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A Multiscale Approach to Unravelling the Structure and Infrared Spectra of Astronomically Relevant Nanosilicates

Joan Mariñoso Guiu



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Memòria presentada per

Joan Mariñoso Guiu

Per optar al grau de Doctor per la Universitat de Barcelona

Programa de doctorat en Química Teòrica i Modelització Computacional

**A Multiscale Approach to Unravelling the Structure
and Infrared Spectra of Astronomically Relevant
Nanosilicates**

Dirigida per:

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Universitat de Barcelona &

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Tutora:

Dr. Mercè Deumal Solé

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l'estructura i els espectres infrarojos de
nanosilicats rellevants en astronomia**

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*We are stardust brought to life, then empowered by the universe
to figure itself out—and we have only just begun.*

Neil deGrasse Tyson

Abstract

Silicates are ubiquitously found both terrestrially and throughout the universe where they are often found as small particles. In the interstellar medium (ISM), these particles undergo high-energy processes that cause them to shatter into ultrasmall grains, resulting in a vast population of nanosilicates. These nanosized grains are likely to play a crucial role in various chemical processes in space, such as catalysing the formation of molecules. Infrared (IR) spectroscopy is the primary tool for identifying silicate grains and analysing their properties and chemical composition. Such analyses are typically performed by empirical comparisons of astronomical observations with spectra of laboratory-made samples. However, this approach only provides indirect information about atomistically detailed properties and typically employs bulk silicate samples. Consequently, most knowledge about nanosilicates relies on top-down extrapolations from bulk properties. As such, much of our current understanding of nanosilicate grains is likely to be unreliable due to the known strong size dependence of structure and properties of materials at the nanoscale.

Thanks to the advances in technology and theoretical methods, computational modelling has revolutionized our ability to interpret experimental results and astronomical observations. In particular, such modelling can probe materials at conditions that are challenging to replicate in the laboratory. (*e.g.* at very small sizes and under extreme environments). In the case of nanosilicates, computational modelling offers a powerful alternative approach to improve our understanding of their properties and to potentially help confirm their presence and abundance in the universe together with astronomical observations and laboratory experiments.

This thesis expands upon previous theoretical models to study nanosilicates aiming to provide a more comprehensive study of their properties. Here, the main particular focus is on improving our knowledge and understanding of these nanosystems through their IR spectra. The thesis is structured as follows: first, a general overview of silicates, their astronomical significance, and the important role of nanosilicate grains is

presented, along with a review of the current state-of-the-art computational modelling approaches. Next the theoretical foundations of all the methodologies used to build our models are described in depth, as well as the different software used. Afterwards, the different research publications derived from this work are discussed providing, for each one, an introduction to the theme and motivation of the publication and a brief discussion of the results and the conclusions that can be extracted from them.

First, we explore various methodologies for accurately computing vibrational spectra, emphasizing their ability to incorporate thermal effects. We then compute the heat capacities of small nanograins comparing them with previous estimates and analysing the implications for their IR emission. Next, we investigate the properties of slightly hydroxylated nanosilicates, particularly their ability to emit microwave radiation. This is followed by a collaborative study combining computational and observational modelling to assess the potential detectability of small nanosilicate grains using. We further discuss two additional collaborative works to study cationic and anionic nanosilicates synthesized in the lab, examining their relevance to both astronomy and atmospheric chemistry. Finally, we study the size dependency of different nanosilicate properties, including IR spectra through modelling nucleated nanosilicate growth. The thesis concludes with a summary of the main conclusions derived from these works.

Keywords: Nanosilicates, Cosmic dust, IR Spectroscopy, DFT Calculations

Resum

Els silicats són omnipresents, tant a la Terra com a l'univers, sovint en forma de petites partícules. En el medi interestel·lar, aquestes partícules són sotmeses a processos d'alta energia que les fragmenten en grans nanomètrics, creant una abundant població de nanosilicats. Aquests petits grans tenen un paper fonamental en diversos processos químics espacials, com la formació de molècules complexes. L'espectroscòpia infraroja (IR) és l'eina principal per identificar i analitzar els silicats, tot comparant observacions astronòmiques amb mostres de laboratori. No obstant això, aquesta tècnica només proporciona informació directa sobre grans superiors a $0,1\ \mu\text{m}$, fet que obliga a extrapolar propietats dels nanosilicats a partir dels grans més grans, sovint amb resultats imprecisos.

Els avenços tecnològics i els models computacionals han revolucionat la interpretació de resultats experimentals i observacions astronòmiques, especialment en entorns extrems difícils de reproduir al laboratori. En el cas dels nanosilicats, la modelització computacional permet superar les limitacions dels models tradicionals, millorant el coneixement de les seves propietats i confirmant-ne la possible presència a l'univers.

Aquesta tesi amplia models teòrics anteriors per estudiar les propietats dels nanosilicats, amb especial atenció a les seves freqüències vibracionals. Primer, es presenta una visió general dels silicats i la seva importància astronòmica, així com una revisió dels models computacionals actuals. Després, es descriuen en detall les metodologies i els programes utilitzats. A continuació, es discuteixen els diferents estudis derivats d'aquesta investigació.

En primer lloc, s'analitzen metodologies per calcular espectres vibracionals, considerant els efectes tèrmics. També es comparen capacitats calorífiques dels nanosilicats amb estimacions prèvies i es discuteixen les seves implicacions en l'emissió IR. A més, s'explora la radiació de microones dels nanosilicats lleugerament hidroxilats i es realitza un estudi combinat de models computacionals i observacionals per determinar la detectabilitat d'aquests grans.

També es duen a terme estudis sobre nanosilicats catiònics i aniònics sintetitzats en laboratori i s'investiga la influència de la mida en les seves propietats. La tesi conclou amb un resum de les principals aportacions de la recerca.

Paraules clau: Nanosilicats, Pols còsmica, Espectre IR, Càlculs DFT

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List of Abbreviations

AGB Asymptotic Giant Branch

AIMD *Ab Initio* Molecular Dynamics

AME Anomalous Microwave Emission

ASE Atomic Simulation Environment

BO Born-Oppenheimer

BFM Bulk Fitted Model

DFT Density Functional Theory

FF Forcefield

FHI-aims Fritz-Haber Institute *Ab Initio* Materials Simulations

FWHM Full Width at Half Maximum

GGA General Gradient Approximation

GM Global Minimum

GOFEE Global Optimization with First-Principles Energy Expression

GP Gaussian Processes

GTO Gaussian-Type Orbitals

GULP General Utility Lattice Program

HF Hartree-Fock

HRD Hertzsprung-Russel Diagram

IDP Interplanetary Dust Particle

IP Interatomic Potentials

IR Infrared

ISM Interstellar Medium

JWST James Webb Space Telescope

KS Kohn-Sham

LAMMPS Large-scale **A**tomic/**M**olecular **M**assively **P**arallel **S**imulator

LCAO Linear **C**ombination of **A**tomic **O**rbitals

LDA Local **D**ensity **A**pproximation

LSDA Local **S**pin **D**ensity **A**pproximation

M_⊙ Solar **M**asses

MC Molecular **C**loud

MCBH Monte **C**arlo **B**asin-**H**opping

MD Molecular **D**ynamics

MIRI Mid-**I**R **I**nstrument

ML Machine **L**earning

MSP Meteoric **S**moke **P**articles

NAO Numeric **A**tom-**C**entered **O**rbitals

NLC Noctilucent **C**loud

PAH Polycyclic **A**romatic **H**ydrocarbon

PES Potential **E**nergy **S**urface

RGB Red **G**iant **B**ranch

SN **S**upernova

UV **U**ltraviolet

WF **W**avefunction

XC **E**xchange and **C**orrelation

CHAPTER 1

Motivation and Objectives

Silicates are among the most abundant materials in the universe, forming the primary constituents of planets, asteroids and interstellar dust. Their presence is revealed through characteristic features in the mid-infrared (mid-IR) spectrum, particularly through two prominent absorption bands at wavelengths close to 10 and 20 microns. By comparing these observed features with those of laboratory-synthesized samples, valuable information can be extracted about the composition and structure of silicates in space.

Despite their importance, much of the current knowledge of silicates is based on observations and measurements of amorphous and crystalline bulk grains. However, it is widely accepted that a significant fraction of interstellar silicates may exist as nanosilicates (grains composed of at most a few thousand atoms). Traditionally, the properties of nanosilicates have been inferred by extrapolating those of bulk materials to smaller sizes. Yet, due to their limited size, nanosilicates likely exhibit distinct physical and chemical properties compared to their bulk counterparts.

In recent decades, computational modelling has emerged a powerful approach to studying nanosilicates, offering a more accurate framework for predicting their properties. Nevertheless, significant challenges remain, particularly in the modelling of their vibrational properties, which could be key to confirming their presence in various astrophysical environments.

The research presented in the present thesis aims to advance the modelling of nanosilicates, with a particular focus on their vibrational spectrum. The main objectives of the thesis are as follows:

- Evaluate the reliability of density functional theory (DFT) based calculations using the PBE0 and B3LYP functionals for modelling the harmonic vibrational properties of nanosilicates by benchmarking them against high-level ab initio calculations and experimental data.
- Investigate the influence of temperature on the IR spectra of nanosilicates, with particular attention to the appearance of anharmonic effects such as combination bands and overtones, as well as shifting of peak positions.
- Compare the vibrational mode distribution of small nanosilicates, obtained at DFT level, and assess their deviation from previous models based on the extrapolation of experimental results on bulk samples.
- Reassess the heat capacity of nanosilicates, and their instantaneous temperature rise upon ultraviolet (UV) photon absorption to provide more accurate predictions of their IR emission capabilities.
- Explore the effects of molecular and dissociative water adsorption on the physical and spectroscopic properties of nanosilicates and evaluate their implications as potential carriers of the anomalous microwave emission.
- Compare the IR spectra of diverse nanosilicate populations to those of bulk amorphous silicates, identifying potential diagnostic IR spectral features for future JWST observations of the interstellar medium.
- Provide a structural and spectroscopic characterization of cationic and anionic nanosilicates produced in cluster beam experiments, and clarify their formation mechanisms and relevance to astrophysical and atmospheric environments.

- Use an in-house developed simulation code that models the nucleated growth of nanosilicate grains with up to 1000's of atoms to examine the size-dependence physical and spectroscopic properties of nanosilicates over a range of conditions.
- Analyze the evolution of the IR spectra during nanosilicate grain growth, with a focus on the development and transformation of the characteristic 10-micron silicate IR feature.

CHAPTER 2

Introduction

This thesis explores how modern atomistic computational modeling can contribute to a deeper understanding of cosmic dust and its properties. To provide some context for this work, I begin with a broad introduction to the discovery of cosmic dust, followed by a discussion of its origins and its role in the life cycle of stars. I then examine the various types of cosmic dust, with a particular focus on silicates and their properties. Next, I review the different evidence that supports the presence of silicate dust in the Universe and its importance on a variety of astronomical processes. Finally, I provide a review of the current efforts to model silicate dust using computational techniques.

2.1 History of interstellar dust observations

Since the dawn of civilization, humans have been fascinated by the unknown and vast ceiling covering them during day and night. Initially, observations of the sky were made with the naked eye, in such a way that only the main celestial bodies were clearly recognizable. It is no surprise that ancient people, upon observing these seemingly immortal entities, believed them to be gods and spirits observing the Earth from above¹. This belief drove and expanded the mythologies of different societies around the globe across different periods of history². For example, in ancient Greek mythology Apollo was the god of Sun³, whereas in ancient Egypt the god of Sun was Ra⁴. Viewing the heavens in this way created a connection between what nowadays are called astronomy and astrology.

The link, between observable celestial bodies and myths and beliefs, fostered the idea that priests were the first people devoted to a more complete and exhaustive study of the Universe. These early studies made astronomy the first natural science developed by mankind using precise mathematical theory⁵. These early astronomers aimed to understand the behavior and desires of the gods, to predict phenomena such as floods and droughts, the deaths of princes and kings⁶, or to know whether the gods were on their side or not during a war⁷. It was not until the 16th century that the Copernican Revolution⁸ started the divergence of astrology and astronomy until the eventual total differentiation that we find nowadays.

Modern astronomy is based on the information that is obtained from electromagnetic radiation arriving to the Earth. Initially only the visible part of the electromagnetic spectrum was used by astronomers, but thanks to technological innovations the full spectrum can be used now to study different aspects of the Universe^{9–13}. The first observations of dust trace back to 1785, when William Herschel identified the absence of stars in certain positions of the Milky Way; a phenomenon that he described as a “hole” in the sky¹⁴. Tens of years later, F. G. W. Struve observed that the number of stars per unit of volume decreases in all directions when moving away from the Sun¹⁵. More recent observations of one hundred open star clusters in 1930 revealed that stars are frequently less luminous and redder than expected according to the known spectral distribution of stars¹⁶. Since these effects are not constant in all the observed directions, it was proposed that they must be caused by the presence of something contained in the space between the observed stars and the Earth.

Contrary to what was thought until the 19th century, space is not filled with a substance (*i.e* the aether¹⁷), but a near perfect vacuum containing a combination of radiation and highly disperse matter known as the interstellar medium (ISM). A proportion of this matter, known as cosmic (interstellar) dust, is responsible for the absorption, preferentially of blue light, and scattering of the starlight radiation that is observed from the Earth. The total sum of absorption and scattering is referred to as extinction (see Figure 1 for a schematic representation of how light interacts with cosmic dust). Indeed, it has been estimated that cosmic dust reprocesses more than 30% of all starlight in the Universe^{18,19}.

It is important to highlight at this point that the ISM is not homogeneous, with the properties of different regions depending mainly on the temperature and density of the matter, as shown in Table 1. The amount of dust between a star and an observer can be derived by determining the color excess of a star, *i.e.* the difference between the observed and the theoretical color according to the spectral type of the star^{20,21}.

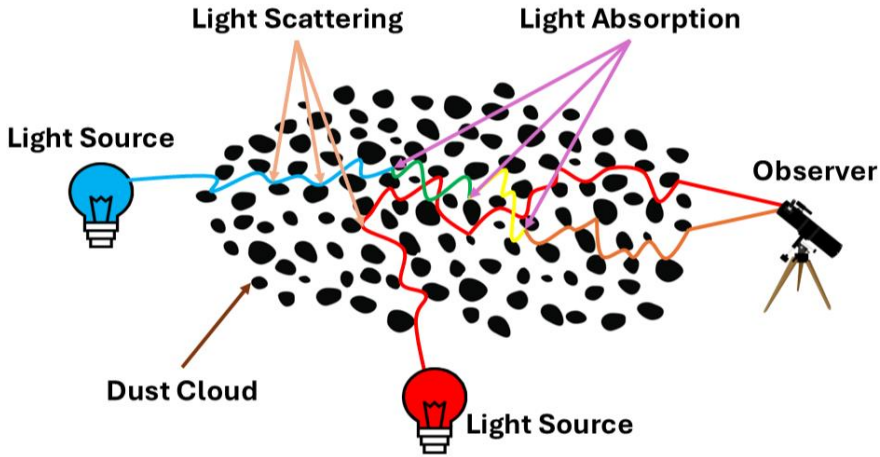


Figure 1: Schematic representation of extinction and reddening due to the presence of cosmic dust cloud. Initial blue light is scattered and absorbed by dust grains leading to a reddening of the light after crossing the dust cloud. Red light is also observable although not travelling initially towards the observer due to scattering.

ISM Zones	Volume fraction	Temperature (K)	Density (particles/cm ³)
Hot Ionized Medium	30-70 %	10 ⁶	0.0065
Warm Neutral Medium	10-20 %	6000-10000	0.2-0.5
Warm Ionized Medium	20-50 %	8000	0.2-0.5
Cold Neutral Medium	1-5 %	50-100	20-50
Molecular clouds	< 1%	10-20	10 ² -10 ⁶

Table 1: Different ISM regions of the Milky Way according to reference 22.

Various models have been proposed to derive the type of dust grains and their size in the ISM. Such work has established that observations cannot be explained by a single grain type with a single or continuous size distribution²³. By fitting the observed extinction over a range of wavelengths, a power-law size distribution for a mixture of grains with different chemical compositions, with ranges between nano and micro sizes, was suggested.²⁴ This model has subsequently improved over the years by including new dust components and adjusting the grain sizes^{25,26}. The presence of small dust grains is also supported by the mid-IR excess of the spectral energy distribution in the Milky Way²⁷, which arises from the IR emission of small grains stochastically heated by absorbing ultraviolet (UV) photons (see section 1.7). All the currently accepted models of dust consider the presence of silicate and carbonaceous grains in the ISM, for reasons we will explain below.

In Figure 2, multiple observations of the molecular cloud (MC) Barnard 68, at different wavelengths, are presented to illustrate the effect of cosmic dust on visible light observations at different wavelengths. Since the size of dust is comparable to the wavelength of blue light (top left image in Figure 2), it absorbs and scatters light, causing the vanishing of the light source. As the wavelength of light increases, photons do not interact as strongly with the dust allowing light to go through the cloud, revealing the light source to the observer.

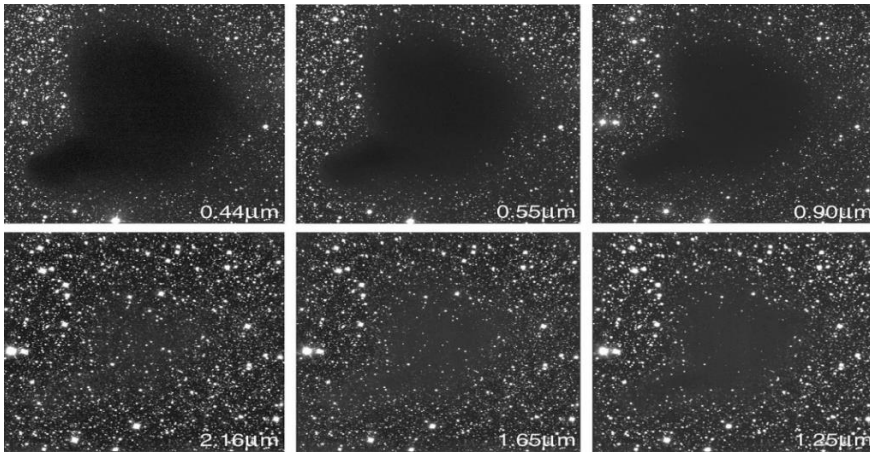


Figure 2: Observations of Barnard 68 molecular cloud at different wavelengths increasing clockwise. **Credit:** European Southern Observatory.

2.2 Stars and dust life cycle

The life cycle of cosmic dust is closely related to that of stars. An understanding of the relation between these two cycles helps us comprehend the origin and processing of dust and why it is present in a vast number of astrophysical environments. To fully understand the sources of dust it is necessary to know the different types of stars, which can be classified by their stage in the stellar life cycle and their current state. The latter can be derived from the relationship between a star's luminosity (or absolute magnitude) and its stellar classification (or effective temperature) as shown in the Hertzsprung-Russell diagram^{28,29} (HRD). Figure 3 shows a schematic representation of HRD.

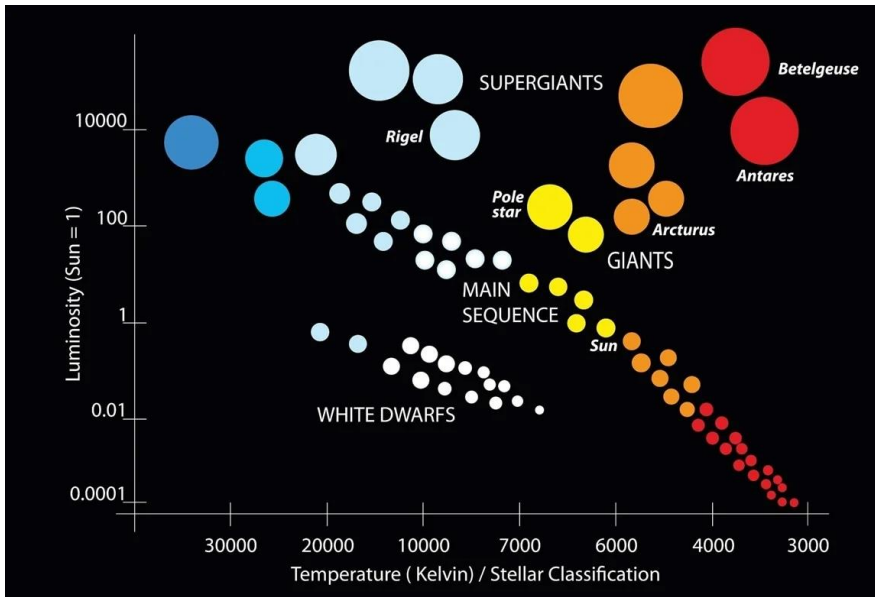


Figure 3: Schematic representation of Hertzsprung-Russell diagram. The Sun is found at luminosity 1 and temperature 5780 K. **Credit:** gstraub/Shutterstock.com

Stars do not remain static throughout their life cycle (see Figure 4 for a schematic representation of their main stages), as various processes continuously alter their properties over time. One of these processes is mass loss, through which stars eject material into ISM, including elements that contribute to dust formation.

The first evidence of stellar mass loss was reported in 1935, based on the observation of blue shifted components in low excitation lines of metals in the spectra of red giant stars³⁰. Stars can lose mass through different mechanisms, with stellar winds being the predominant contributor to this process.³¹ Stellar winds are the continuous outflows of particles ejected from stars driven by radiation pressure³² and have velocities ranging from a few Km/s to over 2000 Km/s, depending on the mass of the star^{33,34}. These winds push out the material in the star's outer layers, where gravitational binding is weaker, ultimately expelling the material into the ISM once the gravitational pull of the star is overcome. Other mechanisms, such as eruptive mass-loss events and binary mass transfer, can also contribute to stellar mass loss, although their impact is generally less significant than stellar winds³⁵.

The origin of stars is found in MCs, made of dust and gas, which are characterized by being cold and dense enough to allow the formation of molecules (as shown in Table 1). MCs are stable for millions of years due to the thermal pressure and the interstellar magnetic field opposition to gravity. However, once the cloud reaches a certain critical mass (known as the Jeans mass), gravity causes the MC to collapse³⁶. This leads to its shrinking and initiates the formation of protostars, which gather dust and gas from the remaining cloud. These protostars are typically found in the upper right part of the HRD corresponding to the initial moments of a star's life. Although obscured by the surrounding dust of the MC, these objects are very bright. Dust that has not been incorporated into the protostar can contribute to the formation of a protoplanetary disk. The initial brightness arises from the conversion of gravitational potential into thermal energy. In addition, protostars have low temperatures, since there is no hydrogen fusion in their core yet.

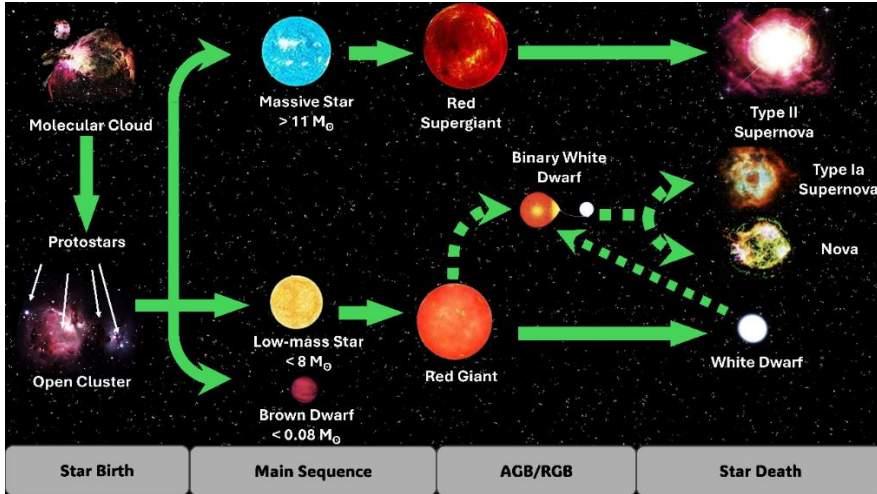


Figure 4: Schematic representation of the stages of the life cycle of stars. Adapted from an original image from Wikipedia by R. N. Bailey

As a protostar accretes more matter and gets denser, radiation becomes trapped inside it and eventually, its core temperature surpasses 10^6 K, enabling the efficient fusion of hydrogen atoms into helium³⁷. In the case of low-mass stars, like our Sun, this process is dominated by the proton-proton chain, which begins with the fusion of two protons into a deuteron and, after different reactions, ends up yielding a helium nucleus³⁸. On the other hand, in stars with masses larger than 1.3 solar masses ($M_{\odot}$) the fusion process is dominated by the carbon-nitrogen-oxygen cycle. This is a catalytic cycle in which carbon nitrogen and oxygen nuclei catalyze the fusion of four protons to obtain helium³⁹. If a protostar does not have enough mass, it cannot reach the temperature needed to sustain stable hydrogen fusion in its core. Such a scenario leads to the formation of brown dwarfs⁴⁰, which are characterized by having masses between that of Jupiter and the stars at the bottom of the main sequence⁴¹.

Once the fusion of hydrogen is established in a star's core, it reaches hydrostatic equilibrium, meaning that the pressure of the nuclear reactions that are taking place, balances out the gravity preventing further collapse. In this stage the star is said to be in its main sequence.

The mass loss of a star in the main sequence is very low, with values ranging from 10^{-14} to $10^{-9} M_{\odot}$ per year^{42,43}. Therefore, during this stage, stars do not contribute significantly to the production of dust. A star remains on the main sequence as long as it has hydrogen to fuse. The rate of hydrogen consumption is clearly dependent on the mass of the star. The more massive a star is, the more hydrogen it will need to fuse to balance out the effects of gravity. Consequently, the larger the star, the less time it stays on the main sequence.

Once the core's hydrogen supply is consumed, gravitational collapse resumes. The core contracts, increasing its temperature, and the outer layers of the star expand reducing their temperature. During this process, the star evolves from the main sequence towards the Red Giant Branch (RGB), in the upper-right part of the HRD⁴⁴. After that, the star reaches a new equilibrium point in which hydrogen burns in a shell around the core, formed by the helium obtained from hydrogen fusion. Once the core reaches a temperature of 10^8 K, the fusion of helium is activated, converting it into heavier elements (mainly carbon and oxygen), by means of the triple-alpha process in which three helium nuclei fuse to produce a carbon nucleus which afterwards can produce oxygen⁴⁵. This process, which is much faster than the burning of hydrogen, leaves a core formed mainly of carbon and oxygen surrounded by shells of burning helium and hydrogen⁴⁶. In this point, the star is found in the Asymptotic Giant Branch (AGB) stage. During the AGB phase, heavier elements can also be formed by the burning of hydrogen and helium, and the capture of neutrons⁴⁷. During this stage, the star's contribution to the production of dust is significantly larger than in the main sequence, with mass loss rate between 10^{-7} and $10^{-4} M_{\odot}/\text{year}$ ⁴⁸.

The evolutionary path that a star follows, after the AGB stage, is determined by its initial mass on the main sequence⁴⁹. If the initial mass was less than $8 M_{\odot}$, they become white dwarfs. In white dwarfs, fusion reactions are no longer viable and therefore they gradually cool down until they become cold black dwarfs. The cooling process is thought to be longer than the current age of the Universe and consequently no black dwarfs are expected yet to exist.

On the other hand, if the original star weights more than $11 M_{\odot}$, due to the sudden gravitational collapse after fusion stops, it explodes as a supernova (SN). There are different types of supernovae (SNe), with their classification depending on their light curves and the absorption lines appearing in their spectra⁵⁰. Finally, the fate of stars having between 8 and $11 M_{\odot}$ is not currently clear.

The main stages of stars during which they produce dust are RGB/AGB and SNe^{51,52}. Nevertheless, other types of stars are also possible sources of cosmic dust, but in a much lower proportion compared to the main contributors⁵³.

Once dust has been formed in circumstellar environments, it is passively transported back into the ISM by means of stellar winds. Once dust has been carried into the ISM, it undergoes different processes. These can be destructive, like for example the fragmentation due to SNs shock waves or constructive by accretion and coagulation in dense regions such as MCs. Finally, this processed dust is incorporated into MCs starting the cycle again. A more extensive discussion of dust processing is given in section 1.6.

Although the nature of interstellar dust sources is quite well established, there are still processes that are not fully understood and that need further research. For example, there is a huge discrepancy between the estimated rates of dust formation in circumstellar environments and the rate of dust destruction due to processing in the ISM. Theoretical studies have predicted that dust is destroyed in the ISM in a period of $\sim 10^8$ years, whereas the stardust injection timescale is calculated to be of the order of 10^9 years^{54,55}. As such it is hard to rationalize the abundance of dust that we observe. Some models have been presented to explain this discrepancy by proposing the possibility of efficient dust growth in the low density conditions of the ISM. In principle, for example, dust growth in such environments could be promoted by means of Coulomb focusing by which a negative grain would actively attract positively charged ions⁵⁶.

However, when a dust grain grows to a certain size, it is expected to become positively charged⁵⁷ and therefore would repel incoming positive ions instead of attracting them, effectively halting dust growth⁵⁸. The issue of destruction versus formation is still a big conundrum in the cosmic dust community.

2.3 Types of interstellar dust

As discussed above, it is generally accepted that a large fraction of the observed dust is formed in circumstellar environments of evolved stars. The process of formation of any kind of molecule in these environments is not easy due to the harsh conditions. In the inner regions of the AGB envelopes, in which there is a relatively high density of particles, the temperature is too high (around 10^4 K) to allow the direct formation of dust⁵⁹. On the other hand, as one moves to regions far from the star, the temperature decreases, but also does the density of particles⁶⁰. Therefore, there are clearly constraints on the nature of cosmic dust. Under circumstellar conditions between these extremes, only highly refractory materials, which contain relatively abundant elements, can be formed at sufficiently large rates. In Table 2, the solar abundances of various elements are presented.

The most abundant elements of this list from which refractory materials can form are carbon and oxygen. AGB stars can be classified according to their atmospheric composition based on the carbon to oxygen (C/O) ratio. Stars with $C/O > 1$ are considered carbon-rich, while those with $C/O < 1$ are classified as oxygen-rich stars⁴⁷. A third category, S-type stars, corresponds to those with $C/O \sim 1$ and are identified by the presence of ZrO molecular bands in their visual spectra⁶¹. Carbon and oxygen initially form carbon monoxide due to its high bond energy (11.11 eV)⁶² which makes it one of the most stable molecules in stellar atmospheres. Once the less abundant element is entirely locked in CO, the remaining element becomes available to form other dust species.

In carbon-rich AGB stars, carbon generates carbonaceous dust, which is thought to mainly form amorphous carbon grains, although graphitic material and polycyclic aromatic hydrocarbons (PAHs) are also formed⁶³. On the other hand, in oxygen-rich AGB stars, oxygen is responsible for the formation of oxides which, according to the relative abundances in Table 2, should be mainly compounds containing Si, Mg and O, such as silicates. It is important to stress that the abundances shown in Table 2 refer to our Sun. However, the order of magnitude of these abundances should not vary with other stars in the main sequence or in AGB. For this reason, they can be taken as a good starting point to understand the available elements for forming interstellar dust.

Element	Abundance (Relative to H)
H	1
He	$8.20 \cdot 10^{-2}$
O	$4.90 \cdot 10^{-4}$
C	$2.88 \cdot 10^{-4}$
Ne	$1.15 \cdot 10^{-4}$
N	$6.76 \cdot 10^{-5}$
Fe	$2.88 \cdot 10^{-5}$
Si	$3.24 \cdot 10^{-5}$
Mg	$3.55 \cdot 10^{-5}$
Al	$2.69 \cdot 10^{-6}$
Ti	$9.33 \cdot 10^{-8}$

Table 2: Solar abundances of different elements relative to H. Data taken from reference 64.

The chemical composition of interstellar dust is not derived just from the analysis of chemical abundances. Various evidence obtained from astronomical observations can also be used to infer the presence of carbonaceous and silicate dust in space. In Table 3, the main features of both types of dust obtained in observational UV and infrared (IR) spectra are listed. It is important to highlight that the position of these signals can shift depending on the composition of the dust (see Table 5 for an example of the silicates features).

The absorption features observed in the IR regions of these spectra are assigned mainly to C-H vibrational modes in the case of carbonaceous dust, while in silicates these features are associated with Si-O vibrations.

A more tangible means to study the composition of cosmic dust grains is by laboratory analysis. For such work, interplanetary dust particles (IDPs)⁶⁵ can be collected by planes flying in the Earth's stratosphere⁶⁶. Crystalline and amorphous silicates have been detected in the samples of both IDPs⁶⁷ and meteorites⁶⁸ with the analysis of oxygen isotopes indicating their pre-solar origin. Moreover, extraterrestrial dust samples collected by the NASA Stardust mission have also been studied⁶⁹. In section 1.5 a discussion on the evidence for the presence of cosmic dust in the ISM is provided.

Wavelength (microns)	Type of dust producing the signal
0.2175	Carbon/aromatic
3.4	Carbon/aliphatic
6.2	PAHs
7.7	PAHs
8.6	PAHs
9.7	Amorphous silicates
9.8	Crystalline silicates
11.2	Crystalline silicates
16.3	Crystalline silicates
18	Amorphous silicates
19.5	Crystalline silicates

Table 3: List of some of the features observed in the UV-IR spectra that are assigned to dust of either carbonaceous or silicate origin. The wavelength of the features can shift depending on chemical composition.

Although both carbonaceous and silicate dust are astronomically relevant in different processes and environments, in the present thesis the focus is on silicates. For this reason, from here on, when mentioning interstellar dust, unless the contrary is stated, it will refer to silicate dust.

2.4 Chemical structure of silicates

Silicates are the most common form of mineral in the solar system and likely beyond it. They are a class of materials that encompass a large variety of chemical composition and physical properties. The basic building block of silicates is the silicate tetrahedron $[\text{SiO}_4]^{4-}$ in which the silicon atom sits in the center of a tetrahedron with oxygen atoms in its vertices. Various silicates structures can be built by linking these tetrahedra structures in different ways. Table 4 shows the classification of silicates depending on the structure resulting from the combination of silicate tetrahedra.

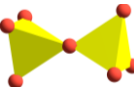
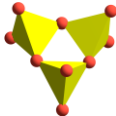
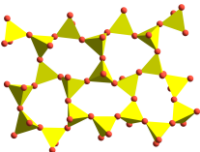
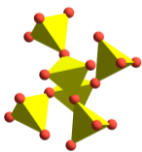
Major group	Structure	Structure description	Chemical formula	Mineral example
Nesosilicates		Isolated tetrahedron	$[\text{SiO}_4]^{4-}$	Olivine
Sorosilicates		Double tetrahedra	$[\text{Si}_2\text{O}_7]^{6-}$	Epidote
Cyclosilicates		Rings	$[\text{Si}_n\text{O}_{3n}]^{2n-}$	Beryl
Inosilicates		Chains	$[\text{Si}_n\text{O}_{3n}]^{2n-}$ (single chain)	Pyroxene
Phyllosilicates		2D Sheets	$[\text{Si}_{2n}\text{O}_{5n}]^{2n-}$	Clays
Tectosilicates		3D Framework	$[\text{Al}_x\text{Si}_y\text{O}_{(2x+2y)}]^{x-}$	Quartz

Table 4: Classification of silicate minerals according to their structure. Oxygen atoms are depicted as red spheres. Inside each tetrahedra there is a silicon atom.

The negative charge of the silicate tetrahedra must be compensated by cations to obtain charge neutral compounds. Depending on the cation used, each of the major groups presented in Table 4 can be subdivided into various subgroups⁷⁰. In the case of astronomically formed silicates, their composition is restricted by the abundance of the counterions in the dust-forming regions. From the data already shown in Table 2, as well as other evidence explained in section 1.5, one can conclude that these counterions should mainly be Mg^{2+} and Fe^{2+} . The silicates found in most astronomical environments are thought to be mainly amorphous and have olivine ($\text{Mg}_{2x}\text{Fe}_{2-2x}\text{SiO}_4$) and pyroxene ($\text{Mg}_x\text{Fe}_{1-x}\text{SiO}_3$) compositions^{71,72}. In olivine isolated silica tetrahedra $[\text{SiO}_4]^{4-}$ are found, whereas in pyroxenes the tetrahedra are linked by oxygen atoms forming chains $([\text{SiO}_3]^{2-})_n$. When silicates are formed around AGB stars they are thought to be more olivinic^{73,74}. However, due to sputtering processes in the ISM, Mg atoms are depleted^{75,76} and an increase in the proportion of pyroxene silicates in these environments is expected⁷⁷.

The reason why olivine and pyroxene can be found with mixtures of Mg^{2+} and Fe^{2+} emerges from the fact that both have the same charge and similar radius⁷⁸. Indeed, their solid solutions show small deviations from ideal mixing⁷⁹. Consequently, both cations can be exchanged between these minerals without altering significantly their crystalline structure. The crystalline endmembers, *i.e.* the cases in which there is only Mg or Fe atoms in the crystal of olivine are known as forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4), whereas for pyroxene they are named enstatite (MgSiO_3) and ferrosilite (FeSiO_3). In Figure 5, the crystal structures of forsterite and enstatite are shown.

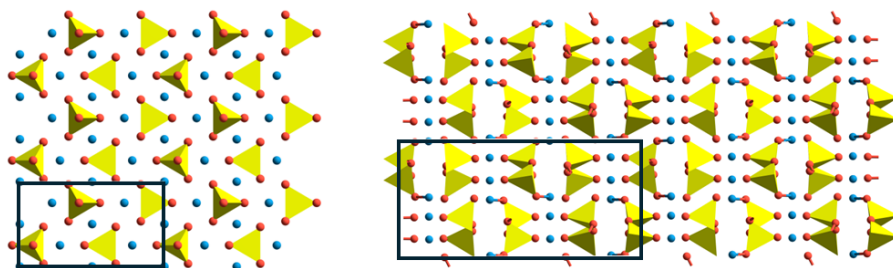


Figure 5: Crystal structures of forsterite (left) and enstatite (right). Oxygen and magnesium atoms are depicted as red and blue spheres respectively. Inside each tetrahedra there is a silicon atom. Black lines correspond to the unit cell of the crystal.

Spectroscopic studies of dust analogs synthesized in the laboratory are a great source to better understand observational data and the physical and optical properties of interstellar dust. In this direction, various studies have been carried out to obtain these properties for both olivinic and pyroxenic silicate bulk materials, containing different proportions of Mg and Fe^{80,81}.

It is important to note that although the olivinic and pyroxenic nature of cosmic dust has been widely accepted, its exact composition is difficult to assess and remains an open question. As was noted in Table 3, amorphous silicates show two features in the infrared at ~ 9.7 and ~ 18 microns which are ubiquitously observed in numerous astronomical environments. Their broadness (see Figure 6) is a clear sign of the amorphous structure of dust. This broadening appears due to the distribution of bond lengths and angles which are characteristic of amorphous silicates⁸².

Multiple efforts have been carried out to fit these two spectral features using laboratory analogs to determine the exact composition of dust. Studies on this topic have shown good agreement between the IR spectra of these analogs and the observational IR spectra of different astronomical environments. These studies used amorphous silicate analogs of both pyroxenic and olivinic composition with a range of $\text{Mg}^{2+}/\text{Fe}^{2+}$ ratios^{73,83,84}. However, the complete characterization of these analogs is a complex procedure because their exact structure and properties can vary depending on the technique used to synthesize them and even at different sites of the same grain⁸⁵. As a matter of fact, differences in the peak position, full widths at half-maximum (FWHM) and strength ratio of the two silicate IR signals have been obtained in materials of similar composition when using different techniques⁸⁴. Moreover, some studies have found that presolar grains contains stoichiometries in-between pyroxene and olivine^{86–88} and therefore, they should also be considered when developing dust models.

In addition, there is an extra problem when trying to fit observational spectra because amorphous silicates of different composition show very similar IR spectra with just small variations in peak position and broadening (see Table 5). Therefore, it is possible to fit one signal with different silicate mixtures. Even the use of crystalline silicates mixtures, with small amount of amorphous dust, has been used to match the 10-micron region of astronomical observations⁸⁹. This issue makes the precise and unambiguous characterization of observed silicate cosmic dust a challenging topic.

Chemical Formula	10 μm signal		18 μm signal	
	Peak position (μm)	FWHM (μm)	Peak position (μm)	FWHM (μm)
$\text{Mg}_x\text{Fe}_{1-x}\text{SiO}_3$				
x = 1.0	9.32	1.64	17.7	5.95
x = 0.95	9.36	1.65	17.8	6.01
x = 0.8	9.35	1.82	17.9	6.33
x = 0.7	9.30	1.95	17.9	6.08
x = 0.6	9.44	2.17	17.8	6.50
x = 0.5	9.25	2.27	17.9	6.64
x = 0.4	8.91	2.29	18.0	6.76
$\text{Mg}_{2x}\text{Fe}_{2-2x}\text{SiO}_4$				
x = 0.5	9.80	2.14	17.1	6.94
x = 0.4	9.78	2.61	16.9	7.53

Table 5: Comparison in peak position and FWHM of the 10 and 18 micron IR features of amorphous silicates with different composition. Data taken from reference 73.

Besides the ubiquitous presence of amorphous silicate dust, crystalline silicates have also been observed^{90–93}. The IR features assigned to crystalline dust are characterized by being sharp, contrary to the broad features of amorphous dust⁹⁴. Their signals appear in a wide range of wavelengths from mid to far IR⁹⁵. Some of these signals appear around the 10-micron region of the spectra which complicates its observation on top of the amorphous dust broad signal.

On the other hand, signals showing up at ~ 11.2 and 16.3 have been used to assess the presence of crystalline dust⁹⁶ and to place an upper limit of $\sim 3\%$ to the mass fraction of crystalline dust in the diffuse ISM^{77,97}. In addition, the comparison with lab-made analogs have shown that the composition of crystalline dust tends to be very magnesium-rich^{90,95}.

Finally, we consider observations related to the initial nucleation of silicate dust grains around oxygen rich AGB stars. Even with their highly refractory characteristics, this process would be very unlikely at temperatures above 1000K ⁹⁸. SiO is one of the most common and discussed species that could be involved in this process, although its capacity to homogeneously nucleate in silicate-forming regions has been a topic of much debate^{99,100}. It is thus likely that silicates would need the presence of more refractory seeds to be previously formed on which to condense on¹⁰¹.

In this context, refractory seeds such as TiO_2 and Al_2O_3 have been studied because of the relatively high Al/Ti abundances and their capacity to form refractory oxides¹⁰²⁻¹⁰⁵. Nevertheless, observational studies focused on Mira stars show that TiO_2 particles condensate at distances around 3.0-5.5 stellar radius from the parent star, where temperatures of few hundred K are present¹⁰⁶. This result contrasts with observations that show the presence of dust at shorter distances of 2-3 stellar radii in AGB stars¹⁰⁷⁻¹⁰⁹. Therefore, dust produced at this distance cannot condensate on TiO_2 grains. On the other hand, observations and models of the distribution of Al-containing grains are more in agreement with that of dust^{103,110} making them more suitable for that purpose.

Computational studies have also shown the possibility of silicate nanoclusters forming without needing to grow on a seed¹¹¹. However, this route still requires the initial dimerization of SiO and its posterior oxidation. Subsequent Mg incorporation and oxidation yields bare or hydroxylated pyroxenic dimers. Other computational work has indicated that mixed oxides such as TiSiO_3 or CaSiO_3 may be suitable refractory seed species for silicate grain growth^{105,112}.

2.5 Evidence of silicate dust in the universe

The presence of silicate dust in the universe can be confirmed by different observations, which at the same time can contain useful information about the chemical composition, size, shape etc.

Two of these observational traits have already been mentioned and discussed in previous sections. On the one hand the extinction and reddening of light caused by dust, from which it is possible to gather information about the size distribution of dust grains¹¹³. On the other hand, the observational IR spectra show two broad features at ~ 10 and ~ 18 microns (Figure 6) which are characteristic of amorphous silicates or sharp features in the mid and far IR, characteristic of crystalline dust (Figure 7).

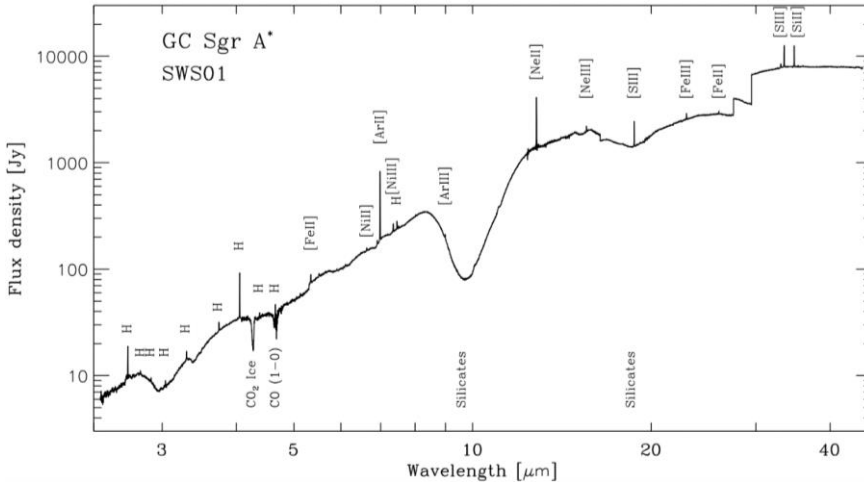


Figure 6: Observational IR spectrum along the line of sight towards the Galactic Center. The observed spikes correspond to atomic emission and are labelled according to the atom producing the emission. The observed dips in the spectrum correspond to absorption features. Spectrum obtained from reference 114.

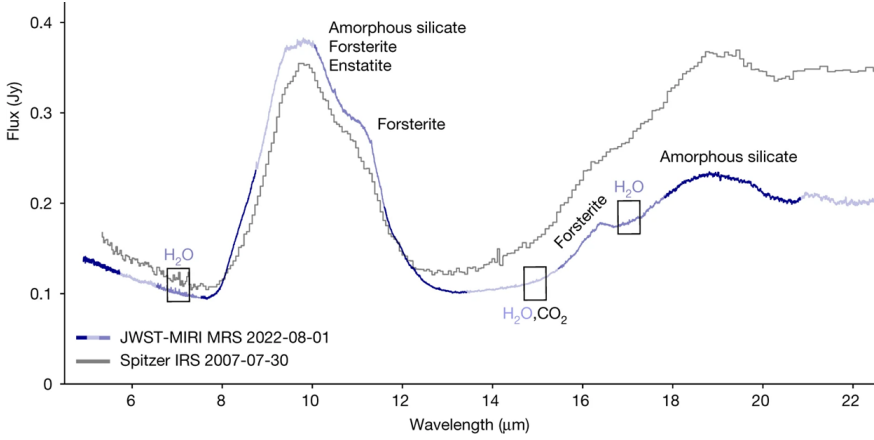


Figure 7: JWST-MIRI MRS IR spectrum (blue line) and Spitzer IRS IR spectrum (grey line) of the PDS 70 protoplanetary disk. The observed signals at ~ 11.30 and ~ 16.40 microns correspond to crystalline silicates. Spectra obtained from reference 96.

The feature at ~ 10 microns correspond to Si-O stretching vibrational modes, while the 18-micron feature is assigned to O-Si-O bending modes¹¹⁵. From the observed IR signals, information about dust composition can be extracted as already discussed in previous sections. The amorphous signals observed in different sources do not always appear at the exact same position nor with the same broadening¹¹⁶ which is an indicator of different compositions and/or degree of processing of dust in these sources. Apart from absorption spectroscopy, information about the crystallinity of dust can also be obtained by looking at its emission¹¹⁷. Characteristic bands of silicate crystals can be also found in the far-IR region of the spectra and could be used to identify the presence of iron in the crystals¹¹⁸.

Another technique that yields information about the presence of dust is polarimetry. This approach is based on the fact that the light emitted from stars is unpolarized *i.e.* it oscillates in all directions. However, when it is scattered by cosmic dust it becomes polarized. From the wavelength-dependence of the linear polarization it is possible to obtain information such as the size and shape of dust^{119,120}.

Moreover, by assuming that dust grains have spheroidal shape *i.e.* two of the axes have the same length, one can derive a range of possible values for the axial to equatorial ratio. This ratio is a measure of the shape of the spheroid, indicating how flat or elongated it is. By fitting polarimetry observations, a range of this ratio between 1.3 and 3.0 has been obtained^{121,122}, which corresponds to prolate shapes.

To study the chemical elements that form cosmic dust, IR spectroscopy is not the only source of information. By analyzing the abundances of elements towards a given line of sight, one can observe which elements are depleted in comparison with assumed standard abundances of the ISM which are taken typically from those in the Sun (as in Table 2) or from meteorites sample analysis. The rarest elements which can form refractory materials, are thought to be condensed into dust grains^{123,124}. An example of the analysis of element depletions is shown in Figure 8.

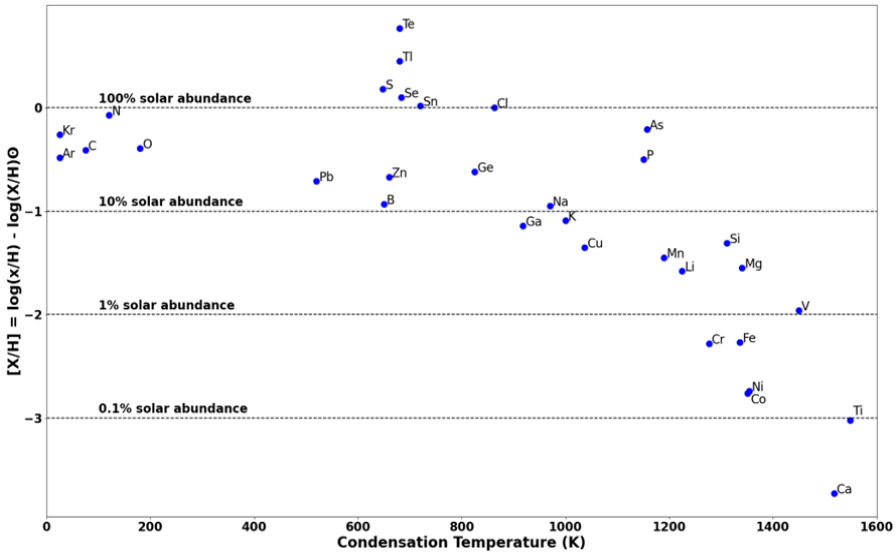


Figure 8: Gas-phase depletion of elements along the line of sight towards the Z Ophiuchus star. Depletions plotted as function of the condensation temperature (temperature at which 50% of an element has been removed). Data taken from reference 125.

Besides the IR part of the spectrum, hints of the presence of silicates can also be obtained by observations in other ranges of the electromagnetic spectrum. First, observations of the foreground component of microwave emission show the presence of a bump in the microwave region between 10 and 60 GHz^{126,127}. The exact origin of this emission remains unsolved and is known as Anomalous Microwave Emission (AME).

Different carriers of AME have been proposed, including small PAHs¹²⁸. However, strong arguments against this idea have been presented which stress that PAHs are mainly non-polar, whereas a certain average dipole is required to have the needed emission¹²⁹. Silicate dust, in particular small silicate grains, has been proposed as an alternative to PAHs^{130,131}. Additionally, recent studies based on *ab initio* quantum mechanics modelling have shown that small nanosilicates can account for the whole observed AME¹³².

The absorption of X-rays has also been recently used to study physical and chemical properties of silicate dust¹³³. This spectroscopic method requires intense X-ray radiation sources, such as black holes¹³⁴, stars¹³⁵ or SNs¹³⁶. By fitting the X-ray absorption fine structure spectra of various astrophysical sources with laboratory spectra of amorphous and crystalline silicate samples of different compositions it has been estimated that up to 12% of dust in the ISM could be in crystalline form¹³⁷. This fraction is notably higher than the estimates derived from observations in the IR (around 3%⁷⁷).

The UV region of the electromagnetic spectrum also provides valuable insights on the presence of silicates. The UV extinction curve exhibits two prominent absorption features. The first is a broad absorption band centered at 2175 Å, first observed in the 1960s^{138,139}. This feature has been extensively studied, revealing that its central wavelength remains remarkably invariant ($\pm 0.46\%$), while its width shows significant variations ($\pm 12\%$).¹⁴⁰ The exact origin of this feature remains uncertain, although its strength suggests that the carrier must be composed of highly abundant elements such as C, Mg, Si or Fe.¹⁴¹ The absence of a scattering component and the fixed peak position indicate that the carrier is likely to be composed of very small grains in the Rayleigh limit.¹⁴²

Numerous models have been proposed to identify the carrier of the 2175 Å feature, with the prevailing hypothesis attributing it to small carbonaceous grains. Graphitic grains were initially suggested as potential carriers^{143,144}, but they struggle to account for the observed variations in the feature's width without altering its central position¹⁴⁵. Alternatively, PAHs have been proposed as plausible carriers¹⁴⁶. The observed bump would therefore be caused by a mixture of different PAHs with the variation in the width of the signal arising from different PAHs populations.

Despite the general consensus favoring PAHs, some studies suggest that silicates may also contribute to this feature. Hydroxylated amorphous silicate grains, of varying compositions exhibit absorptions at 2175 Å with FWHM values consistent with astronomical observations¹⁴⁷. This absorption is thought to arise from OH⁻ ion transitions at low-coordination sites. A positive correlation between silicon depletion and the 2175 Å feature has been reported¹⁴⁸, further supporting the potential involvement of silicates. However, more recent and comprehensive observational studies have not confirmed this correlation, casting doubt on the silicate's contribution¹⁴⁹. The discrepancy between these studies may stem from differing methods of determining silicon depletion and the adopted silicon abundances.

In addition to the 2175 Å feature, UV observations reveal an increase in extinction at wavelengths shorter than 1700 Å, known as the far-UV rise. The exact nature of this rise is still debated, but models combining silicate and carbonaceous dust can successfully reproduce the observed spectrum¹⁵⁰, with some suggesting that small silicate grains dominate the far-UV rise.

2.6 Processing of dust in the universe

Silicate particles freshly formed around stars undergo significant transformations during their journey through the universe. The dynamic and extreme environments of the ISM expose these grains to various high-energy processes, which can profoundly alter their structure and properties.

One of the clearest indicators of dust processing is the clear contrast between the high crystallinity of silicate grains observed in oxygen-rich stars and the predominantly amorphous silicate grains found in the diffuse ISM. While silicate grains are believed to condense preferentially in an amorphous state, implying condensations below its glass temperature⁹⁴, the presence of crystalline silicates around oxygen-rich stars suggest the thermal annealing of these grains in the proximities of dust-forming stars¹⁵¹.

Observational evidence supports the grains transformation in the ISM, revealing a crystalline fraction of 11%-18% in dust-producing environments, compared to only up to 3% in the diffuse ISM⁷⁷. This discrepancy implies that amorphization processes must act on silicate grains during their residence in the ISM. Moreover, signals of crystalline silicates have also been observed in long-period comets¹¹⁷ as well as in protoplanetary disks¹⁵². This is again an indication that dust must be subject to thermal annealing processes after it leaves the diffuse ISM.

The mechanisms responsible for grain transformations can be categorized into destructive and non-destructive processes. Destructive processes include grain sputtering in SNe shockwaves⁵⁵ and high velocity grain-grain collisions¹⁵³, which can completely destroy grains, with subsequent reformation yielding amorphous particles. Grain-grain collisions at lower velocities can also lead to grain growth¹⁵⁴. On the other hand, non-destructive processes, such as high energy cosmic ray absorption¹⁵⁵ or ion irradiation^{156,157}, can amorphize silicate grains without destroying them.

High-energy destructive processes that affect cosmic dust are of particular interest in astronomy, because they are likely to produce a huge population of ultrasmall nanosized dust, which are taken to be grains with radii $\leq 15 \text{ \AA}$ as defined in the work of Li and Draine¹⁵⁸. Their study concluded that up to 10% of interstellar silicon could be locked in these ultrasmall grains without violating any observational constraint. Consequently, they could form the largest population of dust grains by number in the ISM.

Furthermore, due to photoelectric ejection, these small particles would likely be found as cationic species¹⁵⁹, potentially assisting the initial steps of dust nucleation in the ISM¹⁶⁰.

Finally, the recrystallization of silicates observed in protoplanetary disks is most likely to be produced by means of thermal annealing. The high temperatures required for this process suggest that crystallization occurs in the proximity of newly formed stars followed by its transportation, via stellar winds, to outer regions. Nevertheless, alternative mechanisms such as shock waves triggered by gravitational instabilities have also been proposed¹⁶¹. These shocks could locally heat up amorphous grains, inducing their crystallization.

2.7 Astrophysical relevance of dust

Dust is a ubiquitous component in many astronomical environments, accounting for $\sim 1\%$ of the mass in the ISM. Its presence is unequivocally confirmed by a variety of observational techniques, as discussed in previous sections. The continuous improvement in observational capabilities, and the knowledge that can be extracted about the particles responsible for the observed signals, provides a good motivation for carrying out research on cosmic dust. However, the importance of dust extends far beyond its role as a passive component that complicates the stellar observations. Dust actively participates in numerous astrophysical processes across different environments¹⁶², making its study essential for a comprehensive understanding of the universe.

Star Formation

In MCs, dust particles play a crucial role in star formation by acting as efficient coolants. They do this via facilitating the thermal energy transfer from gas to dust, followed by radiative emission, which reduces the thermal pressure opposing gravitational collapse in MCs¹⁶³. This cooling mechanism enhances the likelihood of cloud fragmentation and subsequent star formation (See section 1.2). Moreover, once stars are formed, dust grains absorb stellar radiation and reprocess it in the IR.

Therefore, the detection of IR emission serves as a tracer of star-forming regions, enabling the determination of star formation rates^{164,165} and the evolutionary stage of galaxies¹⁶⁶.

IR emission

Dust does not only emit in the IR when being close to a star. The sporadic absorption of UV photons in the ISM causes temperature spikes with subsequent rapid cooling to ambient ISM temperatures by radiating in the IR. This process, known as stochastic heating, is of particular interest in the case of smaller grains due to their larger temperature spikes as illustrated in Figure 9.

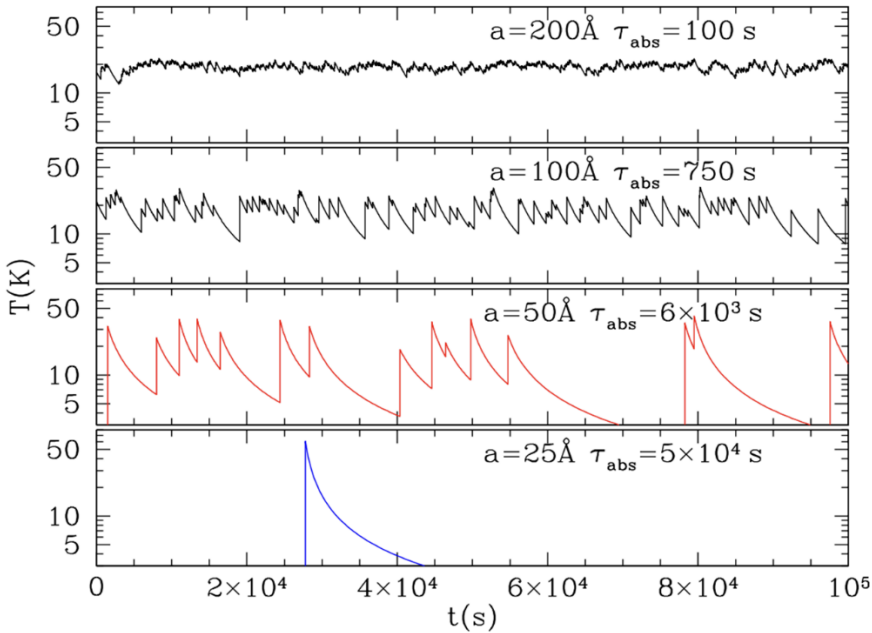


Figure 9: Change in temperature (K) of dust grains with different sizes (increasing from bottom to top) due to stochastic heating with respect to time (seconds). Notice that smaller grains have larger temperature spikes and larger time between UV photon absorption. Figure extracted from reference 63.

Planet Formation

In protoplanetary disks, dust is also a fundamental ingredient in the formation of new planets by providing seeds for nucleation and growth of larger particles. Observations of the 10 μm silicate feature provide evidence for grain growth in these environments¹⁶⁷, although grain growth may also take place in the ISM⁵⁶

The transition from nanometer-sized particles to kilometer-sized planets is a complex process, requiring the aggregation of $\sim 10^{27}$ nanograins to form a single kilometer-sized planet.¹⁶⁸

The evolution of dust growth has been studied via time dependent particle size distribution functions¹⁶⁹, showing that although initially the agglomeration can be relatively quick, it slows down once the grains reach what is known as the meter size barrier¹⁷⁰. This is a size range in which particles have large enough velocities that lead to destructive collisions and quick inward drift towards the central star. Therefore, special trapping mechanisms are likely to be necessary to overcome this limiting barrier to growth¹⁶⁹.

Astrochemical Processes

Dust also plays a pivotal role in astrochemical processes by providing surfaces for a variety of chemical reactions. In dense regions shielded from UV radiation, dust grains act as catalyst for the formation of key molecules such as H_2 ^{171,172} which is essential for the formation of more complex molecules^{173,174}. Without dust, combination reactions ($\text{A} + \text{B} \rightarrow \text{AB}$) would be inefficient due to the lack of a third body to dissipate excess energy. Additionally, species like water, CO, or NH_3 molecules can also form directly on the surface of the grains, leading to the formation of ices¹⁷⁵. Surface reactions on icy grains can also occur leading to the production of complex organic molecules^{176,177}.

Once molecules are formed, they are susceptible to being destroyed by the UV radiation. However, the observation of these molecules^{178–180} indicates that a mechanism to protect them must exist.

Although hydrogen molecules can assist in the shielding from UV radiation if a high enough density of H_2 is present^{181,182}, dust is the main actor shielding molecule formation regions from highly energetic processes^{183,184}.

Nanosilicates Relevance

The study of cosmic dust, and the processes in which it participates, has focused primarily on bulk grains *i.e.* grains with diameters larger than $\sim 0.1 \mu m$. However, recent attention has shifted toward nanosilicate grains due to their expected large population in the ISM as result of dust processing. These ultrasmall grains are believed to play an important role in the dynamic evolution of the ISM by contributing to the heating of diffuse regions via photoelectric emission^{185,186}.

Moreover, they may act as catalyst for chemical reactions such as hydrogen and water formation^{187,188}, similarly to bulk grains.

The reason for the interest in studying these processes on nanosized dust also comes from the expectation that they would exhibit significant differences in their properties compared to their bulk counterparts¹⁸⁹. Traditionally, the properties of nanosized dust grains have been obtained by extrapolating from bulk materials. This top-down approach has been used to approximate properties such as ionization potential and electron affinities¹⁸⁶, as well as heat capacities and IR emission¹⁹⁰. However, this method is not entirely satisfactory, as nanosized particles generally do not behave like bulk materials, making direct extrapolation unreliable¹⁹¹. These differences in properties arise primarily from the large surface to volume ratio of nanoparticles, which makes surface effects dominant over bulk behavior. Additionally, the small size of these particles makes them highly susceptible to quantum effects, further deviating their properties from those of bulk materials¹⁹².

2.8 Nanosilicates: summary and astrophysical context

Although nanosilicates have been mentioned at various points throughout this chapter, this section provides a focused summary of their definition, properties and astrophysical relevance, as they constitute the central theme of this thesis.

Nanosilicates represent a distinct population of silicate grains that may play a critical role in various astrophysical environments¹⁹³. In general, the term “nanosilicate” is used to describe silicate particles with radii in the nanometer regime, typically ranging from a few Å up to few nm. This size range corresponds approximately to clusters containing from a few tens to a few thousand atoms, depending on their composition and degree of structural ordering. Such particles occupy the transitional regime between molecular silicates and bulk dust grains, where their physical and chemical properties are strongly influenced by surface effects, finite-size scaling and quantum phenomena.

From a structural perspective, nanosilicates are commonly assumed to retain basic silicate motifs such as SiO₄ tetrahedra, although significant deviations from bulk structures may occur due to under-coordination, structural disorder, or compositional variability. These features are expected to lead to different properties with respect to those of bulk grains, especially in their vibrational properties.

Nanosilicates have been proposed as potential contributors to several observed interstellar phenomena. Due to their small size, they can absorb UV photons and re-emit in the mid-infrared, producing broad emission features that may overlap with, or complement, those attributed to PAHs and other very small grains. Moreover, their size and composition make them viable candidates to account for part of the UV extinction and polarization excess observed in the diffuse ISM. Their large surface-to-volume ratio and high surface reactivity also suggest a possible role in interstellar surface chemistry, including the formation of complex organic molecules and the modification of ice mantles.

2.9 Current computational modelling of silicate dust

Historically, the study of silicate dust has primarily relied on astronomical observations complemented by laboratory experiments, in which the astronomical conditions are mimicked. Theoretical models have been developed alongside the experiments, enabling the derivation of dust grain properties in cases where direct experimental data was not available. However, these approaches have faced notable limitations, as discussed in previous sections of this chapter.

Over the past two decades, computational modelling techniques have emerged as powerful tools to advance and improve the understanding of cosmic dust. The use of computational models has been successfully applied in the study of various aspects of dust, particularly the modelling of chemical reactions occurring on the surface of bare silicates and ices. These models have been used to explore chemical pathways that lead to the formation of life-building molecular blocks such as glycine¹⁹⁴. Additionally, other astronomical relevant surface reactions, including the formation of H_2 and water on forsterite surfaces have also been modelled^{195,196}.

Despite the rapid progress in modelling surface chemistry on silicates and ices, fewer studies have focused on the intrinsic properties of bare silicate grains. Among these, the vibrational frequencies of bulk silicates, in particular crystalline forsterite and enstatite, have been modelled by quantum chemical methods (see next chapter). These calculations often show remarkable agreement with experimentally measured vibrational frequencies^{197,198}.

Nanosilicates structure and properties have also been modelled using theoretical methods. Although the computational modelling of nanoparticles is well established across various scientific fields^{199–201}, the astronomical community has only recently begun to explore the computational modelling of nano-sized dust grains. In this direction, the potential of TiO_2 and Al_2O_3 nanoparticles as dust condensation seeds have been studied with theoretical methods^{202,203}. A similar approach has been employed to predict the lowest energy structures of $(Mg_2SiO_4)_N$ and $(MgSiO_3)_N$ nanoclusters, for sizes $N = 1-10$.²⁰⁴

Small nanosilicates have also been modelled using highly accurate *ab initio* methods, to obtain the vibrational and rotational spectra of pyroxenic and olivinic monomers and dimers²⁰⁵. This study has highlighted the potential detectability of nanosilicates through astronomical observations due to the strong intensities of their spectral features. The IR spectral region is considered particularly promising for identifying nanosilicates as their spectral features between 8 and 15 microns could provide evidence of their presence in the ISM since some of their signals appear at wavelengths where bulk silicate vibrations are not expected²⁰⁴.

Furthermore, comparison between the IR spectra of crystalline and amorphous nanosilicate grains showed that distinguishing between these structural forms solely based on IR features is not straightforward. Contrary to bulk silicates, crystalline nanograins were found to be energetically metastable, implying that only a small fraction of crystallinity is expected at nanoscale²⁰⁶. Finally, theoretical studies on the rotational spectra of low energy nanosilicates population have demonstrated that these small particles could account for the entirety of the observed AME¹³².

2.10 References

- ¹ Krupp, E. C. *Echoes of the ancient skies: The astronomy of lost civilizations*. New York : Harper & Row, **1983**. ISBN 13: 9780060151010.
- ² Ruggles, C. *Ancient Astronomy: An Encyclopedia of Cosmologies and Myth*. Santa Barbara, California : Bloomsburry publishing, **2005**. ISBN 13: 9781851094776
- ³ Hornblower, S. and Spawforth, A. *The Oxford Classical Dictionary*. Oxford, England : Oxford University Press, **1999**. ISBN 13: 9780198661726.
- ⁴ Hart, G. *The Routledge Dictionary of Egyptian Gods and Goddesses*. Abingdon, Oxon : Routledge, **2005**. ISBN 13: 9780521403405.
- ⁵ Stephenson, B. *Kepler's physical astronomy*. Princeton, N. J : Princeton University Press, **1994**. ISBN 13: 9780691036526
- ⁶ Azzolini, M. The political uses of astrology: predicting the illness and death of princes, kings and popes in the Italian Renaissance. *Studies in History and Philosophy of Science Part C: Studies in History and Philosophy of Biological and Biomedical Sciences*. **2010**, 41(2),135-145.
- ⁷ Mosshammer, A. A. Thales' eclipse. *Transactions of the American Philological Association*. **1981**, 111, 145-155.
- ⁸ Pedersen, O. *Early physics and astronomy: a historical introduction*. Cambridge, England : Cambridge University Press, **1993**. ISBN 13: 9780521408998
- ⁹ Walker, H. J. A brief history of infrared astronomy. *Astronomy & Geophysics*. **2000**, 41(5), 5.10-5.13.
- ¹⁰ Southworth, G. C. Early history of radio astronomy. *The Scientific Monthly*. **1956**, 82(2), 55-66.
- ¹¹ Linsky, J. L. UV astronomy throughout the ages: a historical perspective. *Astrophysics and Space Science*. **2018**, 363(5), 101.
- ¹² Giacconi, R. History of X-ray telescopes and astronomy. *Experimental Astronomy*. **2009**, 25, 143-156.

- ¹³ Pinkau, K. History of gamma-ray telescopes and astronomy. *Experimental Astronomy*. **2010**, 25, 157-171.
- ¹⁴ Herschel, W. XII. On the construction of the heavens. *Philosophical Transactions of the Royal Society of London*. **1785**, 75, 213-266.
- ¹⁵ Struve, F. G. W. *Etudes d'Astronomie Stellaire: Sur la voie lactee et sur la distance des etoiles fixes*. St. Peteresburg : Tip. Acad. Imper., **1847**. ISBN 13: 9781166823801.
- ¹⁶ Trumpler, R. J. Preliminary results on the distances, dimensions and space distribution of open star clusters. *Lick Obs.Bull.* **1930**, 14,154-188.
- ¹⁷ Michelson, A. A. and Morley, E. W. On the relative motion of the Earth and the luminiferous ether. *American journal of science*. **1887**, 3(203), 333-345.
- ¹⁸ Bernstein, R. A.; Freedman, W. L. and Madore, B. F. The first detections of the extragalactic background light at 3000, 5500, and 8000 Å. III. Cosmological implications. *The Astrophysical Journal*. **2002**, 571(1), 107.
- ¹⁹ Witt, A. N. and Gordon, K. D. Multiple scattering in clumpy media. II. Galactic environments. *The Astrophysical Journal*. **2000**, 528(2), 799.
- ²⁰ Savage, B. D.; Bohlin, R. C.; Drake, J. F. and Budich, W. A. survey of interstellar molecular hydrogen. I. *Astrophysical Journal*. **1977**, 216, 291-307.
- ²¹ Bohlin, R. C.; Savage, B. D. and Drake, J. F. A survey of interstellar HI from L-alpha absorption measurements. II. *Astrophysical Journal*. **1978**, 224, 132-142.
- ²² Ferriere, K. M. The interstellar environment of our galaxy. *Reviews of Modern Physics*. **2001**, 73(4), 1031.
- ²³ Greenberg, J. M. in *Interstellar dust and related topics, International Astronomical Union (IAAU) Symposium N° 52*. J. M. Greenberg and H. C. Van de Hulst. Dordrecht: Reidel Publishing Company, **1973**. ISBN 13: 9789401026666

- ²⁴ Mathis, J. S.; Rumpl, W. and Nordsieck, K. H. The size distribution of interstellar grains. *Astrophysical Journal*. **1977**, 217, 425-433.
- ²⁵ Draine, B. T. and Anderson, N. Temperature fluctuations and infrared emission from interstellar grains. *Astrophysical Journal*, **1985**, 292, 494-499.
- ²⁶ Zubko, V.; Swek, E. and Arendt, R. G. Interstellar dust models consistent with extinction, emission, and abundance constraints. *The Astrophysical Journal Supplement Series*. **2004**, 152(2), 211.
- ²⁷ Desert, F.-X.; Boulanger, F. and Puget, J. L. Interstellar dust models for extinction and emission. *Astronomy and Astrophysics*. **1990**, 237, 215-236.
- ²⁸ Hertzsprung, E. Über die Verwendung photographischer effektiver Wellenlaengen zur Bestimmung von Farbenaequivalenten. *Publikationen des Astrophysikalischen Observatoriums zu Potsdam*. **1911**, 22(1).
- ²⁹ Rusell, H. N. Relations Between the Spectra and Other Characteristics of the Stars. *Popular Astronomy*. **1914**, 22, 275-294
- ³⁰ Adams, W. S. and MacCormack, E. Systematic displacements of lines in the spectra of certain bright stars. *Astrophysical Journal*. **1935**, 81, 119.
- ³¹ Lafon, J. -P. J. and Berruyer, N. Mass loss mechanisms in evolved stars. *The Astronomy and Astrophysics Review*. **1991**, 2, 249-289.
- ³² Lamers, H. J. G. L. M and Cassinelli, J. P. *Introduction to stellar winds*. Cambridge: Cambridge university press, **1999**. ISBN 13: 9780521595650.
- ³³ Höfner, S.; Gautschy-Loidl, R.; Aringer, B. and Jørgensen, U. G. Dynamic model atmospheres of AGB stars-III. Effects of frequency-dependent radiative transfer. *Astronomy & Astrophysics*. **2003**, 399(2), 589-601.
- ³⁴ Castor, J. I.; Abbott, D. C. and Klein, R. I. Radiation-driven winds in Of stars. *Astrophysical Journal*. **1975**, 195, 157-174.
- ³⁵ Smith, N. Mass loss: its effect on the evolution and fate of high-mass stars. *Annual Review of Astronomy and Astrophysics*. **2014**, 52(1), 487-528.

- ³⁶ Bonnor, W. B. Jeans' formula for gravitational instability. *Monthly Notices of the Royal Astronomical Society*. **1957**, 117(1), 104-117.
- ³⁷ Moore, B. *Elephants in Space: The Past, Present and Future of Life and the Universe*. Springer International Publishing Switzerland, **2014**. ISBN 13: 9783319056715
- ³⁸ Salpeter, E. E. Nuclear reactions in the stars. I. Proton-proton chain. *Physical review*. **1952**, 88(3), 547.
- ³⁹ Clayton, D. D. *Principles of stellar evolution and nucleosynthesis*. Chicago: University of Chicago Press, **1984**. ISBN 13: 9780226109534
- ⁴⁰ Kumar, S. S. The structure of stars of very low mass. *Astrophysical Journal*. **1963**, 137, 1121.
- ⁴¹ Burrows, A. and Liebert, J. The science of brown dwarfs. *Reviews of Modern Physics*, **1993**, 65(2), 301.
- ⁴² Krtićka, J. Mass loss in main-sequence B stars. *Astronomy & Astrophysics*. **2014**, 564, A70.
- ⁴³ Willson, L. A.; Bowen, G. H. and Struck-Marcell, C. Mass loss on the main sequence. *Comments on Modern Physics, Part C-Comments on Astrophysics*. **1987**, 12, 17-34
- ⁴⁴ Ien Jr, I. Stellar Evolution. VI. Evolution from the Main Sequence to the Red-Giant Branch for Stars of Mass 1 $M_{\odot}$, 1.25 $M_{\odot}$ and 1.5 $M_{\odot}$. *Astrophysical Journal*. **1967**, 147, 624.
- ⁴⁵ Rehder, D. *Chemistry in space: from interstellar matter to the origin of life*. Weinheim: Wiley-VCH, **2010**. ISBN 13: 9783527326891
- ⁴⁶ Herwig, F. Evolution of asymptotic giant branch stars. *Annu. Rev. Astron. Astrophys.* **2005**, 43(1), 435-479.
- ⁴⁷ Habing, H. J. and Olofsson, H. *Asymptotic giant branch stars*. New York: Springer New York, **2003**. ISBN 13: 9781441918437
- ⁴⁸ Engles, D. AGB and post-AGB stars. *arXiv:astro-ph/0508285*, **2005**.

- ⁴⁹ Gail, H. and Sedlmayr, E. *Physics and chemistry of circumstellar dust shells*. Cambridge, UK: Cambridge University Press, **2013**. ISBN 13: 9780521833790.
- ⁵⁰ Cappellaro, E. and Turatto, M. *The influence of binaries on stellar population studies*. Dordrecht: Kluwer Academic Publishers. Astrophys. Space Sci. Library Volume 264, **2001**. ISBN 13: 9780792371045
- ⁵¹ Humphreys, R. M.; Strecker, D. W. and Ney, E. P. Spectroscopic and Photometric Observations of M Supergiants in Carina. *Astrophysical Journal*. **1972**, 172, 75.
- ⁵² Dwek, E. Interstellar dust: what is it, how does it evolve, and what are its observational consequences? *AIP Conference Proceedings*. American Institute of Physics, **2005**. 103-122.
- ⁵³ Dwek, E. The evolution of the elemental abundances in the gas and dust phases of the galaxy. *The Astrophysical Journal*. **1998**, 501(2), 643.
- ⁵⁴ Jones, A. P.; Tielens, A. G. G. M.; Hollenbach, D. J. and McKee, C. F. Grain destruction in shocks in the interstellar medium. *Astrophysical Journal*. **1994**, 433(2), 797-810.
- ⁵⁵ Jones, A. P.; Tielens, A. G. G. M. and Hollenbach, D. J. Grain shattering in shocks: The interstellar grain size distribution. *Astrophysical Journal*. **1996**, 469, 740.
- ⁵⁶ Zhukovska, S.; Henning, T. and Dobbs, C. Iron and silicate dust growth in the galactic interstellar medium: clues from element depletions. *The Astrophysical Journal*. **2018**, 857(2), 94.
- ⁵⁷ Weingartner, J. C. and Draine, B. T. Interstellar depletion onto very small dust grains. *The Astrophysical Journal*. **1999**, 517(1), 292.
- ⁵⁸ Priestley, F. D.; De Looze, I. and Barlow, M. J. The efficiency of grain growth in the diffuse interstellar medium. *Monthly Notices of the Royal Astronomical Society*. **2021**, 502(2), 2438-2445.
- ⁵⁹ Rodgers, B. and Glassgold, A. E. The temperature of the circumstellar envelope of Alpha Orionis. *Astrophysical Journal*. **1991**, 382, 606-616.

- ⁶⁰ Tielens, A. G. G. M. Dust Formation in astrophysical environments: The importance of kinetics. *Frontiers in Astronomy and Space Sciences*. **2022**, 9, 908217.
- ⁶¹ Keenan, P. C. Classification of the S-Type Stars. *Astrophysical Journal*. **1954**, 120, 484.
- ⁶² Kim, H.; Doan, V. D.; Cho, W. J.; Valero, R.; Tehrani, Z. A.; Madrdejós, J. M. L. and Skim, K. S. Intriguing electrostatic potential of CO: Negative bond-ends and positive bondcylindrical-surface. *Scientific Reports*. **2015**, 5(1), 16307.
- ⁶³ Draine, B. T. Interstellar dust grains. *Annual Review of Astronomy and Astrophysics*. **2003**, 41(1), 241-289.
- ⁶⁴ Asplund, M.; Amarsi, A. M. and Grevesse, N. The chemical make-up of the Sun: A 2020 vision. *Astronomy & Astrophysics*. **2020**, 653, A141.
- ⁶⁵ Koschny, D.; Soja, R. H.; Engrand, C.; Flynn, G. J.; Lasue, J.; Chantal, A.; Regourd, L.; Malaspina, D.; Nakamura, T.; Poppe, A. R.; Sterken, V. J. and Trigo-Rodríguez, J. M. Interplanetary dust, meteoroids, meteors and meteorites. *Space science reviews*. **2019**, 215, 1-62.
- ⁶⁶ Warren, J. L. and Zolensky, M. E. Collection and curation of interplanetary dust particles recovered from the stratosphere by NASA. *AIP Conference Proceedings*. **1994**, 310(1), 245-254.
- ⁶⁷ Messenger, S.; Keller, L. P.; Stadermann, F. J.; Walker, R. M. and Zinner, E. Samples of stars beyond the solar system: Silicate grains in interplanetary dust. *Science*. **2003**, 300(5616), 105-108.
- ⁶⁸ Mostefaoui, S. and Hoppe, P. Discovery of abundant in situ silicate and spinel grains from red giant stars in a primitive meteorite. *The Astrophysical Journal*. **2004**, 613(2), L149.
- ⁶⁹ Grün, E.; Sternovsky, Z.; Horanyi, M.; Hoxie, V.; Robertson, S.; Xi, J.; Auer, S.; Landgraf, M.; Postberg, F.; Price, M. C.; Srama, R.; Starkey, N. A.; Hillier, J.K.; Franchi, I. A.; Tsou, P.; Westphal, A. and Gainsforth, Z. Active cosmic dust collector. *Planetary and Space Science*. **2012**, 60(1), 261-273.

- ⁷⁰ Ceer, W. Alexander; H.; Robert A. and Zussman, J. *An introduction to the rock-forming minerals*. Mineralogical Society of Great Britain and Ireland. **2013**. ISBN 13: 9780582300941
- ⁷¹ Gilman, R. C. On the composition of circumstellar grains. *Astrophysical Journal*. **1969**, 155, L185.
- ⁷² Paradaki, I.; Constantini, E.; Rogantini, D.; Mehdipour, M.; Corrales, L.; Zeegers, S. T.; de Groot, F.; den Herder, J. W. A.; Mutschke, H.; Trasobares, S.; de Vries, C. P. and Water, L. B. F. M. Oxygen and iron in interstellar dust: An X-ray investigation. *Astronomy & Astrophysics*. **2023**, 670, A30.
- ⁷³ Dorschner, J.; Begemann, B.; Henning, T.; Jäger, C. and Mutschke, H. Steps toward interstellar silicate mineralogy. II. Study of Mg-Fe-silicate glasses of variable composition. *Astronomy and Astrophysics*. **1995**, 300, 503.
- ⁷⁴ Ferrarotti, A. S. and Gail, H. P. Composition and quantities of dust produced by AGB-stars and returned to the interstellar medium. *Astronomy & Astrophysics*. **2006**, 447(2), 553-576.
- ⁷⁵ Keller, L. P. and McKay, D. S. The nature and origin of rims on lunar soil grains. *Geochimica et Cosmochimica Acta*. **1997**, 61(11), 2331-2341.
- ⁷⁶ Bradley, J. P. Chemically anomalous, preaccretionally irradiated grains in interplanetary dust from comets. *Science*. **1994**, 265(5174), 925-929.
- ⁷⁷ Kemper, F.; Vriend, W. J. and Tielens, A. G. G. M. The absence of crystalline silicates in the diffuse interstellar medium. *The Astrophysical Journal*. **2004**, 609(2), 826.
- ⁷⁸ Shannon, R. D. and Prewitt, C. T. Effective ionic radii in oxides and fluorides. *Acta Cryst*. **1969**, B25, 925-946.
- ⁷⁹ Wood, B. J. and Kleppa, O. J. Thermochemistry of forsterite-fayalite olivine solutions. *Geochimica et Cosmochimica Acta*. **1981**, 45(4), 529-534.
- ⁸⁰ Nuth, J. A. and Donn, B. Laboratory measurements of amorphous silicate smokes and the infrared spectra of oxygen-rich stars. *Astrophysical Journal*. **1982**, 257, L103-L105.

- ⁸¹ Krätschmer, W. and Huffman, D. R. Infrared extinction of heavy ion irradiated and amorphous olivine, with applications to interstellar dust. *Astrophysics and Space Science*. **1979**, 61, 195-203.
- ⁸² Handke, M.; Mozgawa, W. and Nocun, M. Specific features of the IR spectra of silicate glasses. *Journal of molecular structure*. **1994**, 325, 129-136.
- ⁸³ Jäger, C.; Mutschke, H.; Begemann, B.; Dorschner, J. and Henning, T. Steps toward interstellar silicate mineralogy. 1: Laboratory results of a silicate glass of mean cosmic composition. *Astronomy and Astrophysics*. **1994**, 292(2), 641-655.
- ⁸⁴ Speck, A. K.; Whittington, A. G. and Hofmeister, A. M. Disordered silicates in space: a study of laboratory spectra of “amorphous” silicates. *The Astrophysical Journal*. **2011**, 740(2), 93.
- ⁸⁵ Williams, D. A. and Cecchi-Pestellini, C. *The chemistry of cosmic dust*. Cambridge: Royal Society of Chemistry, **2015**. ISBN 13: 9781782620471
- ⁸⁶ Bose, M.; Floss, C.; Stadermann, F. J.; Stroud, R. M and Speck, A. K. Circumstellar and interstellar material in the CO3 chondrite ALHA77307: An isotopic and elemental investigation. *Geochimica et Cosmochimica Acta*. **2012**, 93, 77-101.
- ⁸⁷ Vollmer, C.; Hoppe, P.; Stadermann, F. J.; Floss, C. and Brenker, F. E. NanoSIMS analysis and Auger electron spectroscopy of silicate and oxide stardust from the carbonaceous chondrite Acfer 094. *Geochimica et Cosmochimica Acta*. **2009**, 73(23), 7127-7149.
- ⁸⁸ Floss, C. and Stadermann, F. Auger Nanoprobe analysis of presolar ferromagnesian silicate grains from primitive CR chondrites QUE 99177 and MET 00426. *Geochimica et Cosmochimica Acta*. **2009**, 73(8), 2415-2440.
- ⁸⁹ Bowey, J. E. and Adamson, A. J. A mineralogy of extrasolar silicate dust from 10- μ m spectra. *Monthly Notices of the Royal Astronomical Society*. **2002**, 334(1), 94-106.

⁹⁰ Molster, F. J.; Waters, L. B. F. M.; Tielens, A. G. G. M. and Barlow, M. J. Crystalline silicate dust around evolved stars-I. The sample stars. *Astronomy & Astrophysics*. **2002**, 382(1), 184-221.

⁹¹ Molster, F. J.; Waters, L. B. F. M. and Tielens, A. G. G. M. Crystalline silicate dust around evolved stars-II. The crystalline silicate complexes. *Astronomy & Astrophysics*. **2002**, 382(1), 222-240.

⁹² Waters, L. B. F. M.; Molster, F. J.; de Jong, T.; Beigema, D. A.; Waelkens, C.; Boogert, A. C. A.; Boxhoorn, D. R.; de Graauw, T.; Drapatz, S.; Feuchtgruber, H.; Genzel, R.; Helmich, F. P.; Heras, A. M.; Huygen, R.; Izumiura, H.; Justtanont, K.; Kester, D. J. M.; Kunuze, D.; Lahuis, F.; Lamers, H. J. G. L. M.; Leech, K. J.; Loup, C.; Lutz, D.; Morris, P. W.; Price, S. D.; Roelfsema, Salama, A.; Schaeidt, S. G.; Tielens, A. G. G. M.; Trams, N. R.; Valentijn, E. A.; Vandenbussche, B.; van den Ancker, M. E.; van Dishoeck, E. F.; van Winckel, H.; Wesselius, P. R. and Young, E. T. Mineralogy of oxygen-rich dust shells. *Astronomy and Astrophysics*. **1996**, 315, L361-L364.

⁹³ Sylvester, R. J.; Kemper, F.; Barlow, M. J.; de Jong, T.; Water, L. B. F. M.; Tielens, A. G. G. M. and Omont, A. 2.4-197 micron spectroscopy of OH/IR stars: The IR characteristics of circumstellar dust in O-rich environments. *Astronomy & Astrophysics*. **1999**, 352, 587-599.

⁹⁴ Molster, F. and Kemper, C. Crystalline silicates. *Space Science Reviews*. **2005**, 119, 3-28.

⁹⁵ Jäger, C.; Molster, F. J.; Dorschner, J. Henning, T.; Mutschke, H. and Waters, L. B. F. M. Steps toward interstellar silicate mineralogy. IV. The crystalline revolution. *Astronomy and Astrophysics*. **1998**. 339, 904-916.

- ⁹⁶ Perotti, G.; Christiaens, V.; Henning, T.; Tabone, B.; Water, L. B. F. M.; Kamp, I.; Olofsson, G.; Grant, S. L.; Gasman, D.; Bouwman, J.; Samland, M.; Franceschi, R.; van Dishoeck, E. F.; Schwarz, F.; Güdel, M.; Lagage, P.-O.; Ray, T. P.; Vandenbussche, B.; Abergel, A.; Absil, O.; Arabhavi, A. M.; Argyriou, I.; Barrado, D.; Boccaletti, A.; o Garrati, A. C.; Geers, V.; Glauser, A. M.; Justannont, K.; Lahuis, F.; Mueller, M.; Nehmé, C.; Pantin, E.; Scheithauer, S.; Waelkens, C.; Guadarrama, R.; Jang, H.; Kanwar, J.; Calderón, M. M.; Pawellek, N.; Rodgers-Lee, D.; Schreiber, J.; Colina, L.; Greve, T. R.; Östlin, G. and Wright, G. Water in the terrestrial planet-forming zone of the PDS 70 disk. *Nature*. **2023**, 620(7974), 516-520.
- ⁹⁷ Do-Udy, T.; Wright, C. M.; Fujiyoshi, T.; Glasse, A.; Siebenmorgen, R.; Smith, R.; Stecklum, B. and Sterzik, M. Crystalline silicate absorption at 11.1 μ m: ubiquitous and abundant in embedded YSOs and the interstellar medium. *Monthly Notices of the Royal Astronomical Society*. **2020**, 493(3), 4463-4517.
- ⁹⁸ Gail, H.-P. and Sedlmayr, E. Mineral formation in stellar winds. I. Condensation sequence of silicate and iron grains in stationary oxygen rich outflows. *Astronomy and Astrophysics*, **1999**, 347, 594-616.
- ⁹⁹ Gail, H.-P. and Sedlmayr, E. The primary condensation process for dust around late M-type stars. *Astronomy and Astrophysics*. **1986**, 166(1-2), 225-236
- ¹⁰⁰ Nuth III, J. A. and Ferguson, F. T. Silicates do nucleate in oxygen-rich circumstellar outflows: new vapor pressure data for SiO. *The Astrophysical Journal*. **2006**, 649(2), 1178.
- ¹⁰¹ Gail, H. and Sedlmayr, E. Inorganic dust formation in astrophysical environments. *Faraday Discussions*, **1998**, 109, 303-319.
- ¹⁰² Jeong, K. S.; Winters, J. M.; Le Bertre, T. and Sedlmayr, E. Self-consistent modeling of the outflow from the O-rich Mira IRC-20197. *Astronomy & Astrophysics*. **2003**, 407(1), 191-206.

- ¹⁰³ Gobrecht, D.; Cherchneff, I.; Sarangi, A.; Plane, J. M. C. and Bromley, S. T. Dust formation in the oxygen-rich AGB star IK Tauri. *Astronomy & Astrophysics*. **2016**, 585, A6.
- ¹⁰⁴ Kamiński, T. Molecular dust precursors in envelopes of oxygen-rich AGB stars and red supergiants. *Proceedings of the International Astronomical Union*. **2018**, 14(343), 108-118.
- ¹⁰⁵ Goumans, T. P. M. and Bromley, S. T. Stardust silicate nucleation kick-started by SiO+ TiO₂. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. **2013**, 371(1994), 20110580.
- ¹⁰⁶ Kamiński, T.; Müller, H. S. P.; Schmidt, M. R.; Cherchneff, I.; Wong, K. T.; Brünken, S.; Menten, K. M.; Winters, J. M.; Gottlieb, C. A. and Patel, N. A. An observational study of dust nucleation in Mira (o Ceti)-II. Titanium oxides are negligible for nucleation at high temperatures. *Astronomy & Astrophysics*. **2017**, 599, A59.
- ¹⁰⁷ Norris, Barnaby R. M.; Tuthill, Peter G.; Ireland, Michael J.; Lacour, Sylvestre; Zijlstra, Albert A.; Lykou, Foteini; Evans, Thomas M.; Stewart, Paul and Bedding, Timothy R. A close halo of large transparent grains around extreme red giant stars. *Nature*. **2012**, 484(7393), 220-222.
- ¹⁰⁸ Zhao-Geisler, R.; Quirrenbach, A.; Köhler, R and Lopez, B. Dust and molecular shells in asymptotic giant branch stars-Mid-infrared interferometric observations of R Aquilae, R Aquarii, R Hydrae, W Hydrae, and V Hydrae. *Astronomy & Astrophysics*, **2012**, 545, A56.
- ¹⁰⁹ Sacuto, S.; Ramstedt, S.; Höfner, S.; Olofsson, H.; Bladh, S.; Eriksson, K.; Aringer, B.; Klotz, D. and Maercker, M. The wind of the M-type AGB star RT Virginis probed by VLT/MIDI. *Astronomy & Astrophysics*. **2013**, 551, A72.
- ¹¹⁰ Gobrecht, D.; Plane, J. M. C.; Bromley, S. T.; Decin, L. Cristallo, S. and Sekaran, S. Bottom-up dust nucleation theory in oxygen-rich evolved stars-I. Aluminium oxide clusters. *Astronomy & Astrophysics*, **2022**, 658, A167.

- ¹¹¹ Goumans, T. P. M. and Bromley, S. T. Efficient nucleation of stardust silicates via heteromolecular homogeneous condensation. *Monthly Notices of the Royal Astronomical Society*. **2012**, 420(4), 3344-3349.
- ¹¹² Plane, J. M. C. On the nucleation of dust in oxygen-rich stellar outflows. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. **2013**, 371(1994), 20120335.
- ¹¹³ Kim, Sang-Hee; Martin, P. G. and Hendry, Paul D. The size distribution of interstellar dust particles as determined from extinction. *Astrophysical Journal*. **1993**, 422, 164-175
- ¹¹⁴ Lutz, D.; Feuchtgruber, H.; Genzel, R.; Kunze, D.; Rigopoulou, D. and Spoon, H. W. W. SWS observations of the Galactic center. *Astronomy and Astrophysics*. **1996**, 315, L269-L272.
- ¹¹⁵ Henning, T. Cosmic silicates. *Annual Review of Astronomy and Astrophysics*. **2010**, 48(1), 21-46.
- ¹¹⁶ Shao, Z.; Jiang, B. W.; Li, A.; Gao, J.; Lv, Z. and Yao, J. Probing the 9.7 μm interstellar silicate extinction profile through the Spitzer/IRS spectroscopy of OB stars. *Monthly Notices of the Royal Astronomical Society*. **2018**, 478(3), 3467-3477.
- ¹¹⁷ Wooden, D. H.; Harker, D. E.; Woodward, C. E.; Butner, H. M.; Koike, C.; Witteborn, F. C. and McMurtry C. W. Silicate mineralogy of the dust in the inner coma of comet C/1995 01 (Hale-Bopp) pre-and postperihelion. *The Astrophysical Journal*. **1999**, 517(2), 1034.
- ¹¹⁸ Fabian, D.; Henning, T.; Jäger, C.; Mustschke, H.; Dorschner, J. and Wehrhan, O. Steps toward interstellar silicate mineralogy-VI. Dependence of crystalline olivine IR spectra on iron content and particle shape. *Astronomy & Astrophysics*. **2001**, 378(1), 228-238.
- ¹¹⁹ Cotton, D. V.; Bailey, J.; Kedziora-Chudczer, L.; Bott, K.; Lucas, P. W.; Hough, J. H. and Marshal, J. P. The linear polarization of Southern bright stars measured at the parts-per-million level. *Monthly Notices of the Royal Astronomical Society*. **2016**, 455(2), 1607-1628.

- ¹²⁰ Whittet, D. C. B.; Martin, P. G.; Hough, J. H.; Rouse, M. F.; Bailey, J. A. and Axon, D. J. Systematic variations in the wavelength dependence of interstellar linear polarization. *Astrophysical Journal*. **1992**, 386, 562-577.
- ¹²¹ Gupta, Ranjan; Mukai, T.; Vaidya, D. B.; Sen, A. K. and Okada, Y. Interstellar extinction by spheroidal dust grains. *Astronomy & Astrophysics*. **2005**, 441(2), 555-561.
- ¹²² Das, H. K.; Voschinnikov, N. V. and Il'in, V. B. Interstellar extinction and polarization—a spheroidal dust grain approach perspective. *Monthly Notices of the Royal Astronomical Society*. **2010**, 404(1), 265-274.
- ¹²³ Jones, A. P. Depletion patterns and dust evolution in the interstellar medium. *Journal of Geophysical Research: Space Physics*. **2000**, 105(A5), 10257-10268.
- ¹²⁴ Konstantopoulou, C.; De Cia, A.; Ledoux, C.; Krogager, J. K.; Mattsson, L.; Watson, D.; Heingtz, K. E.; Péroux, C.; Noterdaeme, P.; Andersen, A. C.; Fynbo, J. P. U.; Jermann, I. and Ramburuth, T. H. Dust depletion of metals from local to distant galaxies-II. Cosmic dust-to-metal ratio and dust composition. *Astronomy & Astrophysics*. **2024**, 681, A64.
- ¹²⁵ Savage, B. D. and Sembach, K. R. Interstellar abundances from absorption-line observations with the Hubble Space Telescope. *Annual Review of Astronomy and Astrophysics*. **1996**, 34(1), p. 279-329.
- ¹²⁶ Leitch, E. M.; Readhead, A. C. S.; Pearson, T. J. and Myers, S. T. An Anomalous Component of Galactic Emission. *The Astrophysical Journal*. **1997**, 486(1), L23.
- ¹²⁷ Kogut, A.; Banday, A. J.; Bennett, C. L.; Górski, K. M.; Hinshaw, G.; Smoot, G. F. and Wright, E. L. Microwave emission at high galactic latitudes in the four-year DMR sky maps. *The Astrophysical Journal*. **1996**, 464(1), L5.
- ¹²⁸ Draine, B. T. and Lazarian, A. Electric dipole radiation from spinning dust grains. *The Astrophysical Journal*. **1998**, 508(1), 157.
- ¹²⁹ Draine, B. T. and Lazarian, A. Diffuse galactic emission from spinning dust grains. *The Astrophysical Journal*. **1998**, 494(1), p. L19.

- ¹³⁰ Hoang, T.; Vinh, N.-A. and Lan, N. Q. Spinning dust emission from ultra-small silicates: emissivity and polarization spectrum. *The Astrophysical Journal*. **2016**, 824(1), 18.
- ¹³¹ Hensley, B. S. and Draine, B. T. Modeling the anomalous microwave emission with spinning nanoparticles: no PAHs required. *The Astrophysical Journal*. **2017**, 836(2), 179.
- ¹³² Escatllar, A. M. and Bromley, S. T. Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study. *Astronomy & Astrophysics*. **2020**, 634, A77.
- ¹³³ Costantini, E.; Freyberg, M. J. and Predehl, P. Absorption and scattering by interstellar dust: an XMM-Newton observation of Cyg X-2. *Astronomy & Astrophysics*. **2005**, 444(1), 187-200.
- ¹³⁴ Uttley, P.; Cackett, E. M.; Fabian, A. C.; Kara, E. and Wilkins, D. R. X-ray reverberation around accreting black holes. *The Astronomy and Astrophysics Review*. **2014**, 22, 1-66.
- ¹³⁵ Catura, R. C.; Acton, L. W. and Johnson, H. M. Evidence for X-ray emission from Capella. *Astrophysical Journal*. **1975**, 196, p. L47-L49.
- ¹³⁶ Schlegel, E. M. X-ray emission from supernovae: a review of the observations. *Reports on Progress in Physics*. **1995**, 58(11), 1375.
- ¹³⁷ Zeegers, S. T.; Costantini, E.; Rogantini, D.; de Vries, C.P. Mutschke, H.; Mohr, P.; de Groot, F. and Tielens A. G. G. M. Dust absorption and scattering in the silicon K-edge. *Astronomy & Astrophysics*. **2019**, 627, A16.
- ¹³⁸ Stecher, T. P. Interstellar Extinction in the Ultraviolet. *Astrophysical Journal*. **1965**, 142, 1683.
- ¹³⁹ Stecher, T. P. Interstellar extinction in the ultraviolet. II. *Astrophysical Journal*. **1969**, 157, L125.
- ¹⁴⁰ Fitzpatrick, E. L. and Massa, D. An analysis on the shapes of ultraviolet extinction curves. I-The 2175 Å bump. *Astrophysical Journal*. **1986**, 307, 286-294.

- ¹⁴¹ Draine, B. T. On the Interpretation of the $\lambda 2175$ Å feature. In *Symposium-International astronomical union*. **1989**, 135, 313-327.
- ¹⁴² Mathis, J. S. The origin of variations in the 2175 Å extinction bump. *Astrophysical Journal*. **1994**, 422, 176-186.
- ¹⁴³ Stecher, T. P. and Donn, B. On graphite and interstellar extinction. *Astrophysical Journal*. **1965**, 142, 1681.
- ¹⁴⁴ Draine, B. T. and Lee, H. M. Optical properties of interstellar graphite and silicate grains. *Astrophysical Journal*. **1984**, 285, 89-108.
- ¹⁴⁵ Draine, B. T. and Malhotra, S. On graphite and the 2175 Å extinction profile. *Astrophysical Journal*. **1993**, 414, 632-645.
- ¹⁴⁶ Li, A. and Draine, B. T. Infrared emission from interstellar dust. II. The diffuse interstellar medium. *The Astrophysical Journal*. **2001**, 554(2), 778.
- ¹⁴⁷ Steel, T. M. and Duley, W. W. A 217.5 nanometer absorption feature in the spectrum of small silicate particles. *Astrophysical Journal*. **1987**, 315, 337-339.
- ¹⁴⁸ Haris, U.; Parvathi, V. S.; Gudennavar, S. B.; Bubbly, S. G.; Murthy, J. and Sofia, U. J. Silicon depletion in the interstellar medium. *The Astronomical Journal*. **2016**, 151(6), 143.
- ¹⁴⁹ Mishra, A. and Li, A. Interstellar Silicon Depletion and the Ultraviolet Extinction. *The Astrophysical Journal*. **2017**, 850(2), 138.
- ¹⁵⁰ Muthumariappan, C. Three-component dust models for interstellar extinction. *Journal of Astrophysics and Astronomy*. **2010**, 31, 17-29.
- ¹⁵¹ Fabian, D.; Jäger, C.; Henning, T.; Dorschner, J. and Mutschke, H. Steps toward interstellar silicate mineralogy. V. Thermal evolution of amorphous magnesium silicates and silica. *Astronomy and Astrophysics*. **2000**, 364, 282-292.

- ¹⁵² Watson, D. M.; Leisenring, J. M.; Furlan, E.; Bohac, C. J.; Sargent, B.; Forrest, W. J.; Calvet, N.; Hartmann, L.; Nordhaus, J. T.; Green, J. D.; Kim, K. H.; Sloan, G. C.; Chen, C. H.; Keller, L. D.; D'alessio, P.; Najita, J.; Uchida, K. I. and Houck, J. R. Crystalline silicates and dust processing in the protoplanetary disks of the Taurus young cluster. *The Astrophysical Journal Supplement Series*. **2008**, 180(1), 84.
- ¹⁵³ Drain, B. T. and Salpeter, E. E. Destruction mechanisms for interstellar dust. *The Astrophysical Journal*. **1979**, 231, 438-455.
- ¹⁵⁴ Dominik, C. and Tielens, A. G. G. M. The physics of dust coagulation and the structure of dust aggregates in space. *The Astrophysical Journal*. **1997**, 480(2), 647.
- ¹⁵⁵ Bringa, E. M.; Kucheyev, S. O.; Loeffler, M. J.; Baragiola, R. A.; Tielens, A. G. G. M.; Dai, Z. R.; Graham, G.; Bajt, S.; Bradley, J. P.; Dukes, C. A.; Felter, T. E.; Torres, D. F. and Van Breugel, W. Energetic processing of interstellar silicate grains by cosmic rays. *The Astrophysical Journal*. **2007**, 662(1), 372.
- ¹⁵⁶ Jäger, C.; Fabian, D.; Schrempel, F.; Dorschner, J.; Henning, T. and Wesch, W. Structural processing of enstatite by ion bombardment. *Astronomy & Astrophysics*. **2003**, 401(1), 57-65.
- ¹⁵⁷ Demyk, K.; d'Hendecourt, L.; Leroux, H.; Jones, A. P. and Borg, J. IR spectroscopic study of olivine, enstatite and diopside irradiated with low energy H and He ions. *Astronomy & Astrophysics*, **2004**, 420(1), 233-243.
- ¹⁵⁸ Li, A. and Draine, B. T. On ultrasmall silicate grains in the diffuse interstellar medium. *The Astrophysical Journal*. **2001**, 550(2), L213.
- ¹⁵⁹ Weingartner, J. C. and Draine, B. T. Photoelectric emission from interstellar dust: Grain charging and gas heating. *The Astrophysical Journal Supplement Series*. **2001**, 134(2), 263.
- ¹⁶⁰ Zhukovska, S.; Dobbs, C.; Jenkins, E. B. and Klessen, R. S. Modeling dust evolution in galaxies with a multiphase, inhomogeneous ISM. *The Astrophysical Journal*. **2016**, 831(2), 147.

- ¹⁶¹ Desch, S. J. and Connolly J. A model of the thermal processing of particles in solar nebula shocks: Application to the cooling rates of chondrules. *Meteoritics & Planetary Science*. **2002**, 37(2), 183-207.
- ¹⁶² Williams, D. A. and Herbst, E. It's a dusty Universe: surface science in space. *Surface Science*. **2002**, 500(1-3), 823-837.
- ¹⁶³ Glover, Simon C. O. and Clark, Paul C. Is molecular gas necessary for star formation? *Monthly Notices of the Royal Astronomical Society*. **2012**, 421(1), 9-19.
- ¹⁶⁴ Adelberger, K. L. and Steidel, C. C. Multiwavelength observations of dusty star formation at low and high redshift. *The Astrophysical Journal*. **2000**, 544(1), 218.
- ¹⁶⁵ Bell, E. F. Estimating star formation rates from infrared and radio luminosities: the origin of the radio-infrared correlation. *The Astrophysical Journal*. **2003**, 586(2), 794.
- ¹⁶⁶ Orellana, G.; Nagar, N. M.; Elbaz, D.; Calderón-Castillo, P.; Leiton, R.; Ibar, E.; Magnelli, B.; Daddi, E.; Messias, H.; Cerulo, P. and Slater, R. Molecular gas, dust, and star formation in galaxies-I. Dust properties and scalings in ~1600 nearby galaxies. *Astronomy & Astrophysics*. **2017**, 602, A68.
- ¹⁶⁷ Van Boekel, R.; Water, L. B. F.M.; Dominik, C.; Bouwman, J.; de Koter, A.; Dullemond, C.P. and Parsec, F. Grain growth in the inner regions of Herbig Ae/Be star disks. *Astronomy & Astrophysics*. **2003**, 400(3), L21-L24.
- ¹⁶⁸ Birnstiel, T.; Dullemond, C. P. and Brauer, F. Gas-and dust evolution in protoplanetary disks. *Astronomy & Astrophysics*. **2010**, 513, A79.
- ¹⁶⁹ Brauer, F.; Dullemond, C. P.; Henning, T. Coagulation, fragmentation and radial motion of solid particles in protoplanetary disks. *Astronomy & Astrophysics*. **2008**, 480(3), 859-877.
- ¹⁷⁰ Boley, A. C.; Morris, M. A. and Ford, E. B. Overcoming the meter barrier and the formation of systems with tightly packed inner planets (STIPs). *The Astrophysical Journal Letters*. **2014**, 792(2), L27.

- ¹⁷¹ Navarro-Ruiz, J.; Sodupe, M.; Ugliengo, P. and Rimola, A. Interstellar H adsorption and H₂ formation on the crystalline (010) forsterite surface: a B3LYP-D2* periodic study. *Physical Chemistry Chemical Physics*. **2014**, 16(33), 17447-17457.
- ¹⁷² Wakelam, V.; Bron, E.; Cazaux, S.; Dulieu, F.; Gry, C.; Guillard, P.; Habart, E.; Hornekær, L.; Morisset, S.; Nyman, G.; Pirronello, V.; Price, S. D.; Valdivia, V.; Vidali, G. and Watanabe, N. H₂ formation on interstellar dust grains: The viewpoints of theory, experiments, models and observations. *Molecular Astrophysics*. **2017**, 9, 1-36.
- ¹⁷³ Rednyk, S.; Roučka, Š.; Kovalenko, A.; Tran, T. D.; Dohnal, P.; Plašil, R. and Glosík, J. Reaction of NH⁺, NH₂⁺, and NH₃⁺ ions with H₂ at low temperatures-The pathway to ammonia production in the interstellar medium. *Astronomy & Astrophysics*. **2019**, 625, A74.
- ¹⁷⁴ Zanchet, A.; Lique, F.; Roncero, O.; Goicoechea, J. R. and Bulut, N. Formation of interstellar SH⁺ from vibrationally excited H₂: Quantum study of S⁺⁺ H₂ ⇌ SH⁺⁺ + H reaction and inelastic collision. *Astronomy & Astrophysics*. **2019**, 626, A103.
- ¹⁷⁵ Williams, D. A.; Brown, Wendy, A.; Price, Stephen D. Rawlings, J. M. C. and Viti, S. Molecules, ices and astronomy. *Astronomy & Geophysics*. **2007**, 48(1), 1.25-1.34.
- ¹⁷⁶ Materese, C. K.; Gerakines, P. A.; Hudson, Reggie L. Laboratory studies of astronomical ices: Reaction chemistry and spectroscopy. *Accounts of Chemical Research*. **2020**, 54(2), 280-290.
- ¹⁷⁷ Rimola, A.; Skouteris, D.; Balucani, N.; Ceccarelli, C.; Enrique-Romero, J.; Taquet, V. and Ugliengo, P. Can formamide be formed on interstellar ice? An atomistic perspective. *ACS Earth and Space Chemistry*. **2018**, 2(7), 720-734.
- ¹⁷⁸ Guélin, M. Cernicharo, J. Organic molecules in interstellar space: Latest advances. *Frontiers in Astronomy and Space Sciences*. **2022**, 9, 787567.
- ¹⁷⁹ Henning, T. and Semenov, D. Chemistry in protoplanetary disks. *Chemical Reviews*. **2013**, 113(12), 9016-9042.

- ¹⁸⁰ Martins, Z.; Shan Chan, Q. H.; Bonal, L.; King, A. and Yabuta, H. Organic matter in the solar system—implications for future on-site and sample return missions. *Space Science Reviews*. **2020**, 216, 1-23.
- ¹⁸¹ Draine, B. T. and Bertoldi, F. Structure of Stationary Photodissociation Fronts. *The Astrophysical Journal*. **1996**, 468, 269
- ¹⁸² Chardin, J.; Kulkarni, G. and Haehnelt, M. G. Self-shielding of hydrogen in the IGM during the epoch of reionization. *Monthly Notices of the Royal Astronomical Society*. **2018**, 478(1), 1065-1076.
- ¹⁸³ Hirashita, H. Effects of dust grain size distribution on the abundances of CO and H₂ in galaxy evolution. *Monthly Notices of the Royal Astronomical Society*. **2023**, 522(3), 4612-4625.
- ¹⁸⁴ Li, X.; Heays, A. N.; Visser, R.; Ubachs, W.; Lewis, B. R.; Gibson, S. T.; and van Dishoeck, E. F. Photodissociation of interstellar N₂. *Astronomy & Astrophysics*. **2013**, 555, A14.
- ¹⁸⁵ Spitzer Jr, L. The Temperature of Interstellar Matter. I. *Astrophysical Journal*. **1948**, 107, 6.
- ¹⁸⁶ Weingartner, J. C. and Draine, B. T. Photoelectric emission from interstellar dust: Grain charging and gas heating. *The Astrophysical Journal Supplement Series*. **2001**, 134(2), 263.
- ¹⁸⁷ Oueslati, I.; Kerkeni, B. and Bromley, S. T. Trends in the adsorption and reactivity of hydrogen on magnesium silicate nanoclusters. *Physical Chemistry Chemical Physics*. **2015**, 17(14), 8951-8963.
- ¹⁸⁸ Goumans, T. P. M. and Bromley, S. T. Hydrogen and oxygen adsorption on a nanosilicate—a quantum chemical study. *Monthly Notices of the Royal Astronomical Society*. **2011**, 414(2), 1285-1291.
- ¹⁸⁹ Pokropivny, V.; Lohmus, R.; Hussainova, I.; Pokropivny, A. and Vlassov, S. *Introduction to nanomaterials and nanotechnology*. Tartu: Tartu University Press, **2007**. ISBN 13: 9789949117413

- ¹⁹⁰ Draine, B. T. and Li, A. Infrared emission from interstellar dust. I. Stochastic heating of small grains. *The Astrophysical Journal*. **2001**, 551(2), 807.
- ¹⁹¹ Bromley, S. T.; de P. R. Moreira, I.; Neyman, K. M. and Illas, F. Approaching nanoscale oxides: models and theoretical methods. *Chemical Society Reviews*. **2009**, 38(8), 2657-2670.
- ¹⁹² Johnston, R. L. *Atomic and molecular clusters*. CRC Press, **2002**. ISBN 13: 9780748409310
- ¹⁹³ Bromley, S. T. Nanosilicates and molecular silicate dust species: properties and observational prospects. *Frontiers in Astronomy and Space Sciences*. **2024**, 11, 1523977.
- ¹⁹⁴ Rimola, A.; Sodupe, M. and Ugliengo, P. Deep-space glycine formation via Strecker-type reactions activated by ice water dust mantles. A computational approach. *Physical Chemistry Chemical Physics*. **2010**, 12(20), 5285-5294.
- ¹⁹⁵ Goumans, T. P. M.; Richard, C.; Catlow, C. and Brown, W. A. Formation of H₂ on an olivine surface: a computational study. *Monthly Notices of the Royal Astronomical Society*. **2009**, 393(4), 1403-1407.
- ¹⁹⁶ Molpeceres, G.; Rimola, A.; Ceccarelli, C.; Kästner, J.; Ugliengo, P. and Maté, B. Silicate-mediated interstellar water formation: A theoretical study. *Monthly Notices of the Royal Astronomical Society*. **2019**, 482(4), 5389-5400.
- ¹⁹⁷ De La Pierre, M.; Orlando, R.; Maschio, L.; Doll, K.; Ugliengo, P. and Dovesi, R. Performance of six functionals (LDA, PBE, PBESOL, B3LYP, PBE0, and WC1LYP) in the simulation of vibrational and dielectric properties of crystalline compounds. The case of forsterite Mg₂SiO₄. *Journal of computational chemistry*. **2011**, 32(9), 1775-1784.

- ¹⁹⁸ Demichelis, R.; Suto, H.; Noël, Y.; Sogawa, H.; Naoi, T.; Koike, C.; Chihara, H.; Shimobayashi, N.; Ferrabone, M. and Dovesi, R. The infrared spectrum of ortho-enstatite from reflectance experiments and first-principle simulations. *Monthly Notices of the Royal Astronomical Society*. **2012**, 420(1), 147-154.
- ¹⁹⁹ Woodley, S. M. and Bromley, S. T. Introduction to modeling nanoclusters and nanoparticles. *Frontiers of nanoscience*. **2018**, 12, 1-54.
- ²⁰⁰ Jinnouchi, R. and Asahi, R. Predicting catalytic activity of nanoparticles by a DFT-aided machine-learning algorithm. *The journal of physical chemistry letters*. **2017**, 8(17), 4279-4283.
- ²⁰¹ Morales-García, Á.; Escatllar, A. M.; Illas, F.; Bromley, S. T. Understanding the interplay between size, morphology and energy gap in photoactive TiO₂ nanoparticles. *Nanoscale*. **2019**, 11(18), 9032-9041.
- ²⁰² Sinedl, J. P.; Gobrecht, D.; Helling, Ch. And Decin, L. Revisiting fundamental properties of TiO₂ nanoclusters as condensation seeds in astrophysical environments. *Astronomy & Astrophysics*. **2022**, 668, A35.
- ²⁰³ Gobrecht, D.; Plane, J. M. C.; Bromley, S. T.; Decin, L.; Cristallo, S.; Sekaran, S. Bottom-up dust nucleation theory in oxygen-rich evolved stars-I. Aluminium oxide clusters. *Astronomy & Astrophysics*. **2022**, 658, A167.
- ²⁰⁴ Escatllar, A. M.; Lazaukas, T.; Woodley, S. M. and Bromley, S. T. Structure and properties of nanosilicates with olivine (Mg₂SiO₄)_N and pyroxene (MgSiO₃)_N compositions. *ACS Earth and Space Chemistry*. **2019**, 3(11), 2390-2403.
- ²⁰⁵ Valencia, E. M.; Worth, C. J. and Fortenberry, R. C. Enstatite (MgSiO₃) and forsterite (Mg₂SiO₄) monomers and dimers: highly detectable infrared and radioastronomical molecular building blocks. *Monthly Notices of the Royal Astronomical Society*. **2020**, 492(1), 276-282.
- ²⁰⁶ Zamirri, L.; Escatllar, A. M.; Guiu, J. M.; Ugliengo, P. and Bromley, S. T. What can infrared spectra tell us about the crystallinity of nanosized interstellar silicate dust grains?. *ACS Earth and Space Chemistry*. **2019**, 3(10), 2323-2338.

CHAPTER 3

Methodology

In this chapter, the modelling methods used in this thesis and their theoretical basis are described. First, an overview of different electronic structure methods is provided. Then, the theoretical foundations of Density Functional Theory are described, including the Kohn-Sham formalism and common approximations to the exchange-correlation functional. The following sections outline classical force fields, global optimization methods and molecular dynamics simulations. Finally, the computation of vibrational frequencies through different approaches is discussed, followed by a description of the software packages used to perform the calculations presented in this thesis.

3.1 Overview of electronic structure methods

According to the first postulate of quantum mechanics the state of a given system is completely described, at any moment, by a wavefunction (WF) *i.e.* a complex function of time and the position of each system's particle. Not all complex functions are suitable as wavefunction and they must fulfill some mathematical constraints, such as being twice differentiable, continuous and normalized as in equation 1.

$$\int_{-\infty}^{\infty} \Psi^*(r, t) \Psi(r, t) dr = 1 \quad ; \quad \text{for all } t \quad 1$$

Once the wavefunction of the system is established, one can obtain information about any observable by applying the corresponding operator to it. In the case of the energy, to obtain it for a static system *i.e.* not evolving with time, one needs to solve the time independent Schrödinger equation:

$$\hat{H}\Psi = E\Psi \quad 2$$

where E is the energy of the system and $\hat{H}$ is the Hamiltonian operator, which is the operator corresponding to the total classical energy of the system. The Hamiltonian operator, in atomic units, of a system containing N nuclei and N_e electrons, without considering relativistic effects, is given by:

$$\hat{H} = -\sum_{i=1}^N \frac{\nabla_i^2}{2M_i} - \sum_{i=1}^{N_e} \frac{\nabla_i^2}{2} + \sum_{i=1}^N \sum_{j>i}^N \frac{Z_i Z_j}{R_{ij}} + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^N \sum_{j=1}^{N_e} \frac{Z_i}{r_{ij}} \quad 3$$

∇^2 being the Laplacian operator, M_i the mass of the i^{th} nucleus, Z_i its atomic number, R_{ij} the distance between the i^{th} and j^{th} nuclei and r_{ij} the distance between the i^{th} and j^{th} electron or between the i^{th} nuclei and j^{th} electron.

The first two terms correspond to the kinetic energy of the nuclei and electrons respectively. The remaining terms account for the electronic repulsion among nuclei, between electrons and finally the attraction between nuclei and electrons. Therefore, the Hamiltonian can be rewritten in a more compact way as:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{N-N} + \hat{V}_{e-e} + \hat{V}_{N-e} \quad 4$$

Solving analytically the time independent Schrödinger equation is a difficult task even for small systems. Nevertheless, its resolution can be simplified by introducing the Born-Oppenheimer (BO) approximation¹. This approximation is based on the mass difference between nuclei and electrons. Since the electrons are much lighter than nuclei, one can consider that they adapt instantaneously to the movement of nuclei. Consequently, it is possible to decouple the motion of the electrons allowing one to split the Hamiltonian into two parts. One depending exclusively on the nuclear coordinates (equation 5) and another one depending only on the position of the electrons (equation 6).

$$\text{Dependence on the nuclei: } \hat{T}_N + \hat{V}_{N-N} \quad 5$$

$$\text{Dependence on the electrons: } \hat{H}_{elect} = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{N-e} \quad 6$$

It is important to highlight that the electronic Hamiltonian depends only on the electronic coordinates, although it contains the $\hat{V}_{N-e}$ term, if the position of the nuclei is fixed. This splitting of the Hamiltonian allows one to also split the wavefunction of a given system into a nuclear and an electronic part:

$$\psi(r, R) = \chi_{nucl}(R) \cdot \phi_{elect}(r; R) \quad 7$$

where $\chi_{nucl}(R)$ and $\phi_{elect}(r, R)$ are the nuclear and the electronic wavefunction respectively. If one uses the wavefunction definition shown in equation 7 in equation 2 the following expression is obtained:

$$[\hat{T}_N + \hat{V}_{N-N} + \hat{H}_{elect}] \cdot \chi_{nucl}(R) \cdot \phi_{elect}(r; R) = E\psi(r; R) \quad 8$$

Since the electronic Hamiltonian only depends on the electronic coordinates, its application does not affect the nuclear wavefunction. As a result, its application to the total wavefunction results in:

$$\begin{aligned} \hat{H}_{elect} \cdot \chi_{nucl}(R) \cdot \phi_{elect}(r; R) &= \chi_{nucl}(R) \cdot \hat{H}_{elect} \cdot \phi_{elect}(r; R) \\ &= \phi_{elect}(r; R) \cdot E_{elect} \cdot \chi_{nucl}(R) \end{aligned} \quad 9$$

where E_{elect} is the electronic energy, which is the energy of the Hamiltonian's terms that only depend on the coordinates of the electrons for a given fixed nuclei spatial distribution.

Finally, since $\hat{V}_{N-N}$ is just a multiplicative operator, and neglecting the effect that $\hat{T}_N$ has on the electronic wavefunction, equation 8, in combination with the result in equation 9, can be rewritten as:

$$\begin{aligned} \phi_{elect}(r, R) \cdot [\hat{T}_N + \hat{V}_{N-N} + E_{elect}] \cdot \chi_{nucl}(R) \\ = \chi_{nucl}(R) \cdot E \cdot \phi_{elect}(r; R) \end{aligned} \quad 10$$

where E is the total energy of the system. If one defines now the nuclear Hamiltonian as follows:

$$\hat{H}_{nuc} = \hat{T}_N + \hat{V}_{N-N} + E_{elect} = \hat{T}_N + U(R) \quad 11$$

Then, the nuclear wavefunction must fulfill the following eigenvalues equation:

$$\hat{H}_{nuc} \cdot \chi_{nucl}(R) = E \cdot \chi_{nucl}(R) \quad 12$$

The physical interpretation that can be derived from equations 11 and 12 is the following: Under the BO approximation, the atoms' nuclei move over a potential energy surface (PES) $U(R)$ defined by the nuclear electrostatic repulsion $\hat{V}_{N-N}$ and the attractive effect of the electrons. The latter being responsible for the molecular stability since nuclei always repel each other. The most difficult part to compute under the BO is the electronic energy of the system. To obtain it, there are two main methodologies that can be used. On the one hand, there are methods based on the wavefunction, and on the other hand there are those based on density functional theory (DFT).

Electronic structure approaches based on the wavefunction have their foundation in the Hartree-Fock (HF) method^{2,3}. In this method, the wavefunction of an n -electron system is approximated by a single Slater determinant⁴. The HF method supplies a systematic procedure to obtain the n spin-orbitals in the Slater determinant that minimizes the energy of the system by using the variational principle. Using a Slater determinant as the wavefunction of the system, the antisymmetric nature of the wavefunction is fully considered *i.e.* two electrons with same spin cannot be found at small distances. However, since the Coulombic repulsion of the electrons is approximated by using a mean field potential, electrons with opposite spin are completely uncorrelated and can get arbitrarily close and therefore the HF energy is an upper bound to the real energy of the system. The difference between the real and the HF energy is known as electronic correlation energy. To introduce the electronic correlation into the treatment of the wavefunction, multiple methods have been developed such as Møller-Plesset⁵ and Coupled Cluster⁶. The introduction of correlation is not an easy task, and large computational costs are involved in post-HF methods.

Therefore, although these methods are among the most accurate that one can use, their applicability is restricted to small (e.g. typically < 50 atoms) systems.

For this reason, DFT method, due to its lower computational cost, has become the preferential method to study medium size systems (up to a few 1000 atoms), whereas for larger systems it becomes increasingly challenging to use any *ab initio* method, and more approximate methods such as classical forcefields (FF) are needed. DFT and FFs are the main methods employed in the present thesis and are described in detail in the following sections.

3.1.1 Basis Set

To describe the wavefunction of the system in electronic structure methods, whether based on the WF or DFT, it is essential to obtain the system's spin-orbitals. However, obtaining the exact orbitals is computationally infeasible except for very small systems, such as the hydrogen atom. To overcome this limitation, atomic orbitals are typically represented as mathematical functions. Subsequently, atomic orbitals are linearly combined to build molecular orbitals, an approach known as the linear combination of atomic orbitals (LCAO).

$$\Phi_i = \sum_{k=1}^m c_{ki} \cdot \chi_k \quad 13$$

where χ_k are the basis functions (atomic orbitals) and c_{ki} the coefficients that must be optimized to obtain the lowest energy of the system.

Different types of basis functions can be used for this purpose. In this thesis Gaussian-type orbitals (GTOs) and Numeric Atom-Centered Orbitals (NAOs) were employed to carry out electronic structure calculations using the Gaussian and FHI-Aims software respectively (see section 2.7 for software details).

Gaussian-type orbitals

Gaussian basis sets approximate atomic orbitals using linear combinations of Gaussian-type functions. A Gaussian basis function can be written in polar coordinates as:

$$\chi_{gaus}(r, \theta, \phi) = N \cdot r^l \cdot e^{-\alpha r^2} \cdot Y_{lm}(\theta, \phi) \quad 14$$

where N is a normalization constant, r is the radius from the nucleus, l is the angular momentum quantum number, α controls the width, and $Y_{lm}(\theta, \phi)$ are spherical harmonics functions, used to describe the angular part of the basis function.

These functions are linearly combined to obtain atomic orbitals (ϕ_{AO}) which improve the description of the electron density near the nucleus:

$$\phi_{AO}(r) = \sum_i c_i \cdot \chi_{gaus,i}(r) \quad 15$$

The main advantage of using GTOs is due to the Gaussian product theorem⁷, that eases the calculation of two-electron integrals, making calculations affordable even with large basis set.

Numeric Atom-Centered Orbitals

NAOs have the following expression⁸:

$$\phi_i(r) = \frac{u_i(r)}{r} Y_{lm}(\Omega) \quad 16$$

where $u_i(r)$ is a radial function and $Y_{lm}(\Omega)$ denotes the imaginary ($m = -l, \dots, l$) and real ($m = 0, \dots, l$) parts of complex spherical harmonics. Unlike GTOs, NAOs do not have an analytical expression. Instead, their radial shape is numerically tabulated on a grid allowing full flexibility in their shape. This adaptability enables the optimization of the basis set for each element, ensuring a compact representation while maintaining high accuracy. By definition, NAOs offer a fundamental advantage over GTOs because a well parametrized NAO basis can exactly represent GTOs, whereas the reverse is not possible.

3.2 Density Functional Theory

Compared to available WF-based methods, DFT provides a good balance between the computational cost needed and the accuracy obtained. Consequently, DFT allows to treat much larger system than with WF methods, although with a lower degree of accuracy. The reason behind the decrease in computational cost arises from the fact that with DFT one does not solve directly the time-independent Schrödinger equation (equation 2). To describe the state of the system, DFT uses the electronic density which only depends on three spatial coordinates whereas the WF depends on the coordinates of each electron, hence reducing the computational cost. DFT is based on the Hohenberg and Kohn theorems⁹ and the posterior reformulations based on constrained-search approach^{10,11}. The first theorem states that the ground-state electron density of a non-degenerate polyelectronic system uniquely determines its external potential. Since the external potential defines the Hamiltonian of the system (see the following mathematical development), the wavefunction, and hence all ground-state properties are fully determined by the electron density. On the other hand, the second theorem states that the electronic density that minimizes the total energy is the density of the ground state.

3.2.1 Relationship between monoelectronic density and energy

The electronic density of a polyelectronic system is defined as:

$$\rho(\vec{r}) = n \int \dots \int |\Psi(\vec{r}, \omega_1, \vec{r}_2, \omega_2, \dots, \vec{r}_n, \omega_n)|^2 d\vec{r}, d\omega_1 \dots d\vec{r}_n, d\omega_n \quad 17$$

where n is the total number of electrons, $\vec{r}$ are their spatial coordinates and ω its spin moment.

It is important to highlight at this point that using the electronic density function to describe a system leads to a loss in its information. This is because the complex part of the WF is lost when the modulus is applied. Therefore, there are infinite WFs that can produce the same electronic density (all the WF sharing the same real part).

According to the variational principle, the energy of the ground state of a polyelectronic system must satisfy the following minimization condition:

$$E_0 = \min \langle \Psi | \hat{H} \Psi \rangle \quad 18$$

Since there are infinite WFs with the same electronic density, this minimization can be split in two steps. First, for each density function ρ that can describe the system, the WF, with density ρ , that minimizes the variational integral $\langle \Psi | \hat{H} \Psi \rangle$ is found. Then, from all the WF that minimizes the variational integral, the one with lower energy is selected. This two-step process can be described mathematically as:

$$E_0 = \min_{\rho} \left(\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{H} \Psi \rangle \right) = \min_{\rho} \langle \Psi_{\rho}^{min} | \hat{H} \Psi_{\rho}^{min} \rangle \quad 19$$

where Ψ_{ρ}^{min} is the wavefunction with density ρ that minimizes the variational integral.

Defining the energy functional as:

$$E[\rho] = \langle \Psi_{\rho}^{min} | \hat{H} \Psi_{\rho}^{min} \rangle \quad 20$$

allows to express the minimization condition in a more compact way:

$$E_0 = \min_{\rho} E[\rho] \quad 21$$

Considering the electronic Hamiltonian (equation 6), the energy functional can be rewritten as:

$$E[\rho] = \langle \Psi_{\rho}^{min} | (\hat{T}_e + \hat{V}_{e-e}) \Psi_{\rho}^{min} \rangle + \langle \Psi_{\rho}^{min} | \hat{V}_{N-e} \Psi_{\rho}^{min} \rangle \quad 22$$

It can be proved¹² that the second summand of this equation is the same for any WF that describes the same electronic density and has the following expression:

$$\langle \Psi_{\rho}^{min} | \hat{V}_{N-e} \Psi_{\rho}^{min} \rangle = \int_{\vec{r}} v_{ne}(\vec{r}) \rho(\vec{r}) d\vec{r} \quad 23$$

where $v_{ne}(\vec{r})$ is known as the external potential and is the potential felt by an electron due to the nuclei of the system. This term is easy to calculate once the spatial distribution of the nuclei is fixed and known.

Since all the WFs describing a given electronic density have the same external potential, Ψ_ρ^{min} can be defined either as the WF that minimizes $\langle \Psi | \hat{H} \Psi \rangle$ or that minimizes $\langle \Psi | (\hat{T}_e + \hat{V}_{e-e}) \Psi \rangle$. Combining equations 21, 22 and 23, the energy of the ground state can also be expressed as:

$$E_0 = \min_{\rho} \langle \Psi_\rho^{min} | (\hat{T}_e + \hat{V}_{e-e}) \Psi_\rho^{min} \rangle + \int_{\vec{r}} v_{ne}(\vec{r}) \rho(\vec{r}) d\vec{r} \quad 24$$

It can also be proved¹² that there is always a WF that minimizes the integral $\langle \Psi_\rho | (\hat{T}_e + \hat{V}_{e-e}) \Psi_\rho \rangle$. This integral, that needs to be minimized, is a functional of the electronic density.

$$F[\rho] = \langle \Psi_\rho^{min} | (\hat{T}_e + \hat{V}_{e-e}) \Psi_\rho^{min} \rangle = T_e[\rho] + V_{e-e}[\rho] \quad 25$$

This functional definition is of high importance because it is universal *i.e.* it is the same for any n -electronic system considered. This arises from the fact that $\hat{T}_e$ and $\hat{V}_{e-e}$ depend only on the number of electrons but not on the number nor the position of the nuclei.

Finally, the ground state energy can be written as:

$$E_0 = E[\rho_0] = \min_{\rho} E[\rho] = \min_{\rho} \left\{ F[\rho] + \int_{\vec{r}} v_{ne}(\vec{r}) \rho(\vec{r}) d\vec{r} \right\} \quad 26$$

where ρ_0 is the electronic density that minimizes $F[\rho]$, and $E[\rho]$ is the energy functional. From this result, the importance of the universality of $F[\rho]$ is clear. If the exact expression for the functional is known, then it would only be necessary to minimize $E[\rho]$ to exactly compute the energy of the ground state. However, this expression has not yet been found and parametrizations of the functional are needed to allow the use of DFT method.

3.2.2 The Kohn-Sham approach to obtain $F[\rho]$

In the previous section it has been shown how, using the Hohenberg and Kohn theorems, one can relate the electronic density function with the energy of the ground state of a polyelectronic system. However, these theorems do not provide any practical way to manage the fact that the $F[\rho]$ functional is unknown. The most used methods to approximate the functional are based on the approach proposed by Kohn and Sham¹³.

The main idea behind this approach is to find the Hamiltonian of a polyelectronic system in which the electrons do not interact with each other and in which the electron density is the same as the ground state of the studied system. This system of non-interacting electrons is known as a Kohn-Sham (KS) system.

$$\rho_0^{KS} = \rho_0 \quad 27$$

In the KS system there is no interaction between electrons and therefore, the universal functional (equation 25) does not include the $\hat{V}_{e-e}$ term:

$$F^{KS}[\rho] = T^{KS}[\rho] = \langle \Psi_\rho^{KS} | \hat{T}_{el} | \Psi_\rho^{KS} \rangle \quad 28$$

The electronic repulsion of the real system ($\hat{V}_{e-e}$) can be described, without considering any quantum effects, by using Coulomb's law:

$$J[\rho] = \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad 29$$

With these two definitions, arithmetic transformations can be done to obtain a new way to define $F[\rho]$:

$$F[\rho] = T[\rho] + V_{e-e}[\rho] + T^{KS}[\rho] - T^{KS}[\rho] + J[\rho] - J[\rho] \quad 30$$

$$F[\rho] = T^{KS}[\rho] + J[\rho] + (T[\rho] - T^{KS}[\rho] + V_{e-e}[\rho] - J[\rho]) \quad 31$$

$$E_{xc}[\rho] = (T[\rho] - T^{KS}[\rho] + V_{e-e}[\rho] - J[\rho]) \quad 32$$

$$F[\rho] = T^{KS}[\rho] + J[\rho] + E_{xc}[\rho] \quad 33$$

where $E_{xc}[\rho]$ is the exchange and correlation (XC) functional, which expresses the error of the approximations taken under the KS system. On the one hand, considering the kinetic energy of the KS system to be the same as in the real one. On the other hand, the assumption of classical behavior of electronic repulsion. The XC functional is unknown, and different approaches have been developed to parametrize it.

Finally, using equation 33 in equation 26, a new expression for the energy functional is obtained:

$$E[\rho] = T^{KS}[\rho] + J[\rho] + E_{xc}[\rho] + \int_{\vec{r}} v_{ne}(\vec{r}) \rho(\vec{r}) d\vec{r} \quad 34$$

With this equation, one just needs to determine the electronic density of the system to obtain its energy. To do that, Kohn and Sham proposed an iterative method to determine it.

First, the Hamiltonian of an n-electronic KS system is defined as:

$$\hat{H}^{KS} = \hat{T}_{el} + \hat{V}^{KS} = \sum_{i=1}^n \hat{h}^{KS} = \sum_{i=1}^n \left(-\frac{\nabla^2}{2} + v^{KS} \right) \quad 35$$

where $\hat{V}^{KS}$ is an external potential that reproduces the nuclear attraction and the electronic repulsion of the density *i.e.* the potential felt by an electron in the KS system.

Since this Hamiltonian is separable in monoelectronic terms, it is possible to express the exact WF of the system's ground state as a single Slater determinant of n spin-orbitals:

$$\Psi_0^{KS} = \frac{1}{\sqrt{n!}} | \Phi_1^{KS} \dots \dots \Phi_n^{KS} | \quad 36$$

These spin-orbitals are obtained by solving the KS eigenvalues equation:

$$\hat{h}^{KS} \Phi_i^{KS} = \varepsilon_i \Phi_i^{KS} \quad 37$$

It is not possible to directly solve this equation because the operator $\hat{V}^{KS}$, and consequently $\hat{h}^{KS}$, depends on the electronic density. Therefore, an iterative method must be used to solve it.

To determine the expression of v^{KS} , used in equation 35, a different expression for v_{ne} (equation 23) must be introduced:

$$v_{ne} = -\left(\frac{\partial F[\rho]}{\partial \rho_0}\right) \quad 38$$

Applying this definition to equation 33, and taking into account that for a KS system the previous equation becomes:

$$v^{KS} = -\left(\frac{\partial T[\rho]}{\partial \rho_0}\right) \quad 39$$

and therefore, one obtains the following expression:

$$v^{KS} = v_{ne} + \left(\frac{\partial J[\rho]}{\partial \rho_0}\right) + \left(\frac{\partial E_{xc}[\rho]}{\partial \rho_0}\right) \quad 40$$

The derivative of the coulombic repulsion $J[\rho]$ is:

$$\left(\frac{\partial J[\rho]}{\partial \rho_0}\right) = \int_{\vec{r}_2} \frac{\rho_0(\vec{r}_2)}{r_{12}} d\vec{r}_2 \quad 41$$

and defining the XC potential v_{xc} as:

$$v_{xc} = \left(\frac{\partial E_{xc}[\rho]}{\partial \rho_0}\right) \quad 42$$

equation 40 becomes:

$$v^{KS} = v_{ne} + \int_{\vec{r}_2} \frac{\rho_0(\vec{r}_2)}{r_{12}} d\vec{r}_2 + v_{xc} \quad 43$$

This expression for the external potential of a KS system depends only on the electronic density and therefore it is possible to apply an iterative method to obtain ρ_0 . First, an approximation for the density is used to define the KS external potential. With that information, the KS eigenvalues equation is solved, and the density is recalculated using:

$$\rho(\vec{r}) = \sum_{i=1}^N |\Phi_i(\vec{r})|^2 \quad 44$$

Where Φ_i are the spin-orbitals obtained from the resolution of the KS eigenvalues equation.

This procedure is repeated until the system's electronic density is converged. Knowing the electronic density, one can use equation 34 to obtain the energy of its ground state, for that electronic density.

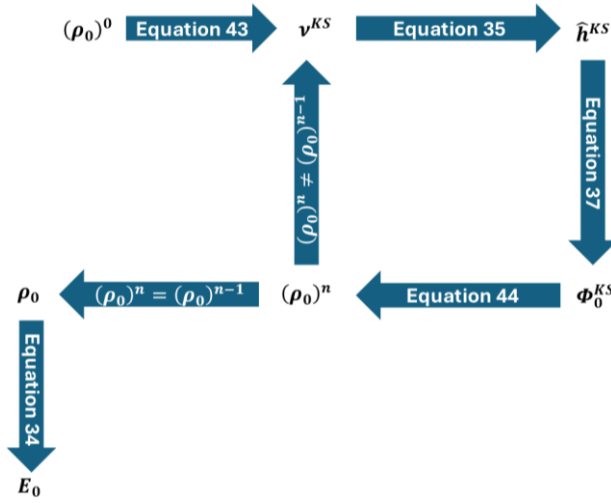


Figure 1: Scheme of the iterative procedure to obtain the energy of the system's ground state using KS method

The only information that is missing to obtain the energy of the system is $E_{xc}[\rho]$. Knowing the exact form of this functional would be of great importance because it would allow the exact energy of any system to be obtained. For this reason, a large amount of work has been done to find approximate forms of the XC functional.

3.2.3 Approximations to obtain $E_{xc}[\rho]$.

There is not much theoretical information about the form that XC functional must have. For this reason, many diverse proposals have been used. It is of great importance to highlight at this point that any approximation that is proposed and used must be compared with experimental results or accurate WF-based quantum mechanical calculations to determine its accuracy.

The Local Density Approximation (LDA) is based on the assumption that the XC energy arises from the interaction of electrons with a homogeneous field:

$$E_{XC}^{LDA} = \int \rho(r) \varepsilon_{XC}(\rho) d\vec{r} \quad 45$$

This approximation supplies a good approximation to $E_{xc}[\rho]$ in systems with electronic densities that change smoothly with the position. The term $\varepsilon_{XC}(\rho)$ can be separated into an exchange and a correlation part. On the one hand, the exchange part is known analytically and can be expressed as follows¹⁴:

$$\varepsilon_X(\rho) = -\frac{3}{4} \left(\frac{3\rho}{\pi} \right)^{1/3} \quad 46$$

On the other hand, no analytical expression is available for the correlation part. Nevertheless, approximations based on the interpolation of computed values for various uniform densities have been obtained to overcome this limitation¹⁵.

XC functionals based on LDA can yield good results in predicting metal properties because their periodicity and electron delocalization make the electronic density almost constant. On the contrary, they are not generally suitable for the study of molecules since they are non-homogeneous. In these cases, LDA tends to underestimate exchange energies and overestimate correlation energies respectively¹⁶.

An improvement of the LDA functionals can be obtained by including, apart from the electron density at a given point, its gradient.

This approach is known as General Gradient Approximation (GGA) and the exchange and correlation is defined energy as:

$$E_{XC}^{GGA} = \int \rho(r) \varepsilon_{XC}(\rho(r), \nabla \rho(r)) d\vec{r} \quad 47$$

There are many GGA functionals that have been developed. Different functionals are built from decomposing E_{XC}^{GGA} into exchange and correlation contributions obtained from theoretical considerations and in some cases the inclusion of fitted empirical parameters. Different combinations of the exchange and correlation parts lead to different functionals such as BLYP^{17,18} (based on fitted parameters) and PBE¹⁹ (without empirical parameters). GGA functionals generally yield good results for equilibrium geometries, energies, dipoles and vibrational frequencies in comparison with experimental values²⁰.

Finally, a more accurate set of functionals, known as hybrid functionals, have been extensively used in recent years. These functionals combine a fraction of the exchange obtained from HF calculation with GGA functionals. Different amounts of HF exchange can be combined with GGA functionals using fitted parameters. Examples of hybrid functionals are B3LYP^{18,21} and PBE0²². B3LYP exchange and correlation energy has the form:

$$E_{XC}^{B3LYP} = (1 - a) \cdot E_X^{LSDA} + a \cdot E_X^{HF} + b \cdot E_X^{B88} + (1 - c) \cdot E_C^{VWN} + c \cdot E_C^{LYP} \quad 48$$

where E_X^{LSDA} and E_C^{LSDA} are the exchange and correlation energies obtained from Local Spin Density approximation (LSDA), *i.e.* the extension of LDA to spin-polarized systems. E_X^{HF} is the HF exchange energy, E_X^B is the Becke 88 exchange functional¹⁷, E_C^{VWN} is the Vosko-Wilk-Nusair correlation energy¹⁵ and E_C^{LYP} is the Lee-Yang-Parr correlation energy¹⁸. The parameters a , b and c take the values 0.2, 0.72 and 0.81 respectively. In the case of the PBE0 functional, it has the following form:

$$E_{XC}^{PBE0} = a \cdot E_X^{HF} + b \cdot E_X^{PBE} + E_C^{PBE} \quad 49$$

where E_X^{HF} is the HF exchange energy, E_X^{PBE} and E_C^{PBE} are the PBE exchange and correlation energies respectively. The parameters a and b take the values 0.25 and 0.75 respectively.

PBE, PBE0 and B3LYP are the functionals that are used to carry out DFT calculations in the present thesis.

3.3 Force Fields

Quantum mechanical calculations, even with the use of DFT-based methods, are restricted to relatively small systems (typically a few 100 atoms at most) because of the large computational cost that these kind of calcs require. An approach that has been successful to study systems with a large number of atoms (i.e. several 1000s) is based on forcefields (FFs). In this method, the potential energy of a given system can be obtained as a series expansion of terms that depend on the position of one, two or more atoms that has the following general expression for the potential energy of the system:

$$V(r_N) = \sum_{i=1}^N V_1(\vec{r}_i) + \sum_{i=1}^N \sum_{j \neq i}^N V_2(\vec{r}_i, \vec{r}_j) + \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots \quad 50$$

where N is the number of atoms, V_1 is the one-body term (only meaningful for atoms in presence of an external field), V_2 the two-body term and so on. Each of these terms contains different analytical functions with parameters that are fitted using experimental data or accurate quantum mechanical calculations to correctly reproduce the potential energies of the studied material for different atoms arrangement. The use of FFs drastically reduces the computational time, compared to DFT-based calculations, but with the issue of reducing the accuracy of the obtained results.

A huge variety of FFs have been developed and are currently available to study different systems. Not all FFs include the same number nor type of terms to compute the potential energy and their exact form depends on the materials to study.

For instance, FFs for ionic materials, which are of most interest in the present dissertation, are based on an ionic description²³. In this type of FF, the main interactions that are considered are Coulombic interactions, van der Waals attraction and Pauli repulsion.

The Coulombic interactions are treated considering the atoms as point-charges. For a N -atoms systems, these interactions are defined by Coulomb's Law:

$$V_{ij}^{Coulomb} = \sum_{i=1}^N \sum_{j \neq i}^N \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad 51$$

Where q_i is the charge of the i^{th} atom, ϵ_0 the vacuum permittivity and r_{ij} the distance between the i^{th} and j^{th} atoms. Treating the atoms as point-charges have some limitations when treating polarizable atoms, such as oxygen. To overcome this limitation and include polarization effects, the FF can be improved by using the core-shell model²⁴.

In this model, the atoms are divided in two parts: a massive core with a positive point-charge and a massless polarizable shell with negative charge. The core and the shell are bonded according to a harmonic potential:

$$V_{C-S} = \frac{1}{2}kr^2 \quad 52$$

where r is the distance between the core and the shell, and k is the constant of the harmonic potential which must be fitted in each FF. When using the core-shell model, the Coulombic interactions are evaluated for all the pairs of shells and cores belonging to different atoms, but not for those on the same atom.

To include van der Waals interactions and Pauli repulsion, multiple analytical potentials can be used. The most commonly used potentials for this purpose are Morse²⁵, Lennard-Jones²⁶ and Buckingham²⁷ potentials, with the latter often being the preferred selection for ionic materials. The Buckingham potential is described by:

$$V_{ij}^{Buck} = Ae^{-Br} - \frac{C}{r_{ij}^6} \quad 53$$

where A , B and C are fitted parameters and r_{ij} the distance between the i^{th} and j^{th} atoms. The first term of the potential corresponds to the Pauli repulsion whereas the second term is responsible for the description of the attraction due to van der Waals forces.

3.4 Global optimization

Chemical systems in nature rarely exist as a single isomer. Instead, a population of different isomers for a given chemical composition are typically found. Therefore, when experimentally measuring a property, the obtained result is the average of the properties of all the isomers in the population. Consequently, obtaining representative isomers is a crucial step when modelling a system using computational techniques.

The distribution of isomers in a system is typically determined by Boltzmann distribution. In general, for moderate temperatures, only the lowest energy isomer has non-negligible populations. For this reason, the finding of the most stable structure, or a small set of low energy isomers, for a given chemical composition, is in many cases enough to explain experimental results. The obtention of low energy isomers has, for example, been applied successfully to explain the infrared (IR) spectra of metal clusters obtained in cluster beam experiments^{28–31}.

The number of possible stable isomers, for a given chemical composition, *i.e.* isomers which lay on an energy minimum of the PES, depends exponentially on the number of atoms of the system. Therefore, even for small systems with just ~ 10 atoms, the number of possible isomers is often too large to try to exhaustively search for the minimum energy structure by hand. For this reason, different methodologies have been developed to speed up this process. It is important to bear in mind that these methodologies are commonly probabilistic and therefore one can never be sure that the obtained structure is the lowest energy one since the PES is not fully explored.

3.4.1 Monte Carlo Basin-Hopping

A methodology that has been successfully applied to efficiently explore the PES and search for low energy isomers in system with few tens of atoms is Monte Carlo Basin-Hopping (MCBH)³². In MCBH a transformation of the PES is applied defining the transformed energy $\tilde{E}$:

$$\tilde{E}(X) = \min\{E(X)\} \quad 54$$

where X is the vector of nuclear coordinates of the system and $\min$ indicates that an energy minimization, using any desired method, is carried out starting from the coordinates defined in X . In that way, one manages to avoid the full exploration of the PES. Instead, only the minima positions of the PES, although probably not all the minima, are explored. Figure 2 depicts the difference between the real PES and the one explored with MCBH algorithm.

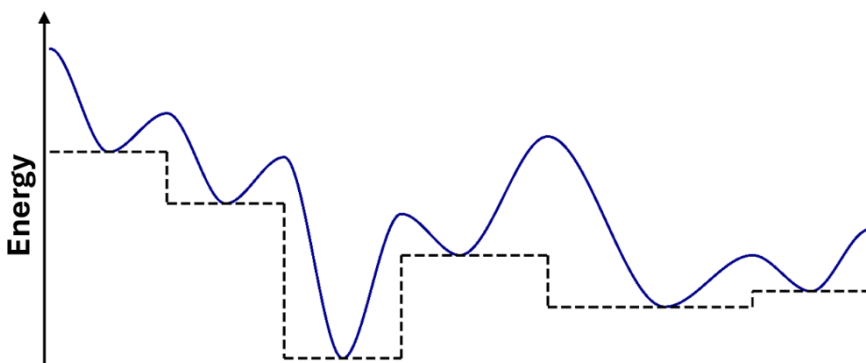


Figure 2: Real PES of a fictitious system (blue solid line) and PES explored by the MCBH algorithm (black dashed line) for the same system.

The procedure followed by the MCBH algorithm can be summarized in the following scheme:

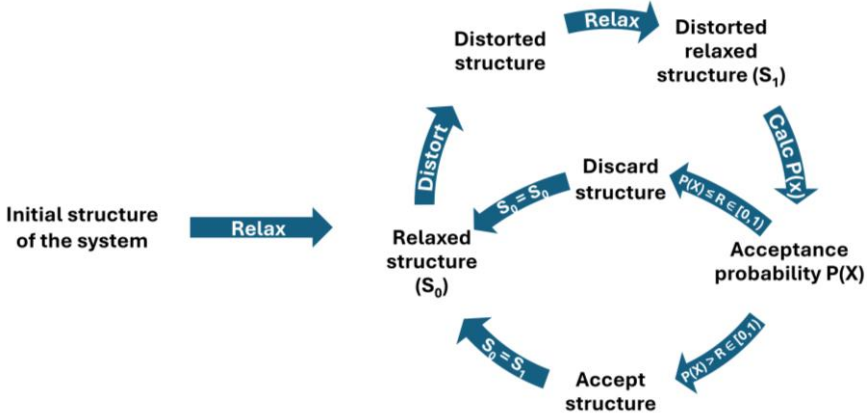


Figure 3: Schematic of the steps followed in MCBH algorithm

The distortion of the structures in the algorithm is carried out in a random way. The coordinates of all the atoms of the system are displaced by a random number between -1 and 1, multiplied by a parameter defined by the user. The acceptance probability is calculated as indicated in equation 55.

$$P(X) \begin{cases} = 1 ; & E(S_1) < E(S_0) \\ = e^{-\Delta E/k_B T} ; & E(S_1) > E(S_0) \end{cases} \quad 55$$

where ΔE is the energy difference between the S_1 and S_0 structures, k_B the Boltzmann constant and T a temperature without physical meaning.

If the energy of the current optimized structure (S_1) is lower than the previous one (S_0), the new structure is always accepted. Otherwise, a random number between 0 and 1 is compared to the Boltzmann distribution value. If the random number is lower, the structure is accepted and discarded if it is larger. The acceptance of structures that are energetically unfavorable compared to the current one allows to move away from deep regions of the PES. Indeed, there are versions of MCBH, as the one used in the present thesis, that allow the temperature in the Boltzmann distribution to be automatically adapted to obtain a value of the acceptance ratio fixed by the user, typically between 60-80%.

To efficiently explore the PES of any system and therefore to obtain good global minimum (GM) candidates, it is necessary to run MCBH for thousands of iterations and to use independent runs with different initial conditions. In consequence the computational cost needed to globally optimize a molecular system is huge since in each iteration an optimization is carried out. Although the optimization step can be performed using either FF or *ab initio* methods, the large number of needed iterations limit the use of relatively computationally expensive electronic structure methods (*e.g.* DFT) to very small systems.³³

For this reason, the use of FFs have been widely used within MCBH to accelerate GM searches. The main concern that one must face when using FFs is to be sure that there is a good correspondence between the relative energies obtained with the employed FFs and DFT energies. In consequence, the choice of a FF that is suitable to correctly describe the studied system is crucial to obtain well energy-ordered isomers. Nevertheless, a posterior relaxation of the lower energy isomers obtained in MCBH, with more accurate methods, is needed to assure which GM candidate is the lowest in energy. For this reason, in all the global optimization searches using MCBH carried out in the present thesis, the 50 energetically lowest lying obtained isomers were reoptimized with accurate DFT calculations.

The use of core-shell FFs adds another difficulty when using MCBH due to the difficulty in optimizing highly distorted isomers containing polarized ions. To solve this problem, a new variant of MCBH was developed in previous studies³⁴. This variant splits the optimization step into two phases. First, the distorted structure is optimized with a FF not containing shells. Next, another optimization with the FF containing shells is carried out to refine the final structure and energies. This version of the MCBH algorithm was employed in all the calculations on the present dissertation.

3.4.2 Global Optimization with First-principles Energy Expression

As mentioned in previous subsection, the use of MCBH is preferentially used with FFs capable of reasonably reproducing relative energies from DFT, or any other accurate *ab initio* method. However, one does not always have a suitable FF for the system that wants to study and making a suitable FF could be computationally expensive and technically hard to achieve. The direct use of DFT would of course solve the issue of needing a FF, however the use of DFT within MCBH, would increase exponentially the computational cost of the searches. Nevertheless, if one wishes to carry out the energy calculations at DFT level, machine-learning (ML) techniques can be used to reduce the time needed.

One such approach trains an ML model with a database of structures and properties obtained at DFT level. Afterwards, the search, including local relaxations, can be carried out on the machine-learned surrogate energy landscape which drastically reduces the search time. This approach has a drawback, that comes from the fact that it requires the generation of an extensive and diverse dataset to be used as training data, with the corresponding computational cost. A more efficient approach consists in applying the philosophy of active learning³⁵. Starting from a small and incomplete set of training data, the database is augmented *on the fly* by only computing the energies and properties of relevant structures. The selection of the next structure to analyze is not a straightforward step and must be chosen appropriately to carry out the searches in an efficient manner. A particular strategy that follows this idea is the global optimization with first-principles energy expression (GOFEE)³⁶.

This methodology has shown good results for obtaining low energy isomers that reproduce the IR spectra of cationic species obtained in cluster beam experiments³⁷. GOFEE uses a surrogate model based on Gaussian Processes (GP) to approximate the PES of the system. The main steps carried out in GOFEE are explained in detail below and summarized in Figure 4.

- 1- The first step in the process is to create a set of initial structures which are evaluated carrying out single point calculations using DFT to obtain its energies.

- 2- A ML surrogate model is trained using this initial dataset. The GP infers a distribution of functions consistent with the dataset of structures $X = (x_1, x_2, \dots, x_n)^T$ and their corresponding energies $E = (E_1, E_2, \dots, E_n)^T$. GP are defined by a mean $\mu(X)$ and a covariance function $k(x_i, x_j)$. The mean function is the expected value of the modeled function whereas covariance encodes assumptions about its smoothness and variability.
- 3- Multiple new candidate isomers are obtained by applying mutation operations to the current dataset.
- 4- The new structures obtained in step 3 are relaxed within the surrogate model.
- 5- Energies and uncertainty of the relaxed isomers (x_*) are predicted using equations 56 and 57 respectively.

$$E_{sur}(x_*) = k_*^T (K + \sigma_n^2 I)^{-1} [E - \mu(X)] + \mu(X) \quad 56$$

$$\sigma_{sur}(x_*)^2 = k(x_*, x_*) - k_*^T (K + \sigma_n^2 I)^{-1} k_* \quad 57$$

Here, $K = k(X, X)$ is the covariance matrix of the training data, $k_* = k(X, x_*)$ the covariance vector between training data and the mutated structure and finally, σ_n^2 is the noise variance.

- 6- To determine which candidate is the most promising one, an acquisition function is used. Multiple acquisition functions can be used such as the lower confidence bound:

$$f(x) = E_{sur}(x) - \tau \cdot \sigma_{sur}(x) \quad 58$$

where τ is a tunable parameter used to set the emphasis on the predicted uncertainty and therefore the degree of exploration in the search.

- 7- The isomer with the lowest acquisition function is selected and a single-point DFT calculation is carried out to obtain its “true” energy. In addition, a perturbed version of the selected isomer is also evaluated with DFT to obtain more information of the PES near the selected isomer.
- 8- The new isomer is added into the dataset of isomers and steps 2-8 are repeated until a certain number of iterations have been carried out or a convergence criterion reached.

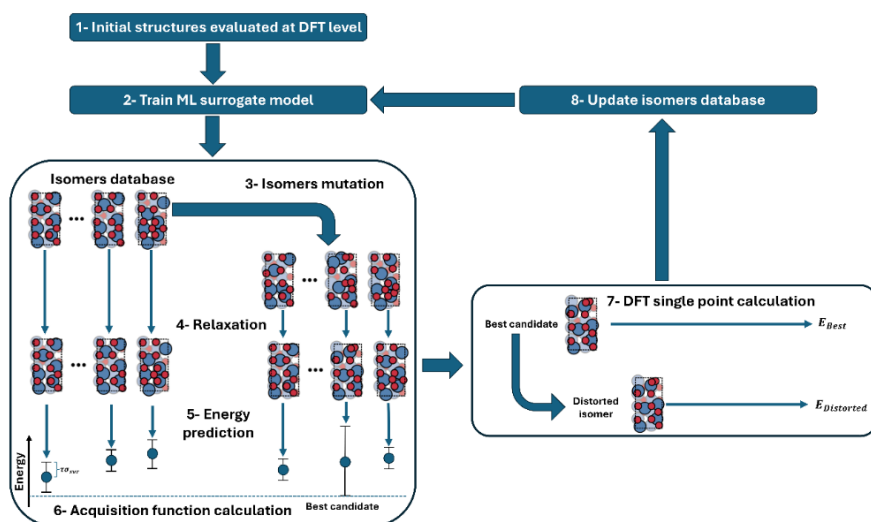


Figure 4: Schematic representation of the steps followed in the GOFEE algorithm. Adapted from reference 36.

3.5 Molecular Dynamics

Molecular Dynamics (MD) is a computational method used to study and analyze the physical motions of atoms and molecules. The interest in developing MD techniques dates as early as seventeenth century with the development of many of the numerical methods that are used nowadays. The first MD simulations using computers were carried out in 1955 to explore the effects of non-linearity in dynamical systems, results which would later raise questions related to irreversibility³⁸. Due to the improvement of computational hardware and software over the years, MD simulations grew in importance and now they are widely used with different objectives, such as to obtain transport properties³⁹ and IR spectra⁴⁰. The obtention of properties through MD is achieved by relating microscopic properties with macroscopic observables through statistical mechanics.

There are different approaches to carry out MD simulations. On the one hand, one can build the PES of the studied system by computing the energies of diverse conformations and afterwards use this data to fit an analytical expression or to train a ML-based PES. Then, the forces acting on the atoms during the simulation are obtained from the fitted PES. This approach has been successfully applied to obtain vibrational bound states of noble gases containing molecules of astronomical interest⁴¹. On the other hand, the energies and forces can be obtained *on the fly* for each conformation that the system undergoes during the MD simulation. This approach is the one used in the present dissertation. Their steps are summarized in Figure 5 and explained below.

First, from the initial position of the atoms, the forces acting in each atom are computed as the derivative of the potential energy, which can be obtained from quantum mechanical (*e.g.* DFT) or FF calculations. If one uses quantum mechanical methods, the MD simulations are known as *ab initio* MD (AIMD) whereas classical MD refers to the use of FFs to obtain the forces.

$$F_i = -\frac{\partial U}{\partial r_i} \quad 59$$

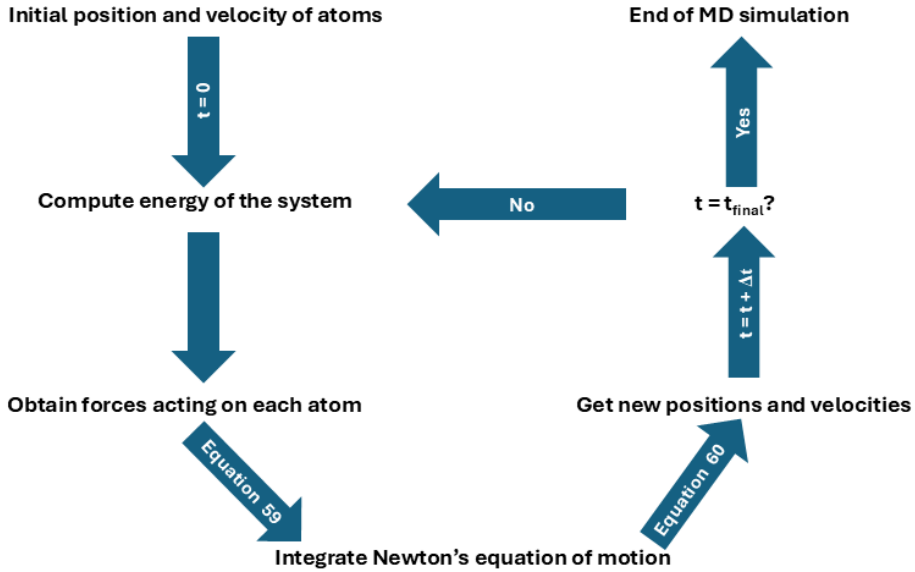


Figure 5: Schematic of the steps in a MD simulation.

Then, assuming that the nuclei are heavy enough to behave classically, Newton's second law is applied to obtain the new velocities of each atom:

$$m\ddot{r} = F \quad 60$$

where m is the mass of the atom, $\ddot{r}$ the second derivative of the position of the atom as a function of time *i.e.* its acceleration, and F the force acting on the atom.

Since the forces acting on each atom depends on the position of the rest, to obtain them one must solve a system of N coupled second order nonlinear differential equations. It is important to note that the resolution of Newton's equation of motion are deterministic *i.e.* there is a unique solution for a given set of initial positions and velocities. This solution is not trivial and analytical solutions cannot be obtained except in particular cases. Instead, they are discretized and solved by an iterative numerical procedure known as integrator. Different integrators are available such as leapfrog or Verlet algorithms.

An important property of the equations of motion is that they conserve the Hamiltonian of the system⁴² and in consequence, the total energy of the system is conserved. Therefore, the states explored using the equations of motion correspond to the microcanonical (*i.e.* NVE) ensemble *i.e.* during the dynamics the number of particles (N), the volume (V) and the energy (E) are constant. Other ensembles can also be used in MD simulations. For example, simulations of a system at constant temperature can be achieved by using the canonical ensemble. In this case, it is necessary to introduce the use of thermostat, which regulates the temperature of the system to keep it constant with the minimum possible fluctuations in temperature.

There are different thermostats that one can use in a MD simulation, each of which modifies in a different manner the Newton's equation of motion. For example, Berendsen thermostat⁴³ is mainly used in the relaxation phase of the MD simulations because it is very efficient to relax the system to reach the target temperature and because it does not correctly generate a canonical ensemble⁴⁴. For the production phase thermostats such as Nosé-Hoover^{45,46} or Bussi-Donadio-Parrinello⁴⁷ are suitable since they correctly sample the canonical ensemble.

Finally, one must also pay attention to the chosen timestep of the simulation *i.e.* the increase in time between two iterations. To assure numerical convergence of the integrators, the timestep must be small enough. However, a too small timestep would unnecessarily increase the number of iterations and in consequence the computational cost. For this reason, a good rule of thumb is to use a timestep that is one order of magnitude smaller than the fastest vibration of the system.

3.6 Vibrational frequency calculations

Interaction between matter and radiation is a powerful source of information to characterize materials and molecules. Depending on the energy of the radiation used different transitions can be studied giving rise to the vast field of spectroscopy which is of high importance in disciplines such as astronomy and chemistry.

For example, microwave spectroscopy allows to study transitions between the rotational levels of a molecule whereas IR spectroscopy gives information about ro-vibrational transitions. IR spectroscopy has been widely used to identify the composition of both organic and inorganic molecules in the laboratory⁴⁸. IR spectroscopy has also been used to gather information about molecules found in space such as polyaromatic hydrocarbons⁴⁹ (PAH) and silicates⁵⁰.

The vibrational IR spectra of a molecule can also be modelled using computational methods. In the following subsections the mathematical foundations for modelling IR spectra in different ways is presented.

3.6.1 Mathematical treatment of matter-radiation interaction

The Hamiltonian of a system interacting with an electromagnetic wave can be expressed as:

$$\hat{H} = \hat{H}^0 + \hat{H}_{m-r}(t) \quad 61$$

where $\hat{H}^0$ is the Hamiltonian of the system without interaction and $\hat{H}_{m-r}(t)$ describes the perturbation due to electromagnetic interaction. It can be described as follows:

$$\begin{aligned} \hat{H}_{m-r}(t) = & V_0 q - \vec{F}_0 \hat{\vec{d}} - \vec{B}_0 \hat{\vec{\mu}} \\ & - \frac{1}{2} \left[\left(\frac{\partial F_x}{\partial x} \right)_0 \hat{Q}_{xx} + \left(\frac{\partial F_x}{\partial y} \right)_0 \hat{Q}_{xy} + \dots \right. \\ & \left. + \left(\frac{\partial F_z}{\partial z} \right)_0 \hat{Q}_{zz} \right] \end{aligned} \quad 62$$

where the subscript 0 indicates the origin of coordinates, $\vec{F}$ and $\vec{B}$ are the electric and magnetic field vectors respectively, $\hat{\vec{d}}$ and $\hat{Q}$ are the electric dipole and quadrupole moments and $\hat{\vec{\mu}}$ is the magnetic dipolar moment.

Assuming that the matter-radiation interaction is not very intense, the system's WF evolution can be expressed as a linear combination of the eigenfunctions of the unperturbed Hamiltonian (ϕ_k):

$$\psi(t) = \sum_k c_{fi}(t) e^{-iE_f t/\hbar} \phi_f \quad 63$$

where the subindex i indicates that the coefficients are dependent on the initial state (ϕ_i).

Using time dependent perturbation theory, the coefficients c_{fi} can be expressed as:

$$c_{fi}(t) = \frac{1}{i\hbar} \int_{t_{initial}}^{t_{final}} e^{i\omega_{fi}t} \langle \phi_f | \hat{H}_{m-r}(t) | \phi_i \rangle dt \quad 64$$

where $t_{initial}$ and t_{final} indicate the duration of the interaction and ω_{fi} is the energy difference between the state ϕ_i and ϕ_f in units of angular frequency:

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} \quad 65$$

If one neglects the quadrupole, and higher order, terms in $\hat{H}_{m-r}(t)$, and assumes that the electromagnetic wave that interacts with the system is linearly polarized, equation 64 can be rewritten as¹²:

$$c_{fi}(t) = \frac{F \langle \phi_f | \left(\hat{d}_x + \frac{1}{c} \hat{u}_y \right) | \phi_i \rangle}{2\hbar} \left(\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} \right) \quad 66$$

With the obtention of these coefficients, the evolution of the system's WF during the interaction with radiation is determined applying equation 63. Therefore, it is now possible to calculate the probability of measuring a given energy of the system:

$$P_t(E_f) = |c_{fi}(t) e^{-iE_f t/\hbar}|^2 = |c_{fi}(t)|^2 \quad 67$$

If the measured energy is different from the initial one, the system is said to have undergone an energy transition and its probability is known as transition probability. By substituting equation 66 into equation 67 it is possible to derive the following expression for the transition probability¹²:

$$P(f \leftarrow i) = \frac{F^2}{\hbar^2} \left| \langle \phi_f | \left(\hat{d}_x + \frac{1}{c} \hat{\mu}_y \right) \phi_i \rangle \right|^2 \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} \quad 68$$

The probability function has a maximum when $\omega_{fi} = \omega$ and is ≈ 0 in other cases. Therefore, the transitions will be restricted to cases in which the radiation's frequency (ω) fulfills the following:

$$E_f - E_i = \hbar\omega \quad 69$$

Finally, by considering a polychromatic radiation, the probability transition can be expressed as follows:

$$P(f \leftarrow i) = \frac{t}{2\hbar^2\epsilon_0} \left| \langle \phi_f | \hat{d}_x \phi_i \rangle + \frac{1}{c} \langle \phi_f | \hat{\mu}_y \phi_i \rangle \right|^2 u(\omega_{fi}) \quad 70$$

where $u(\omega_{fi})$ is the energy density per angular frequency unit and ω_{fi} is expressed as:

$$\omega_{fi} = \frac{(E_f - E_i)2\pi}{h} \quad 71$$

From equation 70 one can conclude that the transition probability is non-zero when the integrals $\langle \phi_f | \hat{d}_x \phi_i \rangle$ or $\langle \phi_f | \hat{\mu}_y \phi_i \rangle$ are non-zero. The contribution of the second integral can be neglected since the contribution of the magnetic dipole is in general small. The first integral is non-zero in the cases in which the vibrations produce a change in the total dipole of the system. From the transition probability, the transition rules of IR absorption spectroscopy for polyatomic systems can be derived¹². These rules are summarized as:

$$\Delta v = +1(+2, +3, \dots) \text{ if } \Delta J = 0 \quad 72$$

$$\Delta v = +1 \text{ if } \Delta J = \pm 1 \quad 73$$

Where Δv and ΔJ indicate a change in the vibrational and rotational levels respectively. A schematic representation of the allowed transitions with $\Delta v = +1$ is depicted in Figure 6.

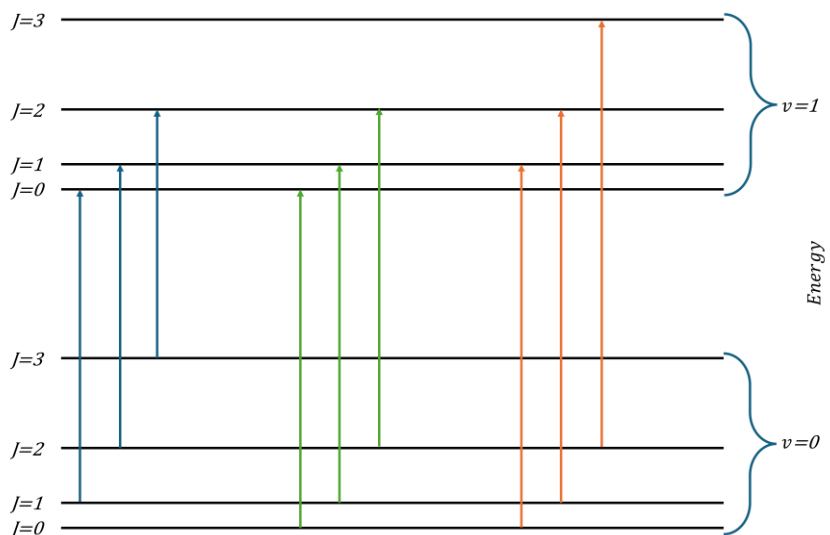


Figure 6: Schematic of the transitions with $\Delta v = +1$ and $\Delta J = -1$ (blue lines), $\Delta J = 0$ (green lines) or $\Delta J = +1$ (Orange lines)

The transition between the vibrational levels 0 and 1, with the rotational level being 0 is known as fundamental band. This is in general the most probable transition because the ground state is usually the most populated one. The transitions of the type $v_n \rightarrow v_{n+1}$ with $n \neq 0$ are known as hot bands and are observable when not only the vibrational ground state is populated. Finally, the transitions $v_n \rightarrow v_n$ with $n > 1$ and $\Delta J = 0$ are known as overtones.

These are not the only signals that are observed in an IR spectrum. For example, combinations bands appear when two vibrational modes couple giving rise to a new signal with frequency approximately being the sum or the difference of the separated frequencies. If the coupling is between a fundamental transition and an overtone or a combination band the vibration is known as Fermi resonance.

3.6.2 IR spectra calculation using the harmonic approximation

The harmonic approximation is one of the most used methods to compute the IR spectra of molecules due to its simplicity and accuracy. The main idea in this approach is to approximate the PES, near the equilibrium position, to a harmonic oscillator (see Figure 7). To do so, Taylor series near the equilibrium position is obtained:

$$U(q_1, \dots, q_{3N}) = U_e + \sum_{k=1}^{3N} \left(\frac{\partial U}{\partial q_k} \right)_e q_k + \frac{1}{2} \sum_{k=1}^{3N} \sum_{l=1}^{3N} \left(\frac{\partial^2 U}{\partial q_k \partial q_l} \right)_e q_k q_l + \dots \quad 74$$

where the subindex e indicates that derivatives must be taken in the equilibrium position and q_k are the mass-weighted displacements of each atom in the 3 spatial directions:

$$q_1 = (X_1 - X_{1equil})\sqrt{m_1}; q_2 = (Y_1 - Y_{1equil})\sqrt{m_1}; q_3 = (Z_1 - Z_{1equil})\sqrt{m_1}; \dots \quad 75$$

Since the Taylor expansion is taken in the equilibrium position, the first derivative of the potential energy is 0, and taking as the zero of energy the minimum of the PES U_e is also 0. Finally, by neglecting higher order terms in the Taylor series, the PES can be approximated to a harmonic oscillator:

$$U(q_1, \dots, q_{3N}) = \frac{1}{2} \sum_{k=1}^{3N} \sum_{l=1}^{3N} \left(\frac{\partial^2 U}{\partial q_k \partial q_l} \right)_e q_k q_l \quad 76$$

In this way, one can describe the PES near the equilibrium position in a rather simple, although accurate, manner.

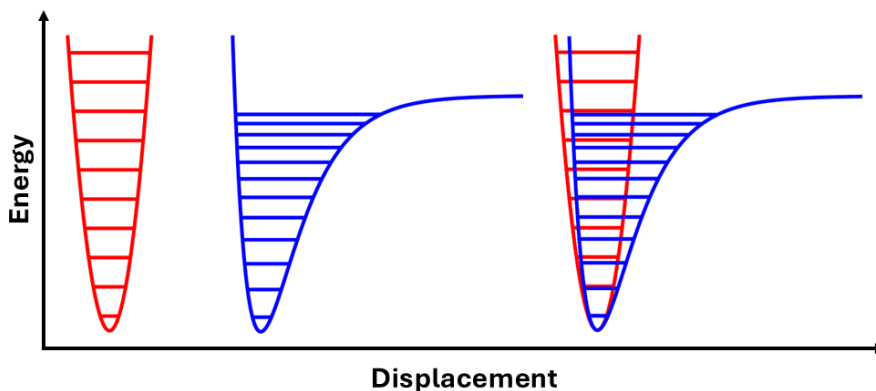


Figure 7: Comparison between the harmonic (red) and the real potential (blue). Horizontal lines correspond to vibrational levels. Notice that in the real potential the levels are closer as the energy increases.

The second derivatives in equation 76 can be expressed as a matrix, which is known as the Hessian. To obtain the harmonic frequencies one needs to diagonalize the Hessian. The $3N$ eigenvalues (λ_i) are then used to obtain the frequencies using the following expression:

$$v_i = \frac{\sqrt{\lambda_i}}{2\pi} \quad 77$$

From the set of $3N$ frequencies that are obtained only $3N-6$ (or $3N-5$ in the case of linear molecules) frequencies must be considered because the rest are due to translational and rotational movements.

Although harmonic approximation gives good results compared to experimental data in many cases, it is not perfect because the real PES is not being used. First, under the harmonic approximation only fundamental transitions can be computed and therefore overtones cannot be obtained. This in principle is not a big problem because in general the overtones are much less intense than fundamental bands and therefore, generally, they are not of great importance to characterize molecules. On the other hand, since under the harmonic approximation each vibration is considered independent from the rest, it is not possible to obtain signals arising from combination bands or Fermi resonances.

Finally, another limitation of this approach that is worth mentioning is that no information about the shape and broadening of the peak can be gathered since only pairs of frequency-intensity are obtained. To have a visual representation of the computed spectrum the normal procedure is to apply Gaussian functions, with a given width characterized by the full width at half maximum (FWHM), in the positions in which the peaks are obtained.

A great advantage of using harmonic approximation, besides its simplicity to compute vibrational frequencies, is that allows to analyze, for each frequency, which kind of vibrational movement produce the signal. Since the matrix of second derivatives is real and symmetric, one can diagonalize it by using a orthogonal transformation matrix:

$$L^t U L = \lambda \quad 78$$

where λ is the diagonalized U matrix. Defining the normal coordinates as:

$$Q_i = \sum_{k=1}^{3N} L_{ki} q_{ki} \text{ for } i = 1, \dots, 3N \quad 79$$

one can rewrite the mass-weighted displacements in equation 75 as:

$$q_k = \sum_{i=1}^{3N} L_{ki} Q_i \quad 80$$

Assuming the harmonic oscillator motion of the nuclei of the system, one must solve the classical equations of motion for a set of 3N independent oscillators. Its resolution leads to the result that each coordinate Q_i oscillates with a sinusoidal movement:

$$Q_i = B_i \sin(2\pi v_i t + b_i) \text{ for } i = 1, \dots, 3N \quad 81$$

where B_i and b_i are arbitrary integration constants and v_i are the frequencies obtained from equation 77.

By substituting equation 81 into equation 80 the general expression for the mass-weighted cartesian coordinates displacement as function of time is obtained.

$$q_k = \sum_{i=1}^{3N} L_{ki} B_i \sin(2\pi v_i t + b_i) \quad 82$$

These equations describe an oscillatory movement of the nuclei near their equilibrium position and can be hard to obtain. However, a particular set of solutions describing especial movements, known as normal modes, can be obtained by cancelling B_i and b_i parameters for all the coordinates except one. For instance, the displacement of the atoms in the j^{th} vibrational frequency can be obtained from:

$$q_k = L_{kj} B_j \sin(2\pi v_j t + b_j) \text{ for } k = 1, \dots, 3N \quad 83$$

3.6.3 Inclusion of anharmonicity in calculations of IR spectra

Although the harmonic approximation generally yields good results, it is important to bear in mind that it is not perfect and that for some systems might lead to incorrect interpretation of experimental results. The first limitation of the harmonic approximation is that it assumes that the vibrational levels are equally spaced whereas in reality, the levels become closer at higher energies (see Figure 7). This causes the harmonic frequencies to appear at lower (larger) wavenumber (wavelength). To solve this problem, an easy, although often practically useful, approach is to apply a scaling factor to the obtained frequency to reduce (augment) its value. Nevertheless, this is not always satisfactory and more robust methods have been developed to obtain better vibrational frequencies. The main idea behind the methods that allow the consideration of anharmonicities is to consider a better approximation of the PES near the equilibrium position by including higher order terms in equation 74. This increases the difficulty of the theoretical treatment of vibrational frequencies and at the same time increases the computational cost of its calculations due to the need of computing higher order derivatives.

The most successful approaches that have been developed to deal with this problem are based on the vibrational self-consistent field⁵¹ or vibrational second-order perturbation theory⁵². The latter being especially efficient in the computation of third and fourth derivatives of the PES by means of numerical differentiation⁵³. Analytical formulas to compute combination bands and overtones have also been obtained^{54,55} as well as methods to obtain anharmonic intensities⁵⁶.

3.6.4 MD-based IR spectra

Another technique that allows to obtain the IR spectra is molecular dynamics. By using MD one can obtain anharmonicities in the frequencies as well as combination bands directly from the atom movements analysis during a period of time.

The transition probability (equation 70) can be also expressed as the Golden Rule of time-dependent quantum-mechanical perturbation theory⁵⁷:

$$P(f \leftarrow i) = \frac{\pi F^2}{2\hbar^2} |\langle \phi_f | \hat{d} \phi_i \rangle|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega)] \quad 84$$

where δ is the Dirac delta function. From this expression one can derive the equation to obtain the absorption cross section⁵⁷:

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c n} \omega (1 - e^{-\beta \hbar \omega}) \sum_f \sum_i p_i |\langle \phi_f | \hat{d} \phi_i \rangle|^2 (\omega_{fi} - \omega) \quad 85$$

p_i being the probability that the studied system is found in the i^{th} vibrational state, c is the lightspeed, n the refraction index of the medium, $\beta = k_B/T$ with k_B being the Boltzmann's constant and T the temperature.

From absorption cross section one can define the absorption lineshape $I(\omega)$ to express the absorption cross section in a different way:

$$I(\omega) = \frac{3\hbar c n \alpha(\omega)}{4\pi^2 \omega (1 - e^{-\beta \hbar \omega})} = 3 \sum_f \sum_i p_i |\langle \phi_f | \hat{d} \phi_i \rangle|^2 (\omega_{fi} - \omega) \quad 86$$

$$\alpha(\omega) = \frac{4\pi^2}{3\hbar c n} \omega (1 - e^{-\beta \hbar \omega}) I(\omega) \quad 87$$

The only term that is necessary to compute to obtain the absorption cross section is the lineshape. Lineshapes can be computed from the Fourier transform of the dipole autocorrelation function:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} C_{\mu}(t) dt \quad 88$$

$$C_{\mu}(t) = \langle \mu(0) \cdot \mu(t) \rangle \quad 89$$

being $\mu(t)$ the total dipole moment of the system at each moment and $\langle \rangle$ indicates the average.

From MD simulations one can obtain the dipole autocorrelation function during the simulation. To do that, it is necessary to first run the MD simulations of the system using either classical or *ab initio* MD. Then, at each step of the simulation the total dipole moment of the system needs to be computed. Finally, with the information of the change of the dipoles the autocorrelation function can be calculated and the IR spectrum obtained.

A more intuitive way to comprehend how to obtain an IR spectrum from MD simulations is to understand what information can be gathered from the autocorrelation function. It allows to find repeating patterns in data series. In the dipole autocorrelation function what is obtained are the dipole moments that are repeated the most during the simulations. Since the IR spectrum signals are related to a change in the dipole moment (equation 70) the dipole moments that are repeated, and therefore captured from autocorrelation function, are the ones that will produce signals in the spectrum.

3.7 Computational modelling software used

This section provides an overview of the different software employed to perform the various calculations throughout this thesis. For each software, a summary of its main features is presented, along with a description of the specific types of calculations carried out using each code.

3.7.1 FHI-aims

The Fritz-Haber Institute *ab initio* materials simulations (FHI-aims)⁸ is a computational modelling software designed to carry out accurate electronic structure calculations based on the DFT method using NAOs as its basis functions. FHI-aims can model both isolated (e.g. molecules and clusters) and periodic systems (e.g. crystals) and, for both, allows efficient use of hybrid functionals.

A distinguishing feature of FHI-aims is its exceptional scalability and parallelization capabilities, which allow for the efficient exploitation of modern high-performance computing architectures.

In this thesis, FHI-aims has been used to carry out the relaxation of nanosilicates structures using DFT, as well as the computing of harmonic vibrational frequencies and AIMD simulations.

3.7.2 Gaussian

Gaussian⁵⁸ is a widely used computational chemistry software package renowned for its capability to perform electronic structure calculations using a diverse range of theoretical methods. The software supports a variety of approaches for electronic structure calculations, including HF, DFT and post-HF methods. Moreover, it also supports various force fields and semi-empirical methods.

A fundamental aspect of Gaussian is its reliance on GTOs for constructing the different available basis set. In that sense, Gaussian provides a wide selection of predefined basis sets with different accuracy. Gaussian is a molecular based code and has very limited capabilities for treating extended periodic systems.

In this thesis, Gaussian software has been employed to compute the 0 K anharmonic IR spectra of nanosilicates.

3.7.3 GULP

The General Utility Lattice Program (GULP)⁵⁹ is a versatile computational modelling software designed to model materials, across different dimensionalities, including 3D crystals, 2D surfaces, 1D polymers and molecules and clusters. The main strength of GULP is its ability to model the materials using FFs. Although this software can carry out MD simulations, its primary focus is on obtaining material properties derived from the energy and its first, second and third derivatives with respect to atomic positions⁶⁰. GULP supports a wide range of interatomic potentials (IP) including those typically required for ionic solids, semiconductors and metals.

In the present thesis GULP has been used to carry out optimization of nanosilicates using different FFs, and to compute their vibrational frequencies.

3.7.4 LAMMPS

The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)⁶¹ is a highly versatile and widely used open-source software package for classical MD simulations. One of the standouts features of LAMMPS is its efficient parallel computing architecture. Additionally, LAMMPS supports hardware accelerators such as GPUs, significantly enhancing computational performance and enabling the efficient simulation of large-scale systems. As in the case of GULP, LAMMPS supports a wide variety of IPs, making it applicable to a wide range of materials and biomolecules.

In the present thesis, LAMMPS has been employed to carry out MD simulations of nanosilicate nucleation processes to handle efficiently the simulation of larger nucleated grains.

3.7.5 Custom codes

In addition to the previously described software packages, a series of custom Python codes developed previously within the research group were employed to perform various computational tasks. These codes were designed to facilitate global optimization searches by leveraging external simulation software through interfaces.

For global optimizations using MCBH method, a Python script was used to manage nanosilicate structures and their structural distortions. This script employs the Atomic Simulation Environment (ASE)⁶² as a framework to handle the system structures and the optimization steps. The structural relaxations were carried out using the GULP software through the interface provided by ASE.

A similar custom code was employed for global optimization searches using GOFEE. In this case ASE was again used as an interface to run the single point energy calculations, which were performed using the FHI-aims software. Additionally, the GOFEE interface, implemented in Python, was integrated into the code to manage the machine learning model training and population handling throughout the search process.

To treat the complex problem of nucleated growth of silicate dust grains a code, previously developed in the research group, was used. This code makes use of ASE and LAMMPS to describe the temperature controlled sequential additions of monomers to a growing grain. This code is described in chapter 9.

3.8 References

- ¹ Born, M. and Oppenheimer, R.; Zur Quantentheorie der Molekeln. *Annalen Der Physik*. **1927**, 389(20), 457-484
- ² Hartree, D. R. The wave mechanics of an atom with a non-Coulomb central field. Part I. Theory and methods. *Mathematical Proceedings of the Cambridge Philosophical Society*. **1928**. 24(1), 89-110.
- ³ Fock, Vladimir. Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Zeitschrift für Physik*. **1930**, 61, 126-148.
- ⁴ Slater, John C. The theory of complex spectra. *Physical review*. **1929**, 34(10), 1293.
- ⁵ Moller, C. and Plesset, Milton S. Note on an approximation treatment for many-electron systems. *Physical review*. **1934**, 46(7), 618.
- ⁶ Čížek, Jiří. On the correlation problem in atomic and molecular systems. Calculation of wavefunction components in Ursell-type expansion using quantum-field theoretical methods. *The Journal of Chemical Physics*. **1966**, 45(11), 4256-4266.
- ⁷ Boys, S. F. Electronic wave functions-I. A general method of calculation for the stationary states of any molecular system. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*. **1950**, 200, 1063, 542-554.
- ⁸ Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. Ab initio molecular simulations with numeric atom-centered orbitals. *Comput. Phys. Commun.* **2009**, 180, 2175– 2196.
- ⁹ Hohenberg, P. and Kohn, W. J. P. R. Density functional theory (DFT). *Phys. Rev.* **1964**, 136, B864.
- ¹⁰ Levy, M. Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem. *Proceedings of the National Academy of Sciences*. **1979**, 76(12), 6062-6065.
- ¹¹ Lieb, E.H. Density functionals for coulomb systems. *Int. J. Quantum Chem.* **1983**, 24(3), 243-277.

- ¹² Paniagua, J. C. and Alemany I Cahner, P. *Química quàntica*. Llibres de l'Índex, **2017**. ISBN 10: 8495317095
- ¹³ Kohn, Walter; Sham, Lu Jeu. Self-consistent equations including exchange and correlation effects. *Physical review*. **1965**, 140(4A), A1133.
- ¹⁴ Dirac, P. A. M. Note on exchange phenomena in the Thomas atom. *Mathematical proceedings of the Cambridge philosophical society*. **1930**. 26(3), 376-385.
- ¹⁵ Vosko, S. H.; Wilk, L. and Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Canadian Journal of physics*. **1980**. 58(8) 1200.
- ¹⁶ Becke, Axel D. Perspective: Fifty years of density-functional theory in chemical physics. *The Journal of chemical physics*. **2014**. 140(18) 18A301.
- ¹⁷ Becke, Axel D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical review A*. **1988**. 38(6), 3098.
- ¹⁸ Lee, Chengteh; Yang, Weitao; Parr, Robert G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical review B*. **1988**. 37(2), 785.
- ¹⁹ Perdew, John P.; Burke, Kieron; Ernzerhof, Matthias. Generalized gradient approximation made simple. *Physical review letters*. **1996**. 77(18), 3865.
- ²⁰ Johnson, Benny G.; Gill, Peter M. W.; Pople, John A. The performance of a family of density functional methods. *The Journal of chemical physics*. **1993**. 98(7), 5612-5626.
- ²¹ D. Becke. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys*. **1993**, 98(7), 5648–5652.
- ²² Adamo, Carlo; Barone, Vincenzo. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *The Journal of chemical physics*. **1999**, 110(13), 6158-6170.
- ²³ Tosi, Mario P. Cohesion of ionic solids in the Born model. *Solid state physics*. **1964**. 16, 1-120.

- ²⁴ Dick J. R. and B. G. and Overhauser, A. W. Theory of the dielectric constants of alkali halide crystals. *Physical Review*. **1958**, 112(1), 90.
- ²⁵ Morse, Philip M. Diatomic molecules according to the wave mechanics. II. Vibrational levels. *Physical review*. **1929**, 34(1), 57.
- ²⁶ Lennard-Jones, John E. Cohesion. *Proceedings of the Physical Society*. **1931**. 43(5), 461.
- ²⁷ Buckingham, Richard A. The classical equation of state of gaseous helium, neon and argon *Proc. R. Soc. Lond. A*. **1938**, 168(933), 264-283.
- ²⁸ Haertelt, M.; Fielicke, A.; Meijer, G.; Kwapien, K.; Sierka, M. and Sauer, J. Structure determination of neutral MgO clusters—hexagonal nanotubes and cages. *Physical Chemistry Chemical Physics*. **2012**, 14(8), 2849-2856.
- ²⁹ Kwapien, K.; Sierka, M.; Döbler, J.; Sauer, J.; Haertelt, M. and Fielicke, A. Structural Diversity and Flexibility of MgO Gas-Phase Clusters. *Angewandte Chemie International Edition*. **2011**, 50(7), 1716-1719.
- ³⁰ Gehrke, R.; Gruene, P.; Fielicke, A.; Meijer, G.; and Reuter, K. Nature of Ar bonding to small Co_n^+ clusters and its effect on the structure determination by far-infrared absorption spectroscopy. *The Journal of chemical physics*. **2009**. 130(3), 034306.
- ³¹ Fielicke, A.; Mitric, R.; Meijer, G. J. M.; Bonacic-Koutecky, V. and Helden, G. J. The structures of vanadium oxide cluster– ethene complexes. A combined IR multiple photon dissociation spectroscopy and DFT calculation study. *Journal of the American Chemical Society*. **2003**. 125(51), 15716-15717.
- ³² Wales, David J. and Doye, Jonathan PK. Global optimization by basin-hopping and the lowest energy structures of Lennard-Jones clusters containing up to 110 atoms. *The Journal of Physical Chemistry A*. **1997**. 101(28), 5111-5116.
- ³³ Jiang, S.; Liu, Y-R.; Huang, T.; Wen, H.; Xu, K-M.; Zhao, W-X.; Zhang, W-J. and Huang, W. Study of $\text{Cl}^-(\text{H}_2\text{O})_n$ ($n = 1-4$) using basin-hopping method coupled with density functional theory. *Journal of Computational Chemistry*. **2014**, 35(2), p. 159-165.

- ³⁴ Cuko, A.; Maciá, A.; Catalayud, M. and Bromley, S. T. Global optimisation of hydroxylated silica clusters: A cascade Monte Carlo Basin Hopping approach. *Computational and Theoretical Chemistry*. **2017**, 1102, 38-43.
- ³⁵ Smith, Justin S.; Nebgen, Ben.; Lubbers, Nicholas; Isayev, Olexandr; Roitber, Adrian E. Less is more: Sampling chemical space with active learning. *The Journal of chemical physics* **2018**, 148(24), 241733.
- ³⁶ Bisbo, Malthe K. and Hammer, Bjørk. Efficient global structure optimization with a machine-learned surrogate model. *Physical review letters*. **2020**, 124(8), 086102.
- ³⁷ De Donato, A. A.; Ghejan, B. A.; Bakker, J. M.; Bernhardt, T. M.; Bromley, S. T. and Lang, S. M. Gas-Phase Production of Hydroxylated Silicon Oxide Cluster Cations: Structure, Infrared Spectroscopy, and Astronomical Relevance. *ACS Earth and Space Chemistry*. **2024**, 8(6), 1154.
- ³⁸ Fermi, E.; Pasta, P.; Ulam, S.; and Tsingou, M. *Studies of the nonlinear problems*. Los Alamos National Laboratory (LANL), Los Alamos, NM (United States), **1955**.
- ³⁹ Aimoli, Cassiano G.; Maginn, Edward J.; Abreu, Charles RA. Transport properties of carbon dioxide and methane from molecular dynamics simulations. *The Journal of chemical physics*, **2014**, 141(13), 134101.
- ⁴⁰ Berens, Peter H.; Wilson, Kent R. Molecular dynamics and spectra. I. Diatomic rotation and vibration. *The Journal of Chemical Physics*. **1981**, v74(9), 4872-4882.
- ⁴¹ Montes de Oca Estévez, María Judit; Valdés, Álvaro and Prosmi, Rita. A kernel-based machine learning potential and quantum vibrational state analysis of the cationic Ar hydride (Ar_2H^+). *Physical Chemistry Chemical Physics*. **2024**, 26(8), 7060-7071.
- ⁴² Tuckerman, Mark E. and Martyna, Glenn J. Understanding modern molecular dynamics: Techniques and applications. *The Journal of Physical Chemistry B*. **2000**, 104(2), 159-178.

- ⁴³ Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A. and Haak, J.R. Molecular dynamics with coupling to an external bath. *The Journal of chemical physics*. **1984**, 81(8), 3684-3690.
- ⁴⁴ Harvey, Stephen C.; Tan, Robert K.-Z.; Cheatham III, Thomas E. The flying ice cube: velocity rescaling in molecular dynamics leads to violation of energy equipartition. *Journal of computational chemistry*, 1998, vol. 19, no 7, p. 726-740.
- ⁴⁵ Nosé, Shūichi. A molecular dynamics method for simulations in the canonical ensemble. *Molecular physics*. **1984**, 52(2), p. 255-268.
- ⁴⁶ Hoover, William G. Canonical dynamics: Equilibrium phase-space distributions. *Physical review A*. **1985**, 31(3), 1695.
- ⁴⁷ Bussi, Giovanni; Donadio, Davide; Parrinello, Michele. Canonical sampling through velocity rescaling. *The Journal of chemical physics*. **2007**, 126(1), 014101.
- ⁴⁸ Coates, John. Interpretation of infrared spectra, a practical approach. *Encyclopedia of analytical chemistry*. **2000**.
- ⁴⁹ Joblin, C.; d'Hendecourt, L.; Léger, A. and Défourneau, D. Infrared spectroscopy of gas-phase PAH molecules. 1: Role of the physical environment. *Astronomy and Astrophysics*. **1994**, 281(3), 923-936.
- ⁵⁰ Angeloni, R.; Contini, M.; Ciroi, S. and Rafanelli, P. Silicates in D-type symbiotic stars: An Infrared Space Observatory overview. *The Astronomical Journal*. **2007**, 134(1), 205.
- ⁵¹ Bowman, Joel M. The self-consistent-field approach to polyatomic vibrations. *Accounts of Chemical Research*. **1986**, 19(7), 202-208.
- ⁵² Willets, A.; Handy, N. C.; Green, W. H. and Jayatilaka, D. Anharmonic corrections to vibrational transition intensities. *Journal of Physical Chemistry*. **1990**, 94(14), 5608-5616.
- ⁵³ Barone, V. Anharmonic vibrational properties by a fully automated second-order perturbative approach. *Journal of Chemical Physics*. **2005**, 122(1), 14108-14108.

- ⁵⁴ Miller, W. H.; Hernandez, R.; Handy, N. C.; Jayatilaka, D. and Willets, A. Ab initio calculation of anharmonic constants for a transition state, with application to semiclassical transition state tunneling probabilities. *Chemical physics letters*. **1990**, 172(1), 62-68.
- ⁵⁵ Vázquez, J. and Stanton, J. F. Simple (r) algebraic equation for transition moments of fundamental transitions in vibrational second-order perturbation theory. *Molecular Physics*. **2006**, 104(3), 377-388.
- ⁵⁶ Barone, V.; Bloino, J.; Guido, C. A. and Lipparini, F. A fully automated implementation of VPT2 Infrared intensities. *Chemical Physics Letters*. **2010**, 496(1), 157-161.
- ⁵⁷ McQuarrie, D. A. Statistical Mechanics. University Science Books, **2000**.
- ⁵⁸ Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT. **2016**.
- ⁵⁹ Gale, J. D. and Rohl, A. L. The general utility lattice program (GULP). *Molecular Simulation*. **2003**, 29(5), 291-341.
- ⁶⁰ Gale, J. D. GULP: Capabilities and prospects. *Zeitschrift für Kristallographie-Crystalline Materials*. **2005**, 220(5-6), 552-554.

⁶¹ Thompson, A. P.; Aktulga, H. M.; Berger, R.; Bolintineanu, D. S.; Brown, W. M.; Crozier, P. S.; Veld, P. J.; Kohlmeyer, A.; Moore, S. G.; Nguyen, T. D.; Shan, R.; Stevens, M. J.; Tranchida, J.; Trott, C. and Plimpton, S. J. LAMMPS—a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Computer physics communications*. **2022**, 271, 108171.

⁶² Larsen, A. H.; Mortensen, J. J.; Blomqvist, J.; Castelli, I. E.; Christensen, R.; Dulak, M.; Friis, J.; Groves, M. N.; Hammer, B. and Hargus, C. The atomic simulation environment—a Python library for working with atoms. *Journal of Physics: Condensed Matter*. **2017**, 29(27), 273002.

CHAPTER 4

How Does Temperature Affect the Infrared Vibrational Spectra of Nanosized Silicate Dust?

4.1 Introduction

The presence of silicates in various astronomical environments can be primarily demonstrated through their absorption and emission features in the IR spectra observed across a wide range of sightlines¹⁻³. As has already been discussed in Chapter 1 the observed broad signals centered around ~10 and ~18 microns have been assigned to bulk silicates of different chemical compositions by fitting observations with laboratory-made analogues. However, nanosized silicate grains are expected to exhibit significant differences in their IR spectra due to their small size, large surface-to-volume ratio, and structural diversity⁴. Although the presence of nanosilicates in the ISM is widely accepted, their identification through observations has not been yet confirmed. Moreover, the potential contribution of nanosilicates to the observed 10- and 18-micron signals of bulk silicates is unclear.

The advent of advanced telescopes, such as the James Webb Space Telescope (JWST) offers an unprecedented opportunity to study the IR spectra with exceptional sensitivity. The mid-IR instrument (MIRI), covering the 5 to 28-micron range⁵, is particularly well-suited to observe (nano)silicates.

The interpretation of these observations and the information that can be gathered from them can be significantly enhanced by computational chemistry tools. In that direction, Macià *et al.*⁶ used computational modelling to obtain the structures and the IR spectra of global optimized nanosilicates (from 1 to 10 units), of both pyroxene (MgSiO_3)_N and olivine (Mg_2SiO_4)_N stoichiometries to assess their differences with respect to bulk silicates. Regarding IR spectra, they found that combining the spectra of all the globally optimized isomers results in a slight blue shift of the 10-micron signal, a broad feature centered at 11.5 microns, and another signal around 15 microns, while no significant signals were obtained around 18 microns. These features are clearly distinct from bulk silicates, highlighting the different behaviour between bulk and nanosilicate materials. Despite providing solid basis for distinguishing between bulk and nanosilicate IR features, the harmonic approximation used in their study introduces some limitations, which are discussed in detail in Chapter 2 (section 2.6).

One could argue that the low temperature in the ISM would make anharmonicities not play a relevant role in the IR spectra making the harmonic results sufficiently accurate for direct comparison with observations. While this argument is valid at low temperatures, nanosilicates are likely to be found in a wide number of environments with varying temperatures. For instance, they are formed in the regions around AGB stars at temperatures between 800 and 1000 K,⁷ and may populate the inner region of protoplanetary disks where typical temperatures reach around 400 K.⁸ These larger temperatures can influence the IR spectra due to anharmonicities, especially in small grains. Even in the cold ISM, small nanosilicates could be stochastically heated to temperatures above 100 K,⁹ potentially leading to discrepancies with respect to ~0 K harmonic IR spectra.

The first computational effort to assess anharmonic effects on nanosilicates IR was conducted by Valencia *et al.*¹⁰ who calculated harmonic and anharmonic modes of pyroxene and olivine monomers using high level ab initio electronic structure methods, establishing benchmark data for these systems.

In this chapter, we extended the study of anharmonicity and temperature effects to pyroxene and olivine dimer clusters using DFT calculations with B3LYP and PBE0 functionals. Initially, we validate our methodology by comparing the harmonic frequencies of the monomers with the benchmark data from Valencia *et al.* To assess temperature effects on the dimers, we derive their IR spectra from AIMD simulations following the procedure detailed in Appendix A. The use of AIMD to obtain anharmonic effects has been previously used in the study of different organic compounds¹¹.

First, we establish the necessary length of the AIMD simulations to obtain a converged spectrum, *i.e.* when the position, intensity and shape of the derived signals do not change significantly. Once convergence is established, we compare the spectra obtained at 400 and 800 K with the 0 K harmonic spectra. To analyze the origin of the difference between the spectra, we computed the 0 K anharmonic spectra *i.e.* considering higher order terms in Taylor expansion to build the PES around the equilibrium position and allowing coupling between vibrational modes. Finally, we made a further study of the AIMD trajectory of the olivine dimer species to analyze the emergence of a new signal as temperature increases.

4.2 Results

To assess the accuracy of our method to obtain vibrational frequencies we compare the frequencies of the pyroxene and olivine monomers obtained using PBE0 and B3LYP functionals with those obtained from state-of-the-art methods in reference 10. The selection of PBE0 and B3LYP functionals is motivated by previous studies where both functionals have successfully reproduced the harmonic frequencies of olivine crystalline bulk material (forsterite) with good agreement with respect to experimental values¹². Moreover, PBE0-based DFT calculations have also yielded good agreement between harmonic and experimental frequencies for enstatite, after a systematic correction¹³.

The results presented in Tables 1 and 2 indicate that harmonic frequencies obtained with both functionals are in good agreement with those considered as benchmark data. In the case of the olivinic monomer (Table 1) both functionals exhibit similar performance, with average deviations $\sim 2.3\%$. On the other hand, for the pyroxenic monomer (Table 2) PBE0 functional has a better agreement with respect to the benchmark data.

Benchmark Frequencies (cm^{-1})	B3LYP Frequencies (cm^{-1})	Ratio B3LYP	PBE0 Frequencies (cm^{-1})	Ratio PBE0
1258.5	1244.2	0.989	1262.2	1.003
1017.6	990.2	0.973	1012.2	0.995
943.9	919.7	0.974	934.6	0.990
782.7	764.5	0.977	774.7	0.990
687.8	677.4	0.985	687.6	1.000
621.1	603.2	0.971	610.8	0.983
550.8	537.7	0.976	543.6	0.987
421.2	408.6	0.970	412.6	0.980
399.9	392.4	0.981	393.0	0.983
298.0	289.5	0.971	291.7	0.979
272.0	270.6	0.995	272.4	1.001
230.9	225.3	0.976	225.7	0.977
139.2	132.8	0.954	126.6	0.909
112.8	110.4	0.979	103.2	0.915
69.3	68.6	0.990	67.9	0.980

Table 1: Comparison of Mg_2SiO_4 monomer frequencies obtained with PBE0 and B3LYP functionals with those obtained using high-level quantum chemistry calculations in reference 10.

Benchmark Frequencies (cm ⁻¹)	B3LYP Frequencies (cm ⁻¹)	Ratio B3LYP	PBE0 Frequencies (cm ⁻¹)	Ratio PBE0
1278.6	1256.2	0.982	1275.5	0.998
872.7	846.4	0.970	873.4	1.001
824.7	806.4	0.978	823.0	0.998
710.1	681.5	0.960	691.3	0.974
618.1	595.1	0.963	606.9	0.982
483.2	465.4	0.963	469.8	0.972
431.6	417.2	0.967	425.3	0.985
310.0	297.0	0.958	301.5	0.973
165.4	159.9	0.967	162.1	0.980

Table 2: Comparison of MgSiO₃ monomer frequencies obtained with PBE0 and B3LYP functionals with those obtained using high-level quantum chemistry calculations in reference 10.

To determine the minimum duration required for an AIMD simulation to obtain converged IR spectra, we performed AIMD simulations for the pyroxene dimer (P-2) and computed its IR spectrum at different time intervals. The obtained spectra are displayed in Figure 1, in which it is possible to observe that an AIMD of 40 ps length is long enough to obtain a converged spectrum.

Once the minimum simulation length has been established, we investigated the effect of temperature on the resulting spectra. For this purpose, we obtained the IR spectra of the P-2 cluster from AIMD simulations at 400 and 800K and compared them with the harmonic spectra using both the PBE0 and B3LYP functionals.

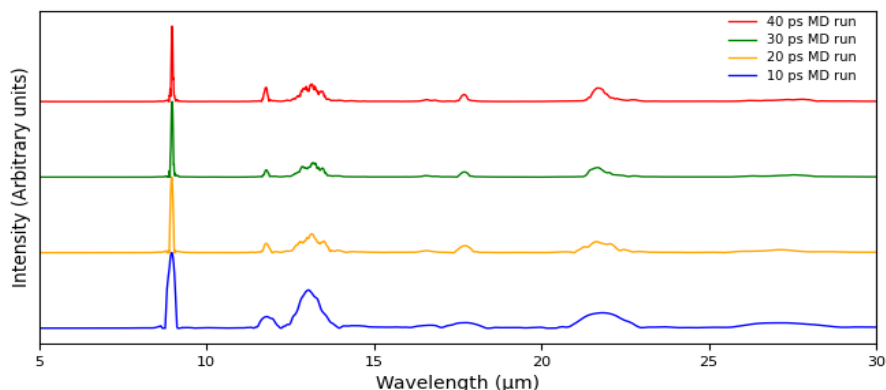


Figure 1: Comparison of the IR spectra of the P-2 cluster obtained from AIMD simulations with different simulation durations. The PBE0 exchange and correlation functional was used. IR Intensities are normalized to the height of the largest signal. Each signal has been broadened with using gaussian functions with 10 cm^{-1} FWHM.

As one can observe from the results shown in figure 2 and 3 the harmonic spectra obtained with both functionals are very similar. However, when temperature effects are included, the IR spectra evolve similarly in both cases, although, the intensities of some of the signals differ depending on the used functional. These differences can be attributed to the difference in the description of the PES, and as a consequence of the deviation of the AIMD trajectory away from the 0 K energy minimum.

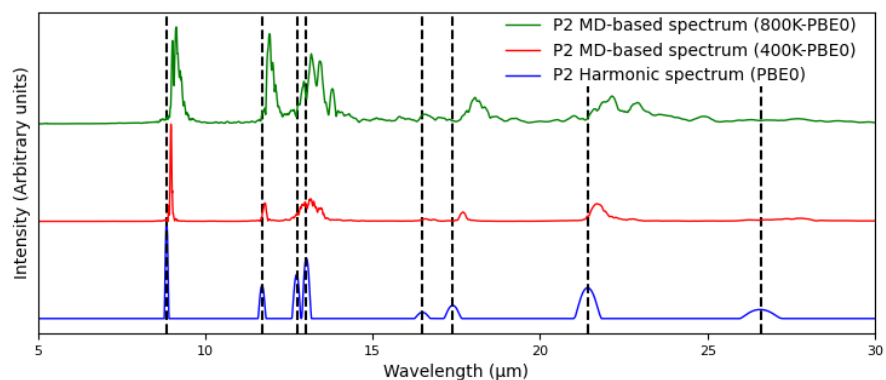


Figure 2: Comparison of the IR spectra obtained using the harmonic approximation (blue) and AIMD at 400 K (red) and 800 K (green) of the P-2 cluster using the PBE0 functional. Dashed vertical lines indicate the position of the harmonic signals. IR Intensities are normalized to the height of the largest signal. Each signal has been broadened with using gaussian functions with 10 cm^{-1} FWHM.

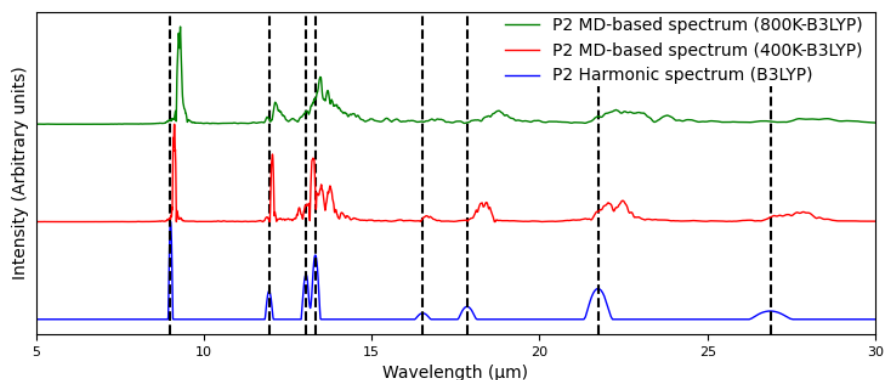


Figure 3: Comparison of the IR spectra obtained using the harmonic approximation (blue) and AIMD at 400 K (red) and 800 K (green) of the P-2 cluster using the B3LYP functional. Dashed vertical lines indicate the position of the harmonic signals. IR Intensities are normalized to the height of the largest signal. Each signal has been broadened with using gaussian functions with 10 cm^{-1} FWHM.

A comparison between the AIMD and harmonic spectra reveals notable discrepancies. First, there is a shift in the position of the peaks towards larger wavelengths, with the magnitude of the shift increasing with temperature. This shift is not uniform across all signals (see Tables 3 and 4). The temperature-dependent increase in the shift can be attributed to the fact that higher temperatures allow the cluster to explore regions of the PES further from the equilibrium position, where the harmonic approximation becomes less accurate. Therefore, the observed shifts are likely the result of anharmonic effects.

On the other hand, the two harmonic peaks around $13 \mu\text{m}$ transform into a multiple signal in the AIMD-based spectra using both functionals. To understand the origin of these multiple peaks, likely arising from combination bands, we computed the 0 K anharmonic IR spectrum (*i.e.* using a more realistic PES and allowing the coupling of vibrational modes which originate combination bands). As shown in Figure 4, the differences between the harmonic and anharmonic spectra are qualitatively similar to those observed between harmonic and AIMD-based spectra. The anharmonic signals are generally shifted towards larger wavelengths, and the double signal $\sim 13 \mu\text{m}$ is formed by multiple signals in the anharmonic one. The analysis of the origin of these new signals reveals that they correspond to combination bands involving low-frequency vibrational modes, including some that are non-active in the harmonic IR.

Harmonic PBE0 (μm)	AIMD 400 K (μm)	Ratio 400K	AIMD 800 K (μm)	Ratio 800 K
8.85	8.98	1.015	9.23	1.043
11.69	11.78	1.001	11.99	1.026
12.73 13.03	13.11	1.018	13.47	1.046
16.47	16.59	1.007	16.61	1.008
17.41	17.71	1.017	18.27	1.049
21.42	21.69	1.013	22.53	1.052
26.53	27.71	1.044	27.69	1.044

Table 3: Comparison of wavelength positions of main signals of the P-2 spectrum in the range 8-28 μm obtained from harmonic and AIMD calculations using the PBE0 functional.

Harmonic B3LYP (μm)	AIMD 400 K (μm)	Ratio 400K	AIMD 800 K (μm)	Ratio 800 K
9.01	9.13	1.013	9.27	1.029
11.95	12.05	1.008	12.17	1.018
12.94 13.05	13.56	1.043	13.69	1.053
16.52	16.64	1.007	16.88	1.022
17.85	18.38	1.030	18.67	1.046
21.77	22.27	1.023	22.61	1.039
26.87	27.74	1.032	28.15	1.048

Table 4: Comparison of wavelength positions of main signals of the P-2 spectrum in the range 8-28 μm obtained from harmonic and AIMD calculations using the B3LYP functional.

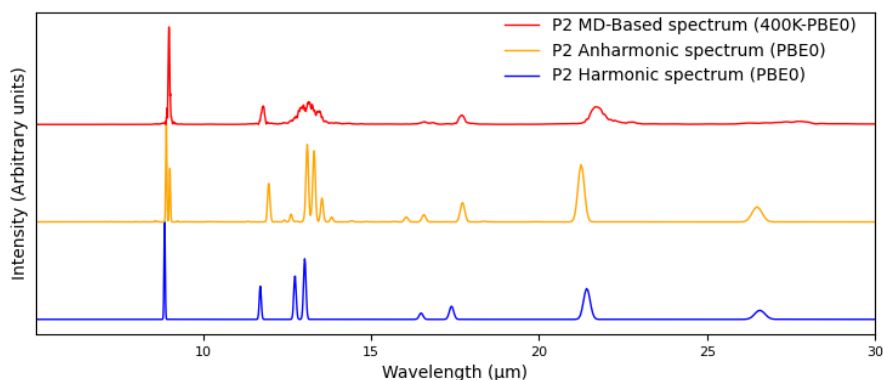


Figure 4: Comparison of the IR spectra obtained using the harmonic approximation (blue), anharmonic (orange) and 400 K AIMD-based (red) IR spectra of P-2. IR Intensities are normalized to the height of the largest signal. Each signal has been broadened with using gaussian functions with 10 cm^{-1} FWHM.

To extend this analysis to clusters with olivinic composition, we carried out the same study on the olivinic dimer (O-2). As in the case of the pyroxenic cluster, the results using PBE0 or B3LYP functionals are very similar with just small variation in the intensities of the AIMD-based signals. The comparison between the harmonic and AIMD-based spectra reveals similar discrepancies, including the appearance of a new signal around $10 \mu\text{m}$ at both 400 and 800 K (see Figure 5).

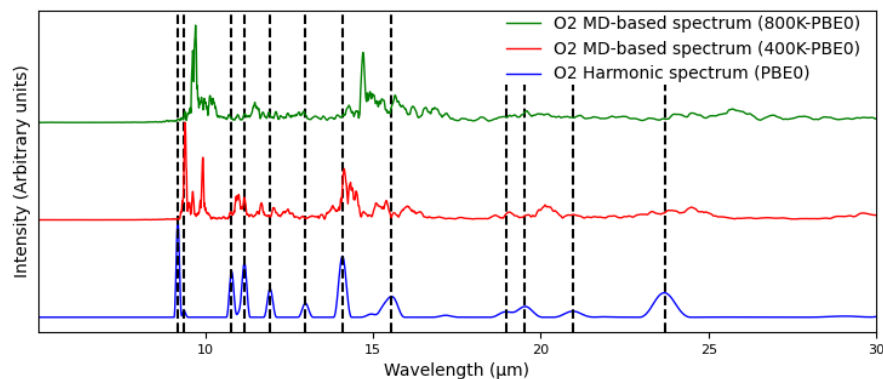


Figure 5: Comparison of the IR spectra obtained using the harmonic approximation (blue) and AIMD at 400 K (red) and 800 K (green) of the O-2 cluster using the PBE0 functional. Dashed vertical lines indicate the position of the harmonic signals. IR Intensities are normalized to the height of the largest signal. Each signal has been broadened with using gaussian functions with 10 cm^{-1} FWHM.

One possible explanation for the emergence of this new signal is the presence of combination bands as observed for the P-2 cluster. However, in this case, the anharmonic spectrum (Figure 6) does not show the presence of any signal around the 10 microns region, indicating that its presence in the AIMD-based spectrum must have a different origin. Indeed, the appearance of the signal is clearly dependent on the temperature because the AIMD-based spectrum obtained at 100 K does not show this signal either.

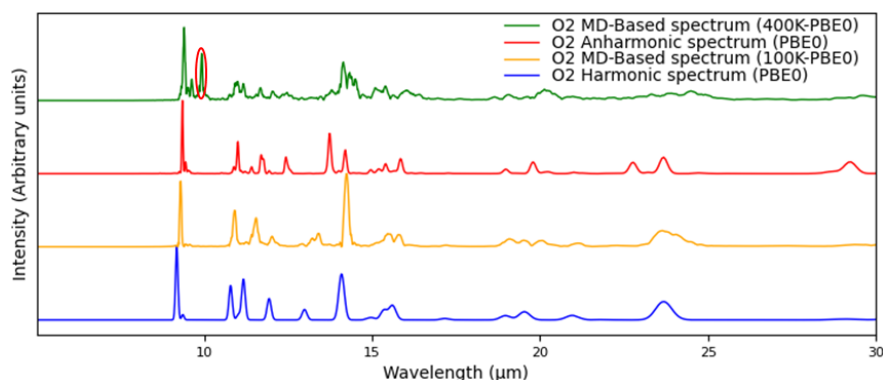


Figure 6: Comparison of the IR spectra obtained using the harmonic approximation (blue) anharmonic (red) AIMD at 100 K (orange) and 800 K (green) of the olivine dimer using the PBE0 functional. IR Intensities are normalized to the height of the largest signal. Each signal has been broadened with using gaussian functions with 10 cm^{-1} FWHM.

To rationalize the origin of this signal, we analyzed the trajectory of the cluster during the different AIMD simulations, finding that in the 400 and 800 K simulations the O-2 cluster undergoes a conformation change (See Figure 7).

This conformational change can be tracked by monitoring the Mg-O distance highlighted in Figure 7. As one can see from the results in Figure 8, at 100 K the cluster does not have enough energy to switch between both conformations. However, at 400 K the energy is enough to allow the cluster to shift between both conformations. Finally, in the 800 K simulation, the Mg-O distance oscillates between the two extreme values. This indicates that the cluster is found in a highly mobile fluxional state between the two conformations. Conformational fluxionality has been already reported at low temperatures in other small oxide clusters¹⁴.

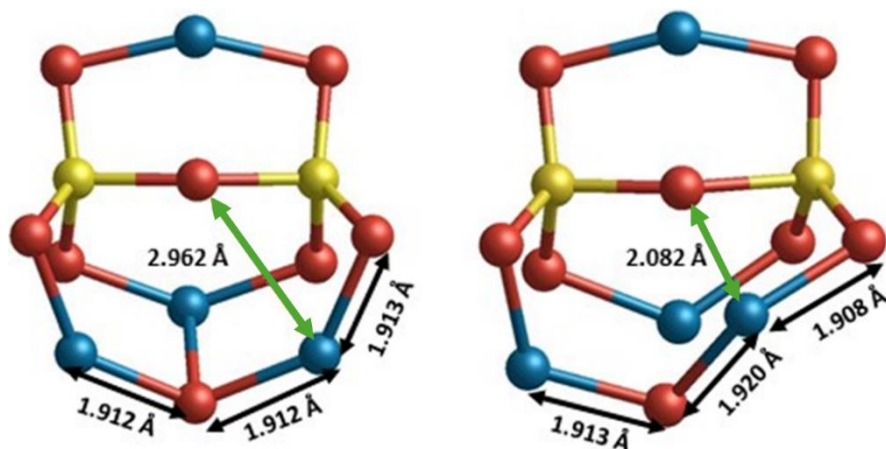


Figure 7: Optimized O-2 conformations that are sampled during the AIMD simulations at 400 and 800 K. Green arrows indicate the Mg-O distance used to track the conformational change in Figure 8. Oxygen, magnesium and silicon atoms are depicted as red, blue and yellow spheres respectively.

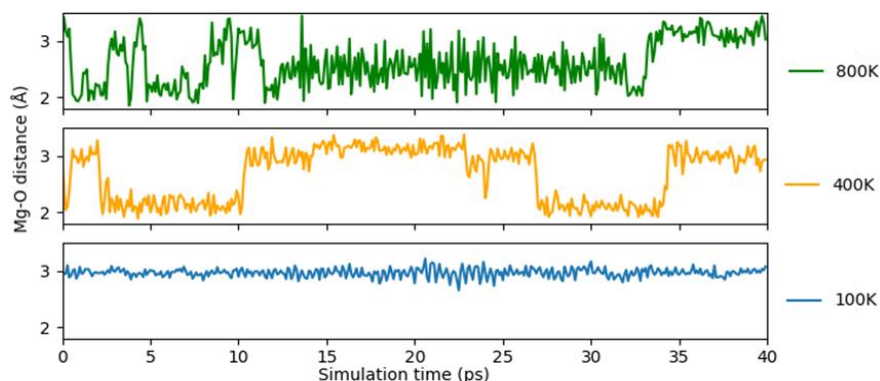


Figure 8: Evolution of the Mg-O distance used to track the conformational change during AIMD simulations at different temperatures.

Finally, in Figure 9, the comparison between the 400 K AIMD-based spectrum and the harmonic spectrum resulting from combining the harmonic spectra of the conformers in Figure 7 is shown. From there, it is possible to observe that there is a much better agreement with respect to the results in Figure 5. This improvement is especially because the signal $\sim 10 \mu\text{m}$ has now its counterpart in the harmonic spectrum, although the rest of the spectrum is now also in better agreement.

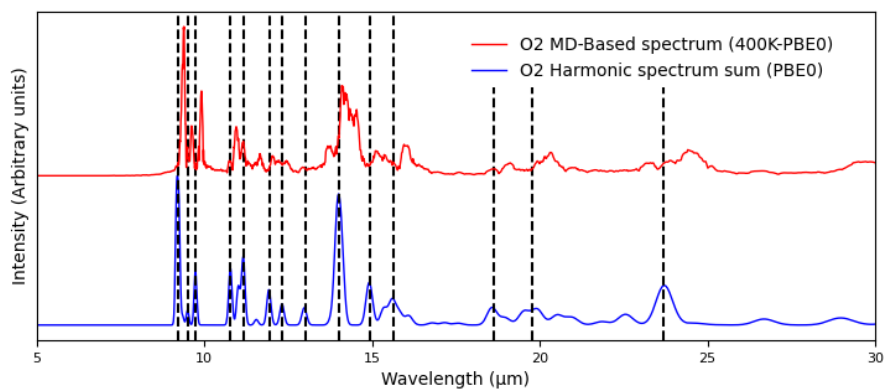


Figure 9: Comparison between the spectrum obtained from summing the harmonic spectra of both O-2 conformers (blue) and the 400 K AIMD-based spectrum (red). Intensities are normalized to the height of the highest signal.

4.3 Conclusions

These findings, combined with the additional data and analysis provided in the accompanying research article, support the following conclusions:

- 1- The use of DFT with the PBE0 and B3LYP functionals give vibrational frequencies that are in good agreement with those obtained from state-of-the-art quantum chemistry calculations. This is especially true for DFT-based spectra obtained using the PBE0 functional.
- 2- We have established the minimum duration that AIMD should have to obtain a converged spectrum using DFT in combination with either the PBE0 or B3LYP functionals. Our results show that a total duration of 40 ps, with 2 ps for the temperature equilibration phase are sufficient to obtain converged IR spectra for the studied nanosilicates.
- 3- The IR spectra of the studied silicate nanoclusters are significantly influenced by temperature specifically at the astronomically relevant temperatures of 400 K (inner regions of protoplanetary disks) and 800 K (circumstellar dust nucleation regions). As temperatures increase, the spectra exhibit larger anharmonic broadenings, redshifts in the signal's wavelength and the appearance of new signals not captured within a 0 K harmonic approach.
- 4- The comparison of the AIMD derived spectra with 0 K anharmonic calcs shows that most of the new signals that are obtained in the AIMD based spectra, either at 400 or 800 K, arise from combination bands of low-frequency modes, including some that are non-active in the 0 K harmonic spectra.

- 5- In the olivine dimer a new signal is observed in the AIMD derived spectra at higher temperatures (*i.e.* 400 and 800 K), which is not the result of combination bands, or any other anharmonic effect. This signal arises from a conformational pre-melting transition between two energetically similar conformers. This causes the resulting AIMD spectra to be a combination of those of the two conformers.

4.4 References

- ¹ Goumans, T. P. M.; Bromley, S. T. Efficient Nucleation of Stardust Silicates via Heteromolecular Homogeneous Condensation. *Mon. Not. R. Astron. Soc.* **2012**, 420, 3344–3349.
- ² Gail, Hans-Peter and Sedlmayr, Erwin. *Physics and chemistry of circumstellar dust shells*. Cambridge, UK: Cambridge University Press, **2013**. ISBN 13: 9780521833790.
- ³ Gobrecht, D.; Cherchneff, I.; Sarangi, A.; Plane, J. M. C. and Bromley, S. T. Dust formation in the oxygen-rich AGB star IK Tauri. *Astronomy & Astrophysics*. **2016**, 585, A6.
- ⁴ Bromley, Stefan T.; de P. R. Moreira, I.; Neyman, Konstantin M. and Illas, Francesc. Approaching nanoscale oxides: models and theoretical methods. *Chemical Society Reviews*. **2009**, 38(8), 2657-2670.
- ⁵ James Webb Space Telescope Home Page, <https://science.nasa.gov/mission/webb/> (accessed 17-02-2025).
- ⁶ Escatllar, A. M.; Lazaukas, T.; Woodley, S. M. and Bromley, S. T. Structure and properties of nanosilicates with olivine (Mg₂SiO₄)_N and pyroxene (MgSiO₃)_N compositions. *ACS Earth and Space Chemistry*. **2019**, 3(11), 2390-2403.
- ⁷ Sogawa, H and Kozasa, T. On the Origin of Crystalline Silicate in Circumstellar Envelopes of Oxygen-rich Asymptotic Giant Branch Stars. *The Astrophysical Journal*. **1999**, 516(1), L33.
- ⁸ Heese, S.; Wolf, S.; Dutrey, A.; Guilloteau, S. Spread of the dust temperature distribution in circumstellar disks. *Astron. Astrophys.* **2017**, 604, A5.

⁹ Draine, B. T. and Li, Aigen. Infrared emission from interstellar dust. I. Stochastic heating of small grains. *The Astrophysical Journal*. **2001**, 551(2), 807.

¹⁰ Valencia, E. M.; Worth, C. J.; Fortenberry, R. C. Enstatite (MgSiO_3) and forsterite (Mg_2SiO_4) monomers and dimers: highly detectable infrared and radioastronomical molecular building blocks. *Mon. Not. R. Astron. Soc.* **2020**, 492, 276–282.

¹¹ Thomas, M.; Brehm, M.; Fligg, R.; Vöhringer, P. and Kirchner, B. Computing vibrational spectra from ab initio molecular dynamics. *Physical Chemistry Chemical Physics*. **2013**, 15(18), 6608-6622.

¹² De La Pierre, M.; Orlando, R.; Maschio, L.; Doll, K.; Ugliengo, P. and Dovesi, R. Performance of six functionals (LDA, PBE, PBESOL, B3LYP, PBE0, and WC1LYP) in the simulation of vibrational and dielectric properties of crystalline compounds. The case of forsterite Mg_2SiO_4 . *Journal of computational chemistry*. **2011**, 32(9), 1775-1784.

¹³ Demichelis, R.; Suto, H.; Noël, Y.; Sogawa, H.; Naoi, T.; Koike, C.; Chihara, H.; Shimobayashi, N.; Ferrabone, M. and Dovesi, R. The infrared spectrum of ortho-enstatite from reflectance experiments and first-principle simulations. *Monthly Notices of the Royal Astronomical Society*. **2012**, 420(1), 147-154.

¹⁴ Viñes, F.; Carrasco, J.; Bromley, S. T. Nanoscale thermal stabilization via permutational premelting. *Phys. Rev. B*. **2012**, 85, 195425.

How Does Temperature Affect the Infrared Vibrational Spectra of Nanosized Silicate Dust?

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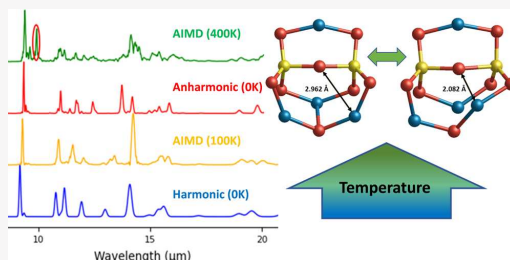


Article Recommendations



Supporting Information

ABSTRACT: Magnesium-rich silicates are pervasive throughout the universe and are found in many astronomical environments as small dust grains. Most of the information we have about such silicate dust comes from infrared (IR) observations, whereby the prominent $\sim 9.7\ \mu\text{m}$ Si–O stretching and $18\text{--}20\ \mu\text{m}$ O–Si–O bending vibrational bands are used as identifying signatures. During the initial stages of silicate dust nucleation around aging stars, the nascent grains are nanosized and heated to $800\text{--}1000\ \text{K}$. Later, the larger fully formed grains are ejected into the cold interstellar medium and are subsequently heavily processed (e.g., by shattering and sputtering), likely leading to an abundant population of nanosilicate grains. Such ultrasmall grains can eventually form a dust component of protoplanetary disks, where they can be again heated to a few hundred degrees. Although nanosilicate grains are astrochemically important and are likely carriers of the ubiquitous anomalous microwave emission, they have yet to be unambiguously identified through observation. The advent of the James Webb Space Telescope, with IR instruments of unrivalled sensitivity covering the $5\text{--}28\ \mu\text{m}$ wavelength range, promises to open a window on these elusive, but presumably abundant, species. Here, we examine Mg-rich ultrasmall silicate clusters with both olivine (Mg_2SiO_4) and pyroxenic (MgSiO_3) stoichiometries and accurately calculate their IR spectra at temperatures between 0 and $800\ \text{K}$. Although this temperature range is below that required to anneal bulk magnesium silicates ($\sim 1000\ \text{K}$), we show that nanosized grains can exhibit significant anharmonic motions and premelted structural conformational fluxionality even at $400\ \text{K}$. As a result, we demonstrate that the IR spectra of nanosilicates are highly sensitive to temperature, which should thus be considered when attempting to identify these species.



KEYWORDS: *Ab initio molecular dynamics, infrared spectra, silicate nanoclusters, cosmic dust grains, olivine, pyroxene, finite temperature modeling*

INTRODUCTION

Silicate nanoclusters (i.e., SiO_2 -containing mineral species possessing between about ten and a few hundred atoms) are likely to be important in numerous astrophysical environments. First, these species are intrinsic intermediates in the high-temperature formation of larger silicate cosmic dust grains around aging stars^{1,2} and supernovae.³ Through dust grain collisions and supernovae shocks, a proportion of these larger grains are shattered into nanoclusters,⁴ likely leading to a significant population of ultrasmall silicate grains throughout the interstellar medium (ISM).⁵ These nanosilicates are likely seeds for the astrochemical formation of H_2 molecules^{6,7} and ices,⁸ and are also strong candidates for being the source of the ubiquitous anomalous microwave emission.^{9–11}

The primary means to obtain information about astronomical silicate dust is through its infrared (IR) spectra.¹² From the comparison of observed IR spectra with those from experimentally prepared bulk silicates, it has been established that astronomical silicates are Mg-rich and tend to have stoichiometries between that of pyroxene (MgSiO_3) and

olivine (Mg_2SiO_4).¹³ Although nanosilicates are likely to be abundant, both their IR intensities and line positions are very dependent on their wide-ranging structure, shape, and size. Nanosilicate IR signals are thus likely to be spread over a wide range of wavelengths, leading to individual signals that are smaller than those of larger dust grains, thus complicating their unambiguous identification. The advent of the highly sensitive James Webb Space Telescope (JWST),¹⁴ with IR instruments covering an ideal range of wavelengths to observe silicates ($5\text{--}28\ \mu\text{m}$), will provide a unique opportunity to provide better estimates of nanosilicate grain prevalence. To prepare for such observations, the IR spectra of these species in different

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astrophysical environments should be accurately determined to assist in their identification.

Although silicate nanoclusters have not yet been experimentally produced, the IR spectra of nanoclusters of other oxides (e.g., MgO ,¹⁵ Si_nO_m ,¹⁶ Al_2O_3 ,¹⁷ Mn_2O_3 ,¹⁸ TiO_2 ¹⁹) have been obtained in cluster beam experiments. In these cases, comparisons of the measured spectra with the calculated IR spectra from density functional theory (DFT)-based calculations have often been useful for determining the nanocluster structures. In such studies, it is typically assumed that the experimental vibrational spectra (i) are due to one, or at most a few, of the lowest energy nanocluster isomers, and (ii) can be well captured by calculations using the harmonic approximation (i.e., that forces on atoms can be derived from harmonic potential energy wells). The first assumption relies on the experiment to provide conditions for the most thermodynamically favored nanocluster isomers to be accessible. Typically, this entails formation at relatively high temperatures in order to overcome isomerization barriers. However, for assumption (ii) to be applicable, the clusters should be at a relatively low temperature during the measurement of their IR spectra. For modern cluster beam experiments on ionic binary oxides, these assumptions appear to hold,^{15,19} indicating that the respective potential energy surface for such isomers is dominated by a very few deep-lying and thermally accessible energy minima. In other cluster beam experiments on more complex bimetallic ternary oxide systems, however, both assumptions appear more open to question.²⁰

The issue of temperature is even more pertinent to silicate clusters in circumstellar environments. Small silicate clusters first form at temperatures between 800 and 1000 K around aging Asymptotic Giant Branch stars.^{21,22} At the other end of the stellar cycle, silicate grains are again heated in the protoplanetary disks of newly forming stars. Here, in the inner part of such disks, smaller nanosized dust grains are typically heated to ~ 400 K.²³ Silicate grains are also thought to be abundant in the atmospheres of hot giant exoplanets,²⁴ where they are heated to ≥ 950 K. Similarly, heated silicate grains are also found in brown dwarf atmospheres, where the presence of small grains has been proposed to explain the observed reddening.²⁵ Even in the cold ISM, very small silicate species of the size considered herein would be stochastically heated to well above 100 K by their interaction with starlight.²⁶

Herein, we focus on the effect of temperature on the IR spectra of small ternary silicate nanoclusters at two astrophysically relevant temperatures (400 and 800 K). We note that larger silicate grains are typically classified as being amorphous or crystalline, where temperatures > 800 K are assumed to be required to anneal the former into the latter.^{27,28} In our study, we consider temperatures below that required for silicate crystallization. In addition, we note that nanosilicates inherently do not exhibit bulk crystalline-like IR spectra, either due to surface reconstruction²⁹ or due to the higher energetic stability of noncrystalline atomic ordering at this small size.³⁰

Although the harmonic approximation often provides IR spectra in good agreement with the experiment, it has limitations arising from the fact that the real potential energy surface (PES) is not being used. The harmonic approximation builds a PES around the 0 K equilibrium geometry of the studied system using a truncated Taylor series. Each vibrational mode is exact and independent in such an approach. As such, harmonic vibrational spectra contain no information about the shape and broadening of the peaks due to couplings between

different vibrational states. Anharmonicities typically reveal themselves in measured IR spectra as asymmetrically broadened and shifted peaks. A widely used procedure to make the calculated harmonic IR spectra better resemble experimental spectra is to empirically broaden the calculated harmonic peaks by applying Gaussian or Lorentzian functions centered at the frequencies of the calculated vibrations. Similarly, if the degree of anharmonicity is known to be small, and mainly leads to only small shifts in peak positions, then one can simply uniformly scale the magnitude of the harmonic frequencies to approximate anharmonic effects.

In addition to not recovering anharmonic broadening/shifts, IR spectra derived using harmonic potentials can only reveal fundamental vibrational transitions. Furthermore, since under the harmonic approximation, each vibrational mode is considered independent, combination bands and Fermi resonances are also not captured. Finally, under the harmonic approximation, the energy difference between all of the vibrational levels is the same. In more realistic anharmonic energy wells, levels become closer in energy as the energy of the vibrational levels increase and the force constant lowers due to the increased distance between atoms. As a result, at higher temperatures, one can observe peaks located near the main peak, with small variations of the frequency due to transitions between closely spaced high-energy vibrational levels (hot bands). Such effects can be accounted for by performing computationally expensive anharmonically corrected vibrational calculations (hereafter referred to as 0 K anharmonic calculations). Although such approaches can often yield good results, real systems vibrate at a finite temperature and, to an extent depending on the temperature and the chemical nature of the bonding, the anharmonic character of the PES will increasingly be sampled as the magnitude of the atomic displacements increase. Herein, we thus focus on how temperature affects the IR spectra of small silicate clusters.

Recently, the 0 K anharmonic IR spectrum of the pyroxenic MgSiO_3 monomer was accurately calculated showing only modest differences with respect to the corresponding harmonic spectrum.³¹ At this very small molecular-like size, silicate monomers appear to show relatively mild anharmonic effects that mainly lead to modest shifts of the harmonic peaks. We note that such high-level quantum chemical 0 K anharmonic calculations represent state-of-the-art benchmark calculations that are only computationally viable for very small species (approximately limited to systems with < 7 light atoms). Herein, using DFT-based calculations, we compare 0 K harmonic and 0 K anharmonic IR spectra, with IR spectra calculated using finite temperature anharmonic *ab initio* molecular dynamics (AIMD) for the 10-atom pyroxenic $(\text{MgSiO}_3)_2$ dimer and the 14-atom olivine $(\text{Mg}_2\text{SiO}_4)_2$ dimer. We note that these dimer species are predicted to be the first stoichiometric pyroxene and olivine silicate species to emerge in heterogeneous nucleation of dust around evolved stars.¹

AIMD-based IR spectra are based on realistic thermally induced atomic motions and are thus particularly suited for taking into account anharmonic effects at finite temperatures.³² Compared to the corresponding 0 K harmonic spectra, we find significant changes in our calculated AIMD IR spectra of both silicate dimer species at astrophysically relevant temperatures of 400 and 800 K. Specifically, we show that multiple anharmonic effects and conformational premelting can play important roles in determining the final IR spectra. Although

only small species, our study demonstrates that small nanosilicates can thus exhibit nontrivial dynamical responses to increased temperatures. The present data will be valuable for helping in identifying nanosilicates in a variety of astronomical environments and/or cluster beam experiments. More generally, our results highlight the potential limitations of calculated harmonic and 0K anharmonic IR spectra for interpreting observed/measured IR spectra of nanosized mineral species at finite temperatures.

■ COMPUTATIONAL DETAILS

Geometry optimizations, harmonic IR spectra calculations, and finite temperature AIMD simulations were carried out using DFT-based calculations with a light-tier 1 numerical atom-centered orbitals (NAO) basis set within the Fritz Haber Institute Ab Initio Molecular Simulations package (FHI-AIMS).³³ Previous studies have shown that this basis set has similar or better quality with respect to valence triple- ζ plus polarization Gaussian-type orbital basis sets.^{34,35} The initial geometries of the low energy (MgSiO_3)₂ pyroxene dimer cluster (P-2) and the (Mg_2SiO_4)₂ olivine dimer cluster (O-2) were obtained by global optimization searches reported in previous work.³⁰

We perform our calculations using both the B3LYP³⁶ and PBE0³⁷ hybrid functionals. Previously, using periodic DFT-based calculations employing both these functionals, the 0 K harmonic spectra of bulk crystalline olivine Mg_2SiO_4 (forsterite) were obtained and compared with the experimental IR spectra.³⁸ Although both functionals performed very well, the PBE0-based calculations were found to provide a more accurate crystal structure. The B3LYP-based calculations were found to be slightly better than the PBE0-based calculations in directly reproducing the forsterite IR spectra. However, once the tendency of the PBE0-based calculations for a slight systematic overestimation of frequencies was corrected, the performance of both approaches was almost the same. For bulk crystalline pyroxenic MgSiO_3 (enstatite), periodic DFT-based 0K harmonic calculations using the PBE0 functional showed very good agreement with experimental IR data, albeit with a systematic correctable small overestimate of frequencies.³⁹

Herein, we also assess the performance of these functionals with respect to calculating accurate IR spectra of clusters using pyroxene and olivine monomers, using the global minima MgSiO_3 and Mg_2SiO_4 cluster structures, respectively.³⁰ In Tables 1 and 2, we compare our DFT-calculated 0 K harmonic spectra for these species, with those obtained using high-level quantum chemistry methods.³¹ Generally, for these ultrasmall silicates, we find that both our PBE0- and B3LYP-based DFT calculations provide 0 K harmonic frequencies that are in good agreement with the benchmark values. For the olivine monomer, the average deviation from the benchmark values is similar for both functionals ($\sim 2.3\%$), whereas, for the pyroxene monomer, the PBE0 functional ($\sim 1.5\%$ deviation) appears to perform better than B3LYP ($\sim 3.3\%$ deviation). We note that these deviations are nearly always negative (i.e., the DFT-based frequencies are lower than the benchmark values). Upon closer inspection of the data, for many astronomically important high-intensity peaks covering the higher-frequency Si–O stretching region, we see that the PBE0 calculations are in remarkable agreement with the benchmark values ($<1\%$ deviation); see blue boxes in Tables 1 and 2. We use both the PBE0 and B3LYP functionals in the present work, but this comparison suggests that the PBE0 results may provide more

Table 1. Comparison of Harmonic Frequencies for the MgSiO_3 Monomer Cluster Obtained from DFT-Based Calculations Using the PBE0 and B3LYP Functionals (This Work) with the Corresponding Frequencies Obtained Using High-Level Quantum Chemistry Calculations in Ref 31^a

0 K harmonic frequencies (ref 31)	present work (B3LYP)	ratio (B3LYP)	present work (PBE0)	ratio (PBE0)
<u>1278.6</u>	1256.2	0.982	<u>1275.5</u>	0.998
872.7	846.4	0.970	<u>873.4</u>	1.001
824.7	806.4	0.978	<u>823.0</u>	0.998
710.1	681.5	0.960	691.3	0.974
618.1	595.1	0.963	606.9	0.982
483.2	465.4	0.963	469.8	0.972
431.6	417.2	0.967	425.3	0.985
310.0	297.0	0.958	301.5	0.973
165.4	159.9	0.967	162.1	0.980
average		0.967		0.985

^aSelected frequencies that are in particularly good agreement with the benchmark values are underlined.

Table 2. Comparison of Harmonic Frequencies for the Mg_2SiO_4 Monomer Cluster Obtained from DFT-Based Calculations Using the PBE0 and B3LYP Functionals (This Work) with the Corresponding Frequencies Obtained Using High-Level Quantum Chemistry Calculations in Ref 31^a

0 K harmonic frequencies (ref 31)	present work (B3LYP)	ratio (B3LYP)	present work (PBE0)	ratio (PBE0)
1258.5	1244.2	0.989	<u>1262.2</u>	1.003
1017.6	990.2	0.973	<u>1012.2</u>	0.995
943.9	919.7	0.974	<u>934.6</u>	0.990
782.7	764.5	0.977	<u>774.7</u>	0.990
687.8	677.4	0.985	<u>687.6</u>	1.000
621.1	603.2	0.971	610.8	0.983
550.8	537.7	0.976	543.6	0.987
421.2	408.6	0.970	412.6	0.980
399.9	392.4	0.981	393.0	0.983
298.0	289.5	0.971	291.7	0.979
272.0	270.6	0.995	272.4	1.001
230.9	225.3	0.976	225.7	0.977
139.2	132.8	0.954	126.6	0.909
112.8	110.4	0.979	103.2	0.915
69.3	68.6	0.990	67.9	0.980
average		0.977		0.978

^aSelected frequencies that are in particularly good agreement with the benchmark values are underlined.

accurate results for small silicate nanoclusters. Based on the PBE0 values, we note that a $\pm 1\%$ error for a high-frequency peak at 1000 cm^{-1} equates to an error of $\pm 0.1\text{ }\mu\text{m}$ for the corresponding wavelength peak at $10\text{ }\mu\text{m}$. For lower frequencies, corresponding to peaks around $20\text{ }\mu\text{m}$, a 2% frequency error results in the same absolute wavelength error. This suggests that, generally, our raw PBE0-based results have an approximate error of $0.1\text{ }\mu\text{m}$.

The AIMD simulations used a time step of 0.0005 ps and were run for a maximum of 40 ps and were split into two steps: (i) a 2 ps equilibration stage using the Berendsen thermostat,⁴⁰ and (ii) a remaining production stage using the Bussi–Donadio–Parrinello thermostat.⁴¹ The initial velocities of each atom were chosen randomly from a Maxwell–Boltzmann distribution at the desired temperature. We note that the final AIMD spectra are independent of the specific choice of initial

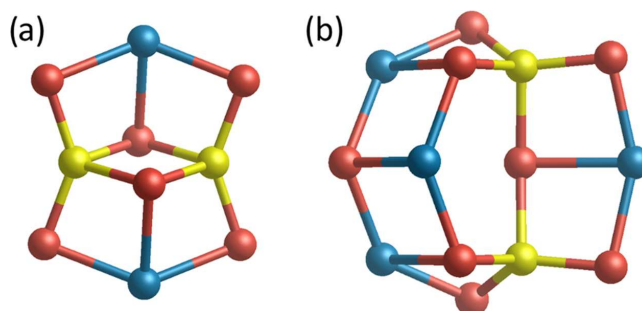


Figure 1. Nanosilicate cluster structures: a) the $(\text{MgSiO}_3)_2$ pyroxene dimer cluster (P-2), and b) the $(\text{Mg}_2\text{SiO}_4)_2$ olivine dimer cluster (O-2). Atom color key: red, oxygen; yellow, silicon; blue, magnesium.

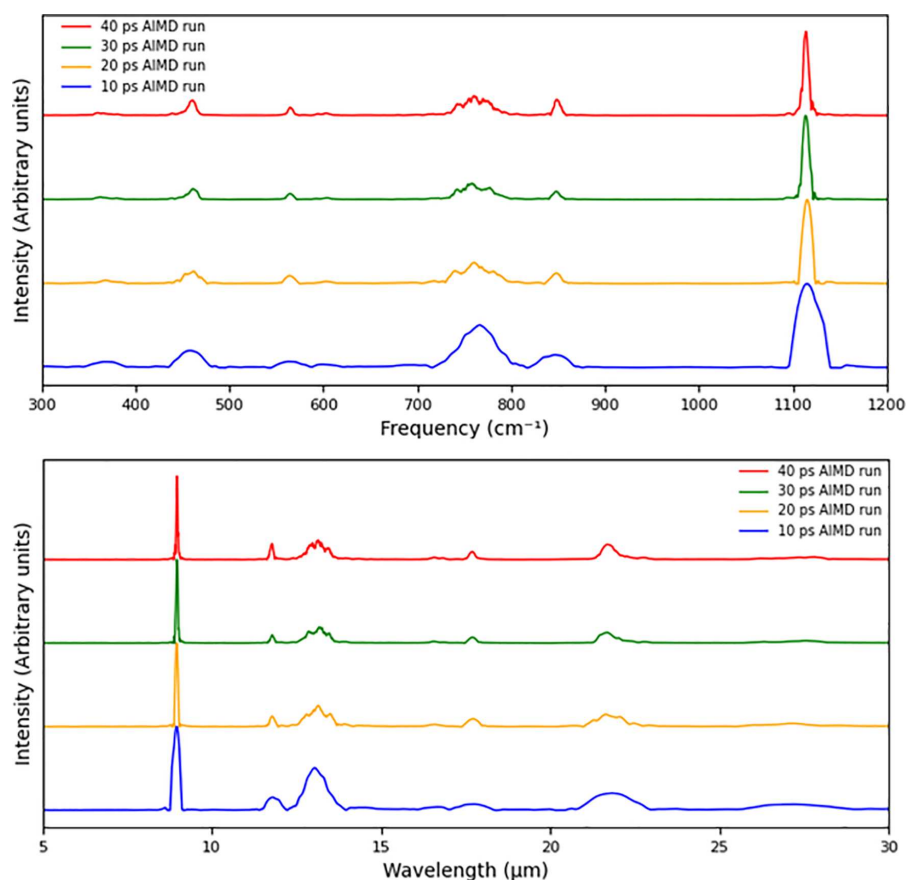


Figure 2. Comparison of P-2 AIMD-based IR spectra from the frequency (top) and wavelength (bottom) perspectives using different AIMD simulation times. Here, the PBE0 functional was used. Intensities are normalized to the height of the highest peak in each spectrum.

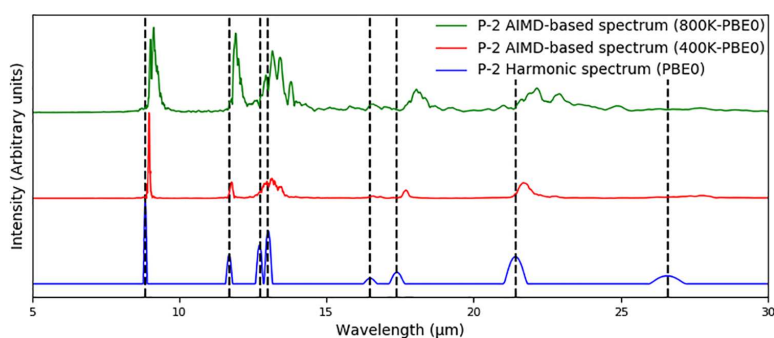
velocities. To obtain the spectral lineshapes, and thus, IR absorption cross sections, it is necessary to obtain the dipole autocorrelation function from our AIMD simulations. To do so, it is necessary to keep track of the total dipole moment of the system at each step of the AIMD simulation. From the

time evolution of the dipole moment, it is then possible to compute the dipole autocorrelation function, and consequently, to obtain the desired AIMD-based IR spectrum (see the [Supporting Information](#) for more details). Our AIMD calculations require a large number of force evaluations

Table 3. Comparison of Wavelength Positions of Main Peaks of the IR spectrum of the P-2 Nanocluster in the Range 8–27 μm , as Obtained from Harmonic (0 K) and AIMD-Based (400 and 800 K) Calculations Using the PBE0 Functional (See Figure 3)

harmonic PBE0 (μm)	harmonic intensity (Debye ² a.m.u./Å ²)	AIMD 400 K ^a (μm)	ratio 400 K	AIMD 800 K ^a (μm)	ratio 800 K
8.85	18.638	8.98	1.015	9.23	1.043
11.69	6.271	11.78	1.001	11.99	1.026
12.73	8.462	13.11	1.018 ^b	13.47	1.046 ^b
13.03	11.674				
16.47	1.215	16.59	1.007	16.61	1.008
17.41	2.508	17.71	1.017	18.27	1.049
21.42	5.907	21.69	1.013	22.53	1.052
26.53	1.719	27.71	1.044	27.69	1.044
		average:	1.6%	average:	3.8%

^aThe positions of signals formed by multiple peaks were obtained from an average of the peak positions. The ratio is calculated as MD signal/harmonic signal. ^bRatio obtained with respect to the average of the two harmonic peaks.

**Figure 3.** Comparison between harmonic (blue) and AIMD-based at 400 K (red) and at 800 K (green) IR spectra of the P-2 cluster using the PBE0 functional. Intensities are normalized to the height of the highest peak. Vertical dashed lines indicate the harmonic peak positions.

(80 000 during a 40 ps trajectory), which is significantly more than required for a 0 K harmonic calculation ($6N$, where N is the number of atoms). Although the progressively updated force evaluations in an AIMD calculation tend to be faster than in a harmonic frequency calculation, the former calculations are approximately two orders of magnitude more computationally expensive.

The DFT-based 0K anharmonic IR spectra were obtained using numerical differentiation to compute anharmonic frequencies, anharmonic vibrational–rotational couplings, and full anharmonic IR intensities,^{42–44} as well as a double zeta polarized 6-31G** basis set within the Gaussian 09 code.⁴⁵ To calibrate the wavelength scale of these anharmonic spectra with our harmonic spectra and AIMD-derived spectra (calculated using the FHI-AIMS code), we also used Gaussian to compute harmonic spectra in each case and extracted the average peak shift between corresponding anharmonic and harmonic spectra. The anharmonic spectra are compared with the harmonic spectra from FHI-AIMS applying this small shift.

RESULTS AND DISCUSSION

Time Convergence of AIMD-Based IR Spectra. First, we determine for how long an AIMD simulation should be run in order to obtain a converged IR spectrum (i.e., such that the shape and position of the spectrum peaks do not significantly change if the simulation time is increased). To study this convergence, we use progressively increasing AIMD simulation times for the P-2 pyroxene dimer (MgSiO_3)₂ cluster (see

Figure 1a) using the PBE0 functional. The resulting computed IR spectra for different AIMD run times are compared in Figure 2. We present these initial results in both frequency units (cm^{-1}) and wavelength units (μm). As our results are particularly relevant to nanosilicates in astronomical environments, we report the remainder of our spectra from the wavelength perspective, as is more common in the astronomical literature.

Generally, we find that at 10 ps, the peak positions are almost the same as in the case of the 40 ps AIMD run. However, the resolution of the peaks increases with increasing AIMD simulation time. This is especially noticeable in the case of the signal centered at $\sim 13 \mu\text{m}$. The increase of the peak resolution can easily be explained by the fact that the longer the dynamics are run, the more the repeating changes in the dipole moments of the cluster are sampled. At 40 ps, we find that the shape of the peaks is almost the same as in the case of 30 ps AIMD simulation time, indicating that 40 ps is sufficient for convergence.

In the converged P-2 spectrum, we find an intense and very sharply peaked signal close to $9 \mu\text{m}$ associated with Si–O stretching modes. We also see a multiply peaked signal around $13 \mu\text{m}$, which is associated with O–Si–O bending modes. These two signals appear at smaller wavelengths than the ones found typically observed for bulk silicates (~ 10 and ~ 18 to $20 \mu\text{m}$, respectively). This difference is due to the constraint of small finite size in the nanoclusters, which increases the bonding strain (and thus the force constant) and the

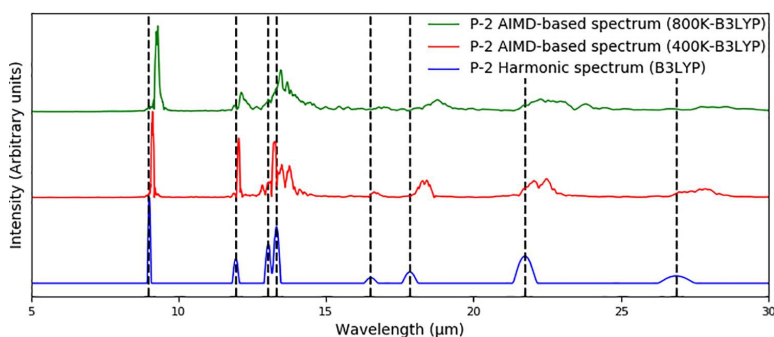


Figure 4. Comparison between harmonic (blue) and AIMD-based at 400 K (red) and at 800 K (green) IR spectra of the P-2 nanocluster using the B3LYP functional. Intensities are normalized to the height of the highest peak. Vertical dashed lines indicate the harmonic peak positions.

Table 4. Comparison of Wavelength Positions of Main Peaks of the IR Spectrum of the P-2 Nanocluster in the Range 8–27 μm , as Obtained from Harmonic (0 K) and AIMD-Based (400 and 800 K) Calculations Using the B3LYP Functional (See Figure 4)

harmonic B3LYP (μm)	harmonic intensity (Debye ² a.m.u./Å ²)	AIMD 400 K ^a (μm)	ratio 400 K	AIMD 800 K ^a (μm)	ratio 800 K
9.01	18.568	9.13	1.013	9.27	1.029
11.95	5.365	12.05	1.008	12.17	1.018
12.94	8.580	13.56	1.043 ^b	13.69	1.053 ^b
13.05	12.225				
16.52	1.164	16.64	1.007	16.88	1.022
17.85	2.415	18.38	1.030	18.67	1.046
21.77	5.832	22.27	1.023	22.61	1.039
26.87	1.565	27.74	1.032	28.15	1.048
		average:	2.2%	average:	3.6%

^aThe positions of signals formed by multiple peaks were obtained from an average of the peak positions. The ratio is calculated as MD signal/harmonic signal. ^bRatio obtained with respect to the average of the two harmonic peaks.

Table 5. Comparison of Mean Average Computed Peak Wavelengths for the Harmonic, and 400 and 800 K AIMD-Based IR Spectra Using the PBE0 and B3LYP Functionals^a

harmonic PBE0: B3LYP (%)	harmonic PBE0: B3LYP (μm)	400 K AIMD PBE0: B3LYP (%)	400 K AIMD PBE0: B3LYP (μm)	800 K AIMD PBE0: B3LYP (%)	800 K AIMD PBE0: B3LYP (μm)
−1.5	−0.23	−2.0	−0.28	−1.3	−0.21

^aAverages are based on values in Tables 1 and 2.

associated vibrational frequencies, thus lowering the wavelengths at which the peaks appear. The spectrum of P-2 also shows individual peaks close to 13, 18, and 22 μm (see also Table 3) due to complex modes involving Si–O–Mg vibrations.

Below, we focus on (i) assessing to what extent anharmonic effects play a role in determining the IR spectra of these nanosilicates, and ii) how the IR spectra of nanosilicates are affected by temperature. For this study, we compute the harmonic, anharmonic, and AIMD-based spectra at 400 and 800 K for the P-2 and O-2 cluster structures using both PBE0 and B3LYP functionals.

P-2 Cluster. We first directly compare the harmonic IR spectra with the AIMD-derived spectra at 400 and 800 K for the P-2 clusters as obtained from calculations using the PBE0 and B3LYP functionals (see Figures 3 and 4, respectively). From visual inspection, one can see that in both cases the harmonic spectra are very similar using both functionals with respect to peak positions and intensities. With the inclusion of temperature, the IR spectra evolve in a broadly similar manner for both functionals, although the intensities of some peaks for

the corresponding AIMD-derived spectra are found to be quite different. These functional-dependent finite temperature intensity differences are likely due to the different way the functionals describe the PES, and thus the resulting dynamics, away from the local energy minimum. As we will see below, these dynamical issues can become very important in understanding the emergence of new IR peaks. Reliable finite temperature IR intensities could be useful to help identify nanosilicates in some astrophysical environments and/or in certain cluster beam experiments; however, here we focus on the positions of prominent peaks. The wavelengths of significant IR peaks are likely to be the main identifying signatures of these species. The main peak positions (and intensities in the harmonic case) from all P-2 IR spectra calculations are compared in Tables 3 and 4. Our full set of calculated harmonic frequencies and intensities for the P-2 cluster can be found in the SI.

In Table 5, we compare the average difference in IR peak positions as predicted by calculations using the PBE0 and B3LYP functionals for the P-2 cluster. For both the harmonic spectra and the AIMD-based spectra, the PBE0 calculations

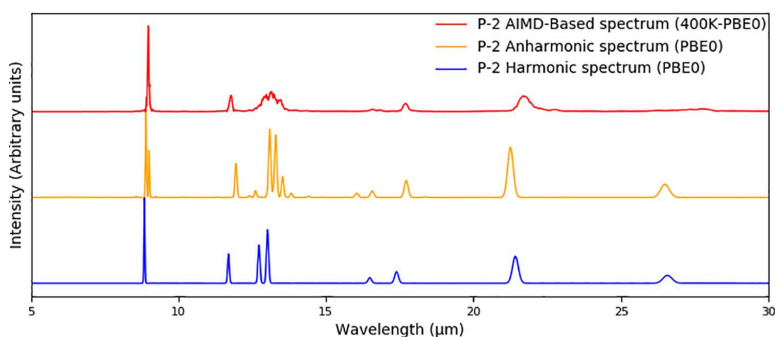


Figure 5. Comparison between harmonic (blue), anharmonic (orange), and 400 K AIMD-based IR spectra (red) of the P-2 nanocluster. Intensities are normalized to the height of the highest peak. The PBE0 functional was used in all cases.

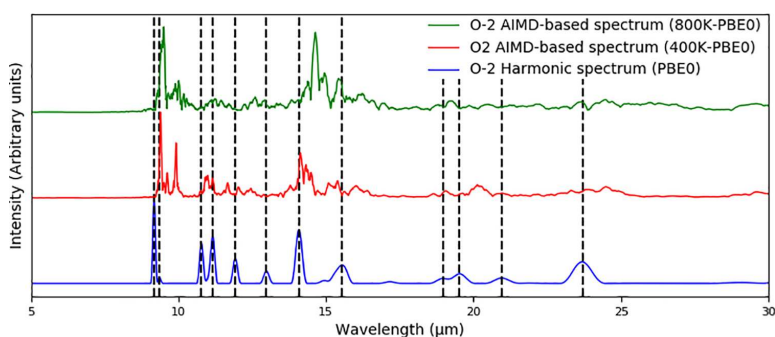


Figure 6. Comparison between harmonic (blue) and AIMD-based IR spectra at 400 K (red) and at 800 K (green) of the O-2 nanocluster using the PBE0 functional. Intensities are normalized to the height of the highest peak. Vertical dashed lines indicate the harmonic peak positions.

tend to give peak wavelengths that are slightly higher (1.3–2.0%) than those from the B3LYP calculations. These results are in line with the results for the monomers (see Tables 1 and 2). Although the harmonic and AIMD-based spectra are broadly similar for P-2, there are two main differences between these spectra that are apparent in calculations using both functionals. First, there is a tendency for peak positions to shift toward larger wavelengths with increasing temperature. Although this temperature-induced shift is not constant for all peaks, it is always positive and amounts to an average increase of 1.6–2.2% for 400 K and 3.6–3.8% for 800 K, depending on the functional used (see Tables 3 and 4). With increasing temperature, the cluster can explore regions of the PES that are progressively further from the 0 K energy minimum. As we move further from the 0 K minimum, we encounter regions that are less and less well fitted with a perfectly symmetric harmonic potential that overestimates the real potential between atoms. We thus expect that the observed peak shifts in the finite temperature spectra are the result of anharmonic effects.

Second, we see that two close peaks around 13 μm in the P-2 harmonic spectrum become a signal with multiple peaks in the AIMD-based spectra. A plausible explanation for this change is that the new peaks observed in the AIMD-based spectra arise from combination bands that inherently cannot be obtained with a 0 K harmonic spectrum. To help confirm the role of anharmonicity in the observed harmonic-to-AIMD

calculations, we also compute the 0 K anharmonic IR spectrum of the P-2 cluster (see Figure 5).

In Figure 5, we compare the 0 K harmonic, 0 K anharmonic, and the 400 K AIMD-derived IR spectra. We can see that the anharmonic spectrum better fits the 400 K AIMD-derived spectrum than the harmonic spectrum. First, in the 0 K anharmonic spectrum, we see the anticipated slight shift of most of the main harmonic peaks toward slightly longer wavelengths. In addition, we also see that the anharmonic spectrum begins to show multiple signals around 13 μm , which are not observed in the harmonic spectrum. Moreover, by analyzing the vibrational transitions in the anharmonic spectrum, we can confirm that the appearance of these multiple peaks is due to combination bands. These extra peaks arise from combinations with various low-frequency modes, including some non-IR-active harmonic frequencies that become active upon combination. We further note that the 0 K anharmonic spectrum also shows a splitting of the harmonic peak close to 9 μm into two close peaks. In the AIMD-derived spectra, this splitting only clearly emerges as a broadened shoulder at 800 K (see Figure 3).

Finally, when the temperature is increased, we observed an increase in the broadening of the peaks. This change is especially clear for the peaks between 11 and 14 μm . These features may be attributable to hot bands (i.e., transitions between excited vibrational states of different vibrational modes).

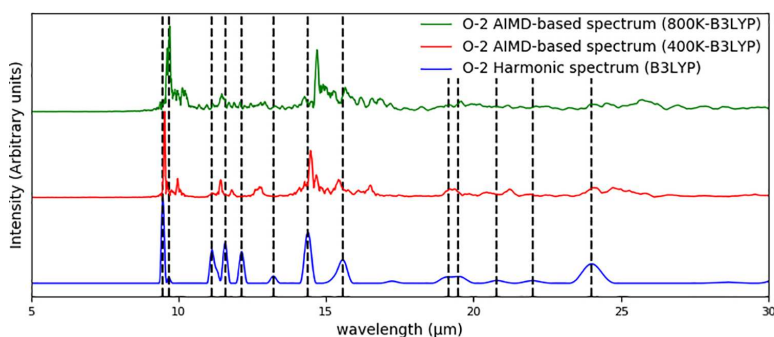


Figure 7. Comparison between harmonic (blue) and AIMD-based IR spectra at 400 K (red) and at 800 K (green) of the O-2 nanocluster using the B3LYP functional. Intensities are normalized to the height of the highest peak. Vertical dashed lines indicate the harmonic peak positions.

Table 6. Harmonic and MD-Based Wavelength Peaks Positions of the O-2 Cluster Using the PBE0 Functional

harmonic PBE0 (μm)	harmonic intensity (Debye ² a.m.u./Å ²)	MD 400 K ^a (μm)	ratio 400 K	MD 800 K ^a (μm)	ratio 800 K
9.27	19.202	9.39	1.013	9.47	1.022
9.45	1.319	9.62	1.034	9.93	1.066
		9.92		10.21	
14.08	12.180	14.34	1.018	14.63	1.039
		average:	2.2%	average:	4.2%

^aThe positions of signals formed by multiple peaks were obtained from an average of the peak positions.

Table 7. Harmonic and MD-Based Wavelength Peaks Positions of O-2 Cluster Using B3LYP Functional

harmonic B3LYP (μm)	harmonic intensity (Debye ² a.m.u./Å ²)	MD 400 K ^a (μm)	ratio 400 K	MD 800 K ^a (μm)	ratio 800 K
9.473	19.548	9.54	1.007	9.66	1.019
9.675	1.395	9.63	1.023	9.93	1.041
		10.16		10.22	
14.390	11.677	14.48	1.006	14.70	1.021
		average:	1.2%	average:	2.7%

^aThe positions of signals formed by multiple peaks were obtained from an average of the peak positions.

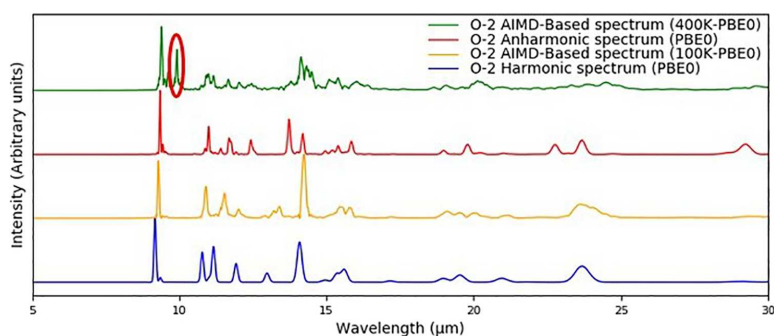


Figure 8. Comparison between 0K harmonic (blue), 100KAIMD-based (yellow), 0K anharmonic (red) and 400 K AIMD-based (green) IR spectra of the O-2 nanocluster using the PBE0 functional. Intensities are normalized to the height of the highest peak. The emergent peak at just above 10 μm is circled in the 400 K spectrum.

O-2 Cluster. Here, we compare the harmonic IR spectra with the AIMD-derived spectra at 400K and 800K for the O-2 cluster as obtained from calculations using the PBE0 (Figure 6) and B3LYP (Figure 7) functionals. The first thing that can be observed is that, as expected, the IR spectrum from the O-2 cluster has more features than the P-2 spectrum since it has more atoms, and therefore, more vibrational modes. The O-2

harmonic spectrum shows an intense peak near 9 μm and some prominent peaks around 14–16 μm that can be assigned to Si-O stretching and O-Si-O bending modes, respectively. Moreover, a group of individual peaks between 11 and 13 μm as well as several signals in the high wavelength region is also found. As in the case of the P-2 cluster, there is reasonable qualitative agreement between the harmonic and the AIMD-

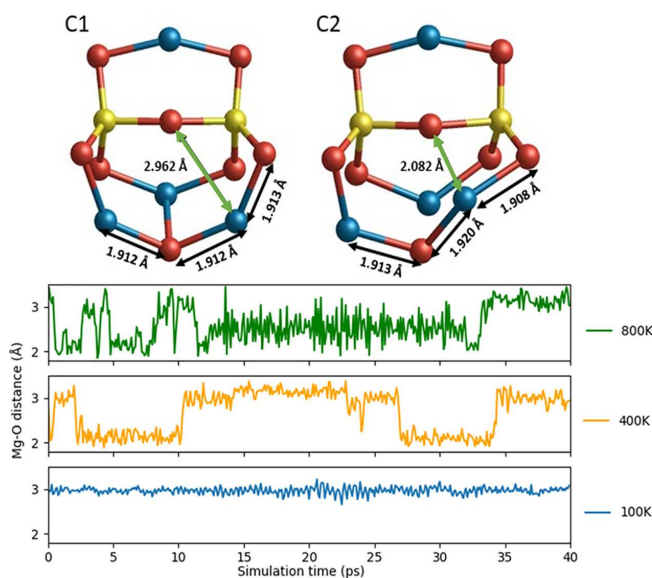


Figure 9. Top: Two optimized O-2 conformations (C1 and C2) with the Mg-O distance that we use to track the structural change marked with a green arrow. Bottom: Evolution of the marked Mg-O distance during AIMD simulations at different temperatures.

based spectra for O-2 using both the PBE0 and B3LYP functionals. As in the case of P-2, there is a general harmonic-to-AIMD upward shifting in the wavelengths of the main peaks, which increases with increasing temperature. Furthermore, it is also observed, as in the P-2 spectra, that at higher temperatures the obtained peaks are much more broadened. These two phenomena are due to anharmonic effects and are especially clear when following how the harmonic peak at $\sim 14 \mu\text{m}$ evolves with increasing temperature. Although only slightly larger than the P-2 cluster, the O-2 cluster gives rise to AIMD-based spectra that involve many more peaks. As such, identification of peaks that clearly correspond to the 0 K harmonic peaks is difficult, especially at 800 K. In Tables 6 and 7, we thus only list the positions of the peaks in the AIMD-based spectra for which we can be reasonably sure of the corresponding harmonic peaks. Our full set of calculated harmonic frequencies and intensities for the O-2 cluster can be found in the SI.

The most remarkable difference between the AIMD-based spectra and the harmonic spectra is the appearance of a peak around $10 \mu\text{m}$ in the former, which is not observed in the latter. This peak is found to some degree in all of the AIMD spectra, but is most clearly seen in the 400 K AIMD spectrum from the PBE0 calculation (see Figure 6 and the circled peak in Figure 8). Following the analysis above, we attempt to rationalize the emergence of this peak by performing a 0 K anharmonic frequency calculation. We also perform an additional AIMD simulation at 100 K to see if this peak persists at lower temperatures. The harmonic and anharmonic spectra and AIMD-derived spectra for 100 and 400 K are compared in Figure 8.

From Figure 8, we see that, as expected, the anharmonic spectrum shows that some of the harmonic peaks become multiple peaks. This is most apparent for the peaks with wavelengths above $12.5 \mu\text{m}$. However, the harmonic peaks

between 10 and $12 \mu\text{m}$ do not change very much when anharmonic effects are considered. In the case of the intense signal at $9 \mu\text{m}$, the anharmonic spectrum shows the presence of small multiple peaks that are also captured in the AIMD-based IR spectra. However, the single prominent peak around $10 \mu\text{m}$, obtained in the 400 K AIMD-based spectrum, does not appear in the anharmonic spectrum. In Figure 8, we clearly see that the 100 K AIMD-based spectrum also does not show the $\sim 10 \mu\text{m}$ peak, indicating that the appearance of this peak is related to increased temperatures.

To further investigate the emergence of the $\sim 10 \mu\text{m}$ peak, we analyzed the AIMD trajectories for the O-2 cluster at 100, 400, and 800 K. Via this analysis, we discovered that at some points during the 400 and 800 K simulations the O-2 cluster undergoes a small reversible conformation change (see C1 and C2 in Figure 9). This conformational change can be tracked by monitoring the highlighted distance between the Mg and O atoms in Figure 9. During the AIMD simulations, this distance stays relatively constant at 100 K indicating that no conformational change occurs. At 400 K, this distance discretely shifts between two extreme values of approximately 2.1 and 3.1 Å every few picoseconds, indicating that the cluster tends to stay in either of two conformations (i.e., C1 or C2) for a few picoseconds before shifting to the other. For 800 K, in addition to the behavior exhibited at 400 K, this distance can oscillate at an intermediate value between the two extremes, indicating that the cluster can persist in a highly mobile fluxional state between two conformations.

As this conformational change occurs at a relatively low temperature, it indicates that both conformations must be very close in energy and have a small transition barrier. Optimizing both C1 and C2 conformations at 0 K using either the PBE0 or B3LYP functional, we find that the total energy difference between the two conformations is always $<0.05 \text{ eV}$. Although this energy difference is below the level for which DFT-based

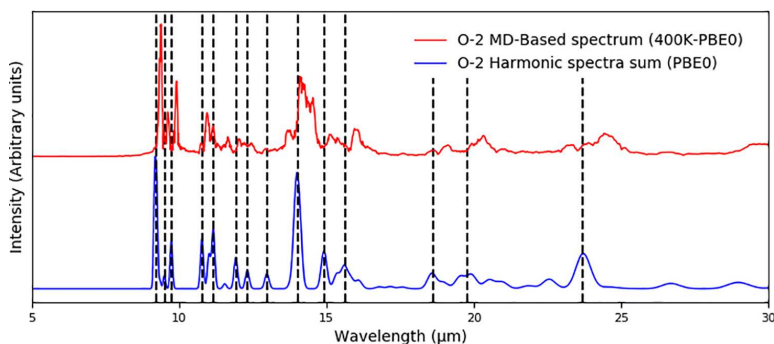


Figure 10. Comparison between the spectrum derived from summing the 0 K harmonic spectra of both O-2 conformers (blue) and the 400 K AIMD-based IR spectrum of the O-2 cluster (red). Intensities are normalized to the height of the highest peak.

calculations can provide accurate predictions, the two conformers are clearly almost energetically degenerate.

To confirm that vibrational contributions from this new conformer are being observed at 400 K, we compare the sum of the harmonic spectra of both C1 and C2 conformers with the 400 K AIMD spectrum (see Figure 10). Here, we see that the agreement between the summed harmonic spectrum and the AIMD-based spectra is improved relative to the corresponding comparison in Figure 6. The most obvious improvement of using the summed spectrum is that the peak just below 10 μm now has a reasonable correspondence in the AIMD-based spectrum. Additionally, there is a better agreement between the summed harmonic spectrum and the AIMD-based spectrum for other signals above 10 μm . The harmonic vibrational frequencies for the C2 conformer are listed in the SI.

We note that conformational fluxionality has been reported at relatively low temperatures in other small oxide clusters, where it can be understood as a premelted phase.⁴⁶ Generally, premelted dynamical effects have been experimentally confirmed in numerous cluster systems,^{47,48} and typically, are associated with anharmonicity, surface melting, and structural transitions. Our observed premelting is thus likely to be common to many other small silicate grains and could thus be an important contributing factor for interpreting the observed IR spectra in warm astrophysical environments or cluster beam experiments.

CONCLUSIONS

Herein, using AIMD simulations, we explicitly show how temperature affects the IR spectra of two small Mg-rich silicate clusters: (i) the pyroxenic (MgSiO_3)₂ dimer and (ii) the olivinic (Mg_2SiO_4)₂ dimer. We take these clusters as being representative of ultrasmall cosmic dust grains and consider grain temperatures typical of inner protoplanetary disks (400 K) and circumstellar dust nucleation regions (800 K). With progressively higher temperatures, anharmonic and premelting dynamics become more prevalent, and the resulting spectra diverge more and more from the corresponding 0 K harmonic/anharmonic spectra. Finite temperature anharmonic effects act to broaden and shift the 0 K harmonic peaks, while also adding new combination bands. These effects become more pronounced with increasing temperature. For the olivine dimer, we also observe a dynamic premelting transition between two nearly energetically degenerate conformers.

This fluxional state leads to the emergence of new IR peaks with respect to that of a single conformer at 100 K, which can be largely understood by considering the sum of the IR spectra of each conformer. Generally, our results show that the IR spectra of nanosized grains can be significantly affected by astrophysically relevant temperatures, which are below that typically considered important for annealing silicate dust (~ 1000 K). These preliminary results strongly suggest that such thermally induced effects should be considered when attempting to identify nanosilicates in a range of astrophysical environments and in cluster beam experiments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsearthspacechem.0c00341>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Goumans, T. P. M.; Bromley, S. T. Efficient Nucleation of Stardust Silicates via Heteromolecular Homogeneous Condensation. *Mon. Not. R. Astron. Soc.* **2012**, *420*, 3344–3349.
- (2) Gail, H.-P.; Sedlmayr, E. *Physics and Chemistry of Circumstellar Dust Shells*; Cambridge University Press: Cambridge, 2013.
- (3) Gobrecht, D.; Cherchneff, I.; Sarangi, A.; Plane, J. M. C.; Bromley, S. T. Dust formation in the oxygen-rich AGB star IK Tauri. *Astron. Astrophys.* **2016**, *585*, A6.
- (4) Hirashita, H.; Kobayashi, H. Evolution of dust grain size distribution by shattering in the interstellar medium: Robustness and uncertainty. *Earth, Planets Space* **2013**, *65*, 1083–1094.
- (5) Li, A.; Draine, B. T. On Ultrasmall Silicate Grains in the Diffuse Interstellar Medium. *Astrophys. J.* **2001**, *550*, L213–L217.
- (6) Oueslati, L.; Kerkeni, B.; Bromley, S. T. Trends in the adsorption and reactivity of hydrogen on magnesium silicate nanoclusters. *Phys. Chem. Chem. Phys.* **2015**, *17*, 8951–8963.
- (7) Kerkeni, B.; Bromley, S. T. Competing mechanisms of catalytic H₂ formation and dissociation on ultrasmall silicate nanocluster dust grains. *Mon. Not. R. Astron. Soc.* **2013**, *435*, 1486–1492.
- (8) Kerkeni, B.; Bacchus-Montabonel, M.-C.; Bromley, S. T. How hydroxylation affects hydrogen adsorption and formation on nanosilicates. *Mol. Astrophys.* **2017**, *7*, 1–8.
- (9) Macià Escatllar, A.; Bromley, S. T. Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study. *Astron. Astrophys.* **2020**, *634*, A77.
- (10) Hensley, Brandon S.; Draine, B. T. Modeling the Anomalous Microwave Emission with Spinning Nanoparticles: No PAHs Required. *Astrophys. J.* **2017**, *836*, 179–192.
- (11) Hoang, T.; Vinh, N.-A.; Lan, N. Q. Spinning Dust Emission from Ultra-Small Silicates: Emissivity and Polarization Spectrum. *Astrophys. J.* **2016**, *824*, 18–28.
- (12) Henning, T. Cosmic Silicates. *Annu. Rev. Astron. Astrophys.* **2010**, *48*, 21–46.
- (13) Jäger, C.; Dorschner, J.; Mutschke, H.; Posch, T.; Henning, T. Steps toward Interstellar Silicate Mineralogy VII. Spectral properties and crystallization behaviour of magnesium silicates produced by the sol-gel method. *Astron. Astrophys.* **2003**, *408*, 193–204.
- (14) James Webb Space Telescope Home Page, <https://www.jwst.nasa.gov/> (accessed 2020-12-14).
- (15) Haertelt, M.; Fielicke, A.; Meijer, G.; Kwapien, K.; Sierka, M.; Sauer, J. Structure determination of neutral MgO clusters-hexagonal nanotubes and cages. *Phys. Chem. Chem. Phys.* **2012**, *14*, 2849–2856.
- (16) Savoca, M.; Langer, J.; Harding, D. J.; Palagin, D.; Reuter, K.; Dopfer, O.; Fielicke, A. Vibrational spectra and structures of bare and Xe-tagged cationic Si_nO_m⁺ clusters. *J. Chem. Phys.* **2014**, *141*, 104313.
- (17) Song, X.; Fagiani, M. R.; Gewinner, S.; Schöllkopf, W.; Asmis, K. R.; Bischoff, F. A.; Berger, F.; Sauer, J. Gas-Phase Vibrational Spectroscopy of the Aluminum Oxide Anions (Al₂O₃)_{1–6}AlO₂[−]. *ChemPhysChem* **2017**, *18*, 868–872.
- (18) Zimmermann, N.; Bernhardt, T. M.; Bakker, J. M.; Landman, U.; Lang, S. M. Infrared photodissociation spectroscopy of dimanganese oxide cluster cations. *Phys. Chem. Chem. Phys.* **2019**, *21*, 23922–23930.
- (19) Weichman, M. L.; Song, X.; Fagiani, M. R.; Debnath, S.; Gewinner, S.; Schöllkopf, W.; Neumark, D. M.; Asmis, K. R. Gas phase vibrational spectroscopy of cold (TiO₂)_n[−] (n = 3–8) clusters. *J. Chem. Phys.* **2016**, *144*, No. 124308.
- (20) Helmich, B.; Sierka, M.; Doebler, J.; Sauer, J. Structure and properties of bimetallic titanium and vanadium oxide clusters. *Phys. Chem. Chem. Phys.* **2014**, *16*, 8441–8447.
- (21) Groenewegen, M. A. T.; Sloan, G. C.; Soszyński, I.; Petersen, E. A. Luminosities and mass-loss rates of SMC and LMC AGB stars and red supergiants. *Astron. Astrophys.* **2009**, *506*, 1277–1296.
- (22) Gail, H.-P.; Wetzel, S.; Pucci, A.; Tamanai, A. Seed particle formation for silicate dust condensation by SiO nucleation. *Astron. Astrophys.* **2013**, *555*, A119.
- (23) Heese, S.; Wolf, S.; Dutrey, A.; Guilloteau, S. Spread of the dust temperature distribution in circumstellar disks. *Astron. Astrophys.* **2017**, *604*, No. A5.
- (24) Gao, P.; Thorngren, D. P.; Lee, G. K. H.; Fortney, J. J.; Morley, C. V.; Wakeford, H. R.; Powell, D. K.; Stevenson, K. B.; Zhang, X. Aerosol composition of hot giant exoplanets dominated by silicates and hydrocarbon hazes. *Nat. Astron.* **2020**, *4*, 951–956.
- (25) Hiranaka, K.; Cruz, K. L.; Douglas, S. T.; Marley, M. S.; Baldassare, V. F. Exploring the Role of Sub-Micron-Sized Dust Grains in the Atmospheres of Red L0–L6 Dwarfs. *Astrophys. J.* **2016**, *830*, 96.
- (26) Draine, B. T.; Aigen, Li. A. Infrared Emission from Interstellar Dust. I. Stochastic Heating of Small Grains. *Astrophys. J.* **2001**, *551*, 807–824.
- (27) Hallenbeck, S. L.; Nuth Iii, J.; Nelson, R. N. Evolving Optical Properties of Annealing Silicate Grains: from Amorphous Condensate to Crystalline Mineral. *Astrophys. J.* **2000**, *535*, 247–255.
- (28) Fabian, D.; Jäger, C.; Henning, T.; Dorschner, J.; Mutschke, H. Steps toward interstellar silicate mineralogy V. Thermal evolution of amorphous magnesium silicates and silica. *Astron. Astrophys.* **2000**, *364*, 282–292.
- (29) Zamirri, L.; Macià Escatllar, A.; Mariño Guiu, J.; Ugliengo, P.; Bromley, S. T. What Can Infrared Spectra Tell Us about the Crystallinity of Nanosized Interstellar Silicate Dust Grains? *ACS Earth Space Chem.* **2019**, *3*, 2323–2338.
- (30) Escatllar, A. M.; Lazaukas, T.; Woodley, S. M.; Bromley, S. T. Structure and Properties of Nanosilicates with Olivine (Mg₂SiO₄)_N and Pyroxene (MgSiO₃)_N Compositions. *ACS Earth Space Chem.* **2019**, *3*, 2390–2403.
- (31) Valencia, E. M.; Worth, C. J.; Fortenberry, R. C. Enstatite (MgSiO₃) and forsterite (Mg₂SiO₄) monomers and dimers: highly detectable infrared and radioastronomical molecular building blocks. *Mon. Not. R. Astron. Soc.* **2020**, *492*, 276–282.
- (32) Thomas, M.; Brehm, M.; Fligg, R.; Vöhringer, P.; Kirchner, B. Computing vibrational spectra from ab initio molecular dynamics. *Phys. Chem. Chem. Phys.* **2013**, *15*, 6608–6622.
- (33) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. Ab initio molecular simulations with numeric atom-centered orbitals. *Comput. Phys. Commun.* **2009**, *180*, 2175–2196.
- (34) Lamiel-García, O.; Ko, K. C.; Lee, J. Y.; Bromley, S. T.; Illas, F. When Anatase Nanoparticles Become Bulklike: Properties of Realistic TiO₂ Nanoparticles in the 1–6 nm Size Range from All Electron Relativistic Density Functional Theory Based Calculations. *J. Chem. Theory Comput.* **2017**, *13*, 1785–1793.
- (35) Jensen, S. R.; Saha, S.; Flores-Livas, J. A.; Huhn, W.; Blum, V.; Goedecker, S.; Frediani, L. The Elephant in the Room of Density Functional Theory Calculations. *J. Phys. Chem. Lett.* **2017**, *8*, 1449–1457.
- (36) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (37) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- (38) de la Pierre, M.; Orlando, R.; Maschio, L.; Doll, K.; Ugliengo, P.; Dovesi, R. Performance of Six Functionals (LDA, PBE, PBESOL, B3LYP, PBE0, and WC1LYP) in the Simulation of Vibrational and Dielectric Properties of Crystalline Compounds. The Case of Forsterite Mg₂SiO₄. *J. Comput. Chem.* **2011**, *32*, 1775–1784.
- (39) Demichelis, R.; Suto, H.; Noël, Y.; Sogawa, H.; Naoi, T.; Koike, C.; Chihara, H.; Shimobayashi, N.; Ferrabone, M.; Dovesi, R. The

infrared spectrum of ortho-enstatite from reflectance experiments and first-principle simulations. *Mon. Not. R. Astron. Soc.* **2012**, *420*, 147–154.

(40) Berendsen, H. J. C.; Postma, J. P. M.; Van Gunsteren, W. F.; Dinola, A.; Haak, J. R. Molecular dynamics with coupling to an external bath. *J. Chem. Phys.* **1984**, *81*, 3684–3690.

(41) Bussi, G.; Donadio, D.; Parrinello, M. Canonical sampling through velocity rescaling. *J. Chem. Phys.* **2007**, *126*, No. 014101.

(42) Califano, S. *Vibrational States*; Wiley, 1976.

(43) Clabo, D. A.; Allen, W. D.; Remington, R. B.; Yamaguchi, Y.; Schaefer, H. F. A systematic study of molecular vibrational anharmonicity and vibration-rotation interaction by self-consistent-field higher-derivative methods Asymmetric top molecules. *Chem. Phys.* **1988**, *123*, 187–239.

(44) Bloino, J.; Barone, V. A second-order perturbation theory route to vibrational averages and transition properties of molecules: General formulation and application to infrared and vibrational circular dichroism spectroscopies. *J. Chem. Phys.* **2012**, *136*, No. 124108.

(45) Frisch, M. J. et al. *Gaussian 16* Revision A.03.; Gaussian Inc: Wallingford CT, 2016.

(46) Viñes, F.; Carrasco, J.; Bromley, S. T. Nanoscale thermal stabilization via permutational premelting. *Phys. Rev. B.* **2012**, *85*, No. 195425.

(47) Breaux, G. A.; Neal, C. M.; Cao, B.; Jarrold, M. F. Melting, Premelting, and Structural Transitions in Size-Selected Aluminum Clusters with around 55 Atoms. *Phys. Rev. Lett.* **2005**, *94*, No. 173401.

(48) Hock, C.; Bartels, C.; Straßburg, S.; Schmidt, M.; Haberland, H.; von Issendorff, B.; Aguado, A. Premelting and Postmelting in Clusters. *Phys. Rev. Lett.* **2009**, *102*, No. 043401.

CHAPTER 5

Efficiency of Interstellar Nanodust Heating: Accurate Bottom-up Calculations of Nanosilicates Specific Heat Capacities

5.1 Introduction

Silicate dust in the ISM predominantly consists of grains with an average radius of approximately 0.1 microns¹. However, the grain size distribution of silicates follows an inverse power law, favouring the formation of populations with a large number of small grains². It is well established that the average temperature of these small grains cannot account for the significant temperature fluctuations that they experience due to sporadic heating upon interaction with UV radiation from the ISM³. The first studies on this effect showed that small dust grains are highly susceptible to sporadic temperature increases following the infrequent absorption of UV photons, with the subsequent rapid cooling to ISM temperatures by radiating in the IR⁴ on timescales shorter than the mean time between consecutive photon absorptions⁵. This effect, commonly referred to as stochastic heating, is now recognized as a key mechanism driving IR emission in astronomical environments. For example, stochastic heating has a significant impact in surface chemistry of small silicate grains^{6,7}.

The temperature that heated nanograins reach after absorption of a UV photon, as well as their IR emissivity, depends on their specific heat capacity⁸. Therefore, accurately determining the heat capacity of nanosilicates is of great interest to the astronomical community for modelling these processes.

The work of Draine and Li⁹ has served as a basis for the calculation of nanodust heat capacities and has been used to study the effect of stochastic heating in chemical processes⁷, dust grains growth¹⁰ and IR emissivity¹¹. In their work they derived the temperature-dependent heat capacity of nanodust (graphitic, PAHs and silicates), based on the distribution of available vibrational modes as a function of frequency, using a bimodal distribution of harmonic vibrations. This approach successfully reproduced the experimental heat capacities of bulk materials such as basalt and graphite. However, while suitable for bulk materials, this method presents significant limitations when applied to silicate nanograins. First, the model fittings rely on empirical materials that do not reflect the magnesium-rich composition of ISM silicates¹². On the other hand, the fittings are purely empirical and do not account for the physical origin of the vibrational modes in nanosilicates. Finally, the fitting is based on bulk samples for which the distribution of vibrational modes is known to be different than those of nanosized grains.¹³

Given the lack of experimental heat capacity data for nanosilicates, computational modelling offers an excellent alternative for deriving more accurate vibrational mode distributions and heat capacities. In this chapter, we determined the heat capacity of different small nanoclusters with different sizes (between 10 and 70 atoms) and chemical compositions (Mg-rich pyroxene and Mg-rich olivine) using computational models based on DFT with the PBE0 functional. We then compare the obtained results with those that can be derived from the bulk fitted model (BFM) to assess its accuracy for nanosilicates.

Our methodology begins with the generation of atomistic structures for the studied nanoclusters, either taken from previous works¹³ or obtained following global optimisation searches. We then compute the vibrational modes of these nanoclusters and compare their vibrational mode spectra with those predicted by the BFM. From these results we compute the heat capacities and analyse the temperature increase experienced by nanosilicates following UV photon absorption, evaluating the discrepancies between our computational model and the BFM across different photon energies.

5.2 Results

To analyse the differences in the predicted vibrational mode spectra between the previously employed BFM and our atomistically detailed model (based on DFT-PBE0 calculations and the harmonic approximation) we selected a set of nanosilicates with varying sizes and chemical compositions obtained from global optimization searches and computed their spectra using both approaches. In Figure 1, the vibrational spectra of the global minimum pyroxene and olivine dimers is compared to the spectra obtained using the BFM for silicate grains containing the same number of atoms. These spectra should be read as follows: For a given energy value (E_x) from the x-axis, the corresponding y value indicates the cumulative number of vibrational modes, with $E_{\text{mode}} \leq E_x$, the grain has.

As seen in these comparisons, there is a considerable difference between the models. The BFM significantly overestimates the number of vibrational modes at frequencies below 600 cm^{-1} , with respect to our model, particularly in the pyroxene dimer case.

In both cases ~66% of the vibrational modes obtained with BFM are found below 400 cm^{-1} whereas in our DFT-based models the same number of modes is reached at approximately 700 cm^{-1} . Moreover, the spectra from our modelled grains exhibit a relatively linear increase in the number of modes, in contrast to the BFM spectra, which show two distinct mode phases arising from the use of a bimodal distribution.

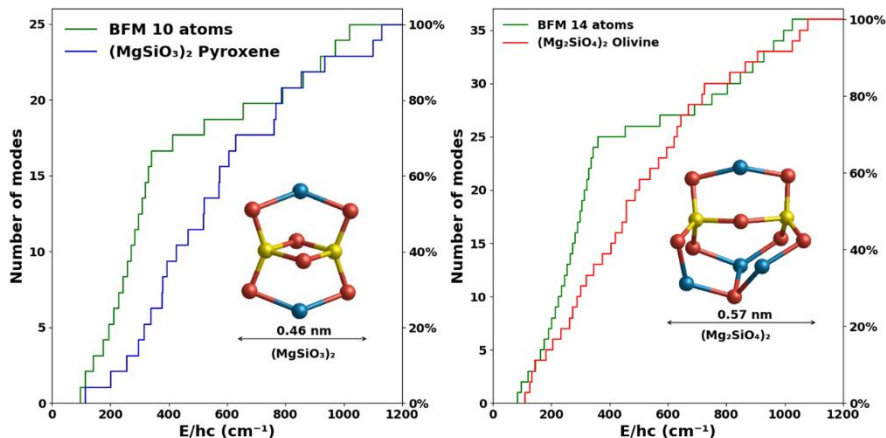


Figure 1: Comparison of the cumulative vibrational mode spectra obtained using our atomistic model for the pyroxene (blue, left) and olivine (red, right) dimers, with respect to the spectra from BFM for silicate grains with the same number of atoms (green). Oxygen, magnesium and silicon atoms are depicted as red, blue and yellow spheres respectively.

A clearer analysis of the observed differences can be performed by counting the number of modes found in regular bins of 100 cm^{-1} and comparing the number of modes in each bin depending on the model used, as shown in Figure 2. These histograms more clearly illustrate the BFM's overestimation of modes in the region below $300\text{-}400 \text{ cm}^{-1}$ and its underestimation between 400 and 800 cm^{-1} . At higher frequencies, both models converge, and the differences are smaller.

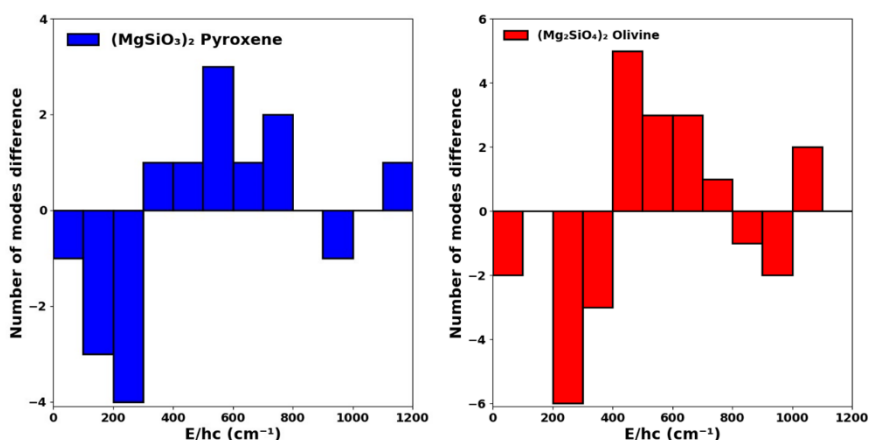


Figure 2: Difference in the predicted number of modes between our atomistic model and BFM with respect to binned frequencies in range of 100 cm^{-1} . Positive (negative) differences indicate that our model spectra have more (less) vibrational modes in a given bin.

Previous estimates using the BFM predict that silicate grains with only a few tens of atoms can be heated to few hundred of Kelvin by absorbing low-energy UV photons (~ 3 eV) (see Figure 8 in reference 9). This temperature, as has been shown in Chapter 3, can induce conformational changes in nanosilicates. To account for this possible structural change, we compared the vibrational spectra of the global minimum dimers, obtained using our models, with the spectra averaging over a set of three low energy isomers, obtained from global minimum searches.

To obtain the average spectra, we repeated the division of the spectra in bins of 100 cm^{-1} and took the average of the total number of vibrational modes per isomer in each bin. Figures 3 and 4 present the comparison for both dimers, showing that the vibrational spectra of the dimers are not significantly affected when multiple low energy isomers are considered. Therefore, the analysis of one single isomer should be sufficient to extract conclusions from the difference with BFM.

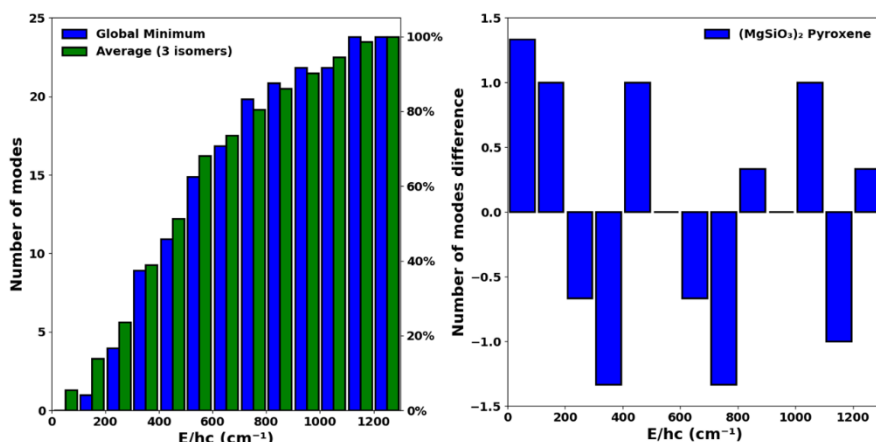


Figure 3: Left: Comparison between the cumulative vibrational spectra of the global minimum pyroxene dimer (blue) and the averaged spectra using three pyroxene dimer isomers (green). Right: Difference in the number of modes between the global minimum and the averaged spectra. Positive (negative) differences indicate that the averaged spectrum has more (less) vibrational modes in a given bin.

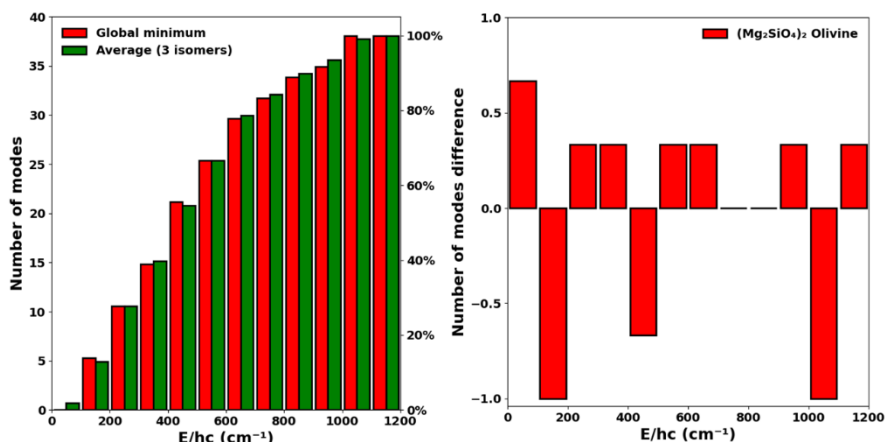


Figure 4: Left: Comparison between the cumulative vibrational spectra of the global minimum olivine dimer (red) and the averaged spectra using three olivine dimer isomers (green). Right: Difference in the number of modes between the global minimum and the averaged spectra. Positive (negative) differences indicate that the averaged spectrum has more (less) vibrational modes in a given bin.

The dimer analysis revealed a significant difference in the vibrational mode distribution of our models with respect to BFM. However, it remains unknown whether this discrepancy persists in larger nanosilicate grains or if on the contrary they would yield spectra more consistent with the BFM. To address this question, we repeated the analysis on figures 1 and 2 but using larger grains containing 35 and 70 atoms.

The spectra presented in Figure 5 indicates that the general trend remains consistent with that of the dimers (Figures 1 and 2). For both grain sizes, the BFM continues to overestimate the number of modes below 400 cm^{-1} , followed by its underestimation with convergence occurring at higher frequencies. However, for the larger grains containing 70 atoms, there are indications of a slope change in the cumulative number of modes around 700 cm^{-1} . This slope change could be linked to the emergence of two distinct signals in the IR, corresponding to the 10- and 18-micron features observed in bulk silicate particles.

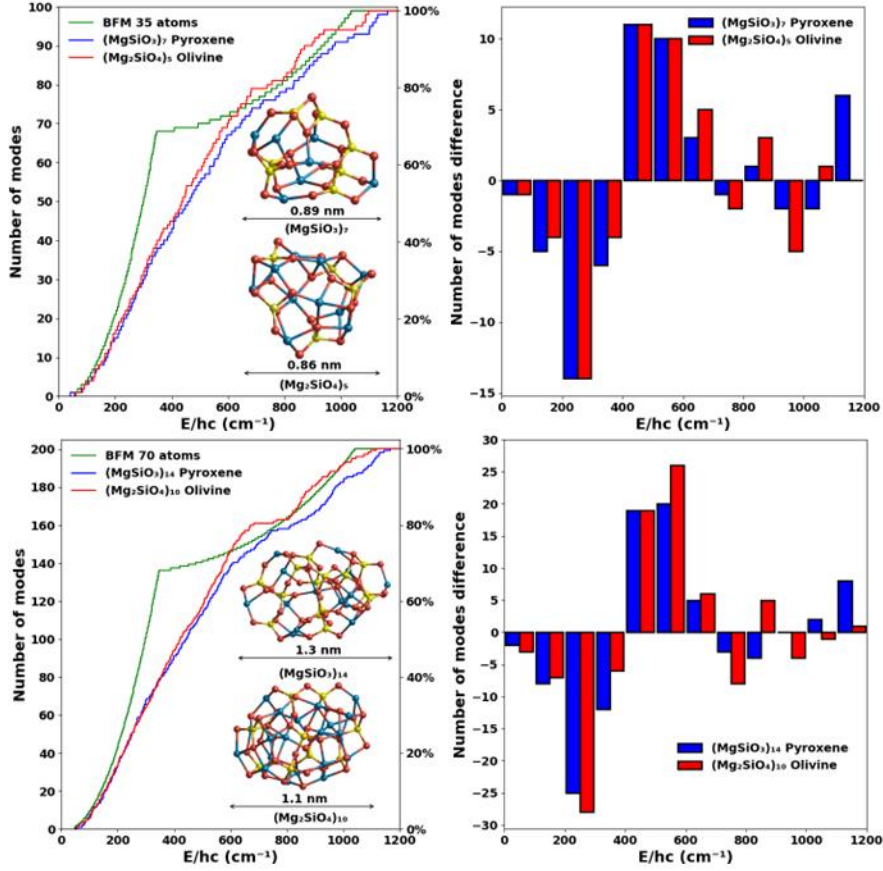


Figure 5: Left: Comparison of the vibrational mode spectra, using our models, of pyroxene (blue) and olivine (red) nanosilicates containing 35 (upper) and 70 atoms (bottom) with respect to the BFM with the same number of atoms (green). Right: Difference in the number of modes between the DFT and BFM spectra with respect to binned frequency ranges of 100 cm^{-1} . Positive (negative) differences indicate that the DFT-based spectra have more (less) vibrational modes in a given bin. Oxygen, magnesium and silicon atoms are depicted as red, blue and yellow spheres respectively.

The results presented so far reveal significant differences in the distribution of vibrational modes computed using DFT and BFM. Therefore, these discrepancies are expected to be reflected, to a certain extent, in the corresponding heat capacities. To quantify this effect, we computed the heat capacities using both approaches across a range of temperatures where there are clear discrepancies for all the previous analysed nanosilicates.

From the computed vibrational frequencies, either using DFT or BFM, it is possible to derive the heat capacity, depending on the temperature, of the grains using standard statistical mechanics¹⁴ by using Equation 1 and 2.

$$\bar{E}(T) = \sum_{j=1}^N \frac{h\nu_j}{\exp\left(\frac{h\nu_j}{k_b T}\right) - 1} \quad 1$$

$$C(T) = \frac{d\bar{E}}{dT} = k_b \sum_{j=1}^N \exp\left(\frac{-h\nu_j}{k_b T}\right) \cdot \left[\frac{h\nu_j}{1 - \exp\left(\frac{-h\nu_j}{k_b T}\right) k_b T} \right]^2 \quad 2$$

The results, presented in Figures 6 and 7, indicate that DFT-derived heat capacities are consistently lower than those obtained using BFM, particularly at low temperatures, with the maximum differences found around 150 K. Additionally, the analysis of larger grains reveals that pyroxenic grains exhibit slightly larger discrepancies between models. This behaviour is consistent with the vibrational spectra, where pyroxenic grains showed less agreement with BFM than in the case of olivinic grains (see Figure 5).

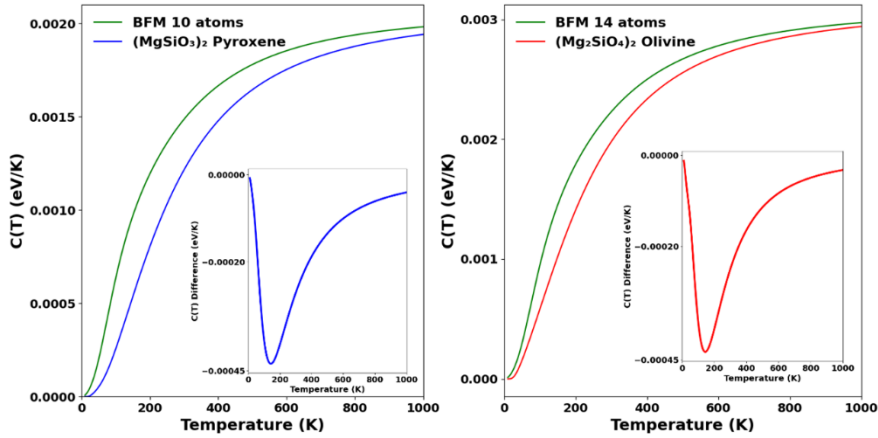


Figure 6: Heat capacity for pyroxene (left) and olivine (right) dimers computed using DFT vibrational modes (blue and red) and with BFM (green). Inset plots show the heat capacity difference between both models.

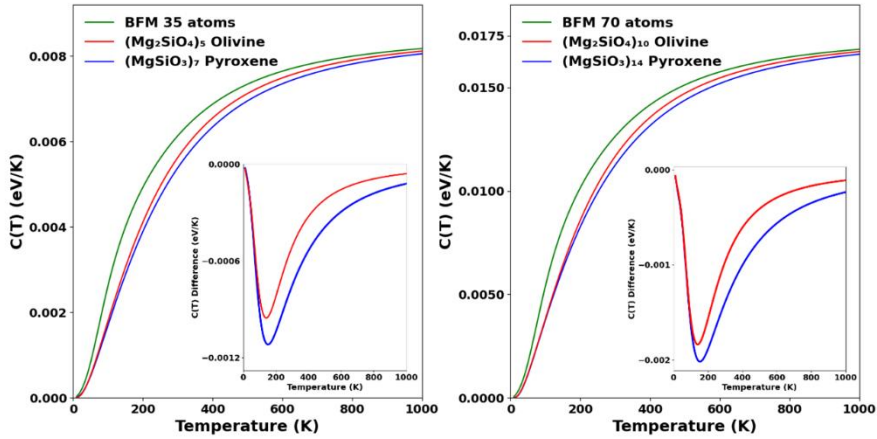


Figure 7: Heat capacity for pyroxene (left) and olivine (right) nanoclusters with 35 (left) and 70 atoms (right) computed using DFT vibrational modes (blue and red) and with BFM (green). Inset plots show the heat capacity difference between both models.

The observed differences between the calculated heat capacities can be directly explained by the differences in the vibrational spectra. As shown in Figures 1 and 5, BFM tends to overestimate the number of low frequency modes. Nanosilicates with more low frequency modes have more degrees of freedom available to distribute modest energy increments, leading to smaller temperature increases and in consequence larger heat capacities.

Finally, to assess the impact of these heat capacity differences on the temperature rise induced by the absorption of UV photons, we computed the temperature increases using equation 1 for a typical range of UV photons energy. The results displayed in Figure 8 show that low energy photons (~ 1.2 eV / $\sim 1.5 \cdot 10^4$ cm) can heat the dimers up to approximately 1000 K. Moreover, the expected underestimation of the temperature rise by the BFM is confirmed, with differences ranging from 50 to 80 K (see insets in Figure 8). This discrepancy could potentially have a relevant impact in improving the modelling of nanosilicates IR emissivity.

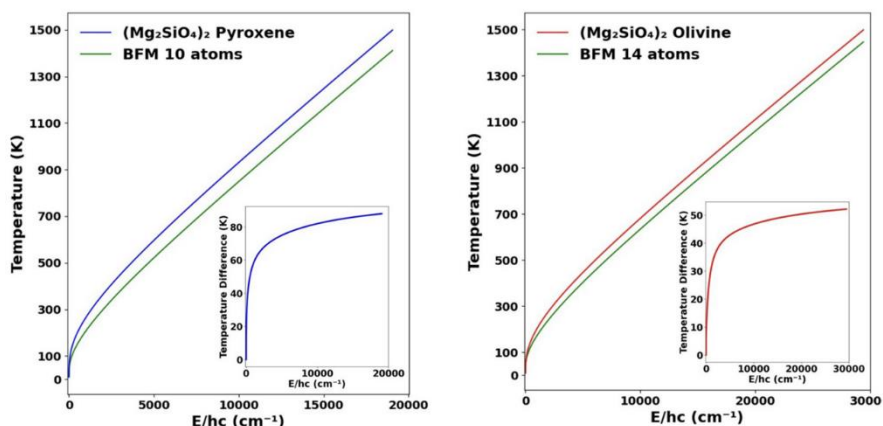


Figure 8: Temperature vs average energy plots for nanosilicate dimers computed from DFT vibrational modes (pyroxene blue, olivine red) and from the BFM spectra (green). Insets show the difference between the DFT and BFM temperatures.

For the larger grains, the absorption of higher energy UV photons is required to achieve a similar heating of 1000 K (see Figure 9), as expected from the larger heat capacities computed in Figure 6. The temperature discrepancies between BFM and DFT are slightly smaller than those observed for dimers, with maximum difference of ~60 K. As anticipated from previous results, the discrepancies are more pronounced in pyroxenic than in olivine grains.

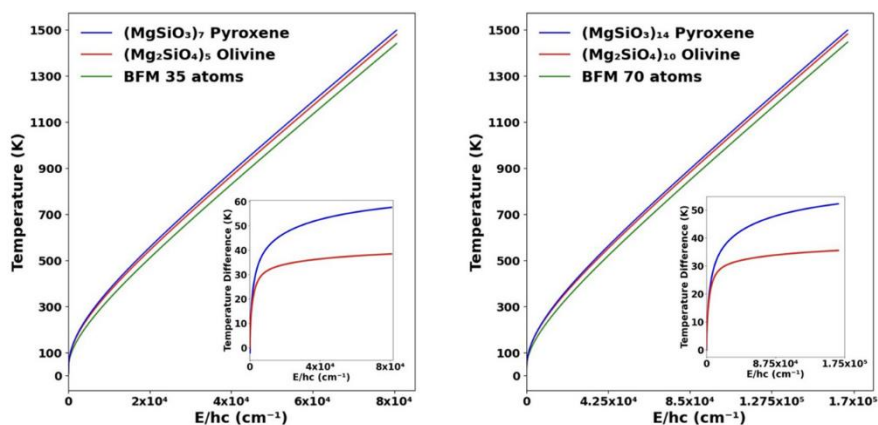


Figure 9: Temperature vs average energy plots for nanosilicate with 35 (left) and 70 atoms (right) computed from DFT vibrational modes (pyroxene blue, olivine red) and from the BFM spectra (green). Insets show the difference between the DFT and BFM temperatures.

For larger grains with few nanometers of radius, stochastic heating derived from BFM, at low temperatures, is predicted to produce temperature increases of just a few tens of Kelvin.^{6,7} From the BFM, and assuming the density and molecular mass of the grains, the heat capacity, at low temperatures, can be expressed as⁶:

$$C(T) = 61.38 \cdot r^3 T^3 \quad 3$$

In Figure 10 we compare the DFT-based heat capacity at low temperatures for the 70 atoms grains with the heat capacity derived in equation 3. By fitting DFT data with an expression of the type $C(T)=A \cdot r^3 T^3$ we observe a good agreement between the two approaches and the fit for the 0-50 K range for olivinic grains. However, for pyroxene grains significant deviations between the DFT-fitted data and BFM are observed. This poorer agreement for pyroxene nanograins likely originates from the experimental materials used to construct the BFM. Specifically, in reference 9 the heat capacities of nanosilicates were derived from fits to basalt glass (composed of approximately 50% SiO₂ and 50% metal oxides) and obsidian (roughly 75% SiO₂ and 25% metal oxides). Therefore, these materials, for which the exact composition is not provided, must have a vibrational modes distribution that resemble those of olivine more closely than those of pyroxene, thus explaining the better match with olivinic grains.

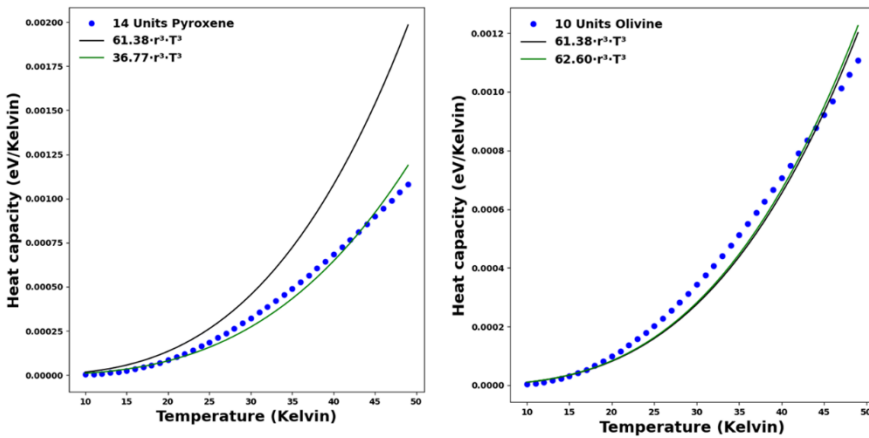


Figure 10: Comparison of the BFM-based heat capacity from Equation 3 (black line) and the DFT derived values for the 70 atoms pyroxene (left) and olivine (right) grains (blue points). Green line indicates the fitting of the DFT data using the same kind of equation as in Equation 3.

5.3 Conclusions

These findings, combined with the additional data and analysis provided in the accompanying research article, support the following conclusions:

- 1- The vibrational mode distribution derived from DFT-PBE0 calculations exhibit significant deviations from those obtained from the BFM across all nanosilicates analysed. These discrepancies are especially significant at frequencies below 700 cm^{-1} .
- 2- The analysis of the vibrational mode distribution for a set of low energy isomers with respect to that of the global minimum structure reveals minor differences indicating that the comparison of a single low energy isomers with respect to the BFM is enough to extract reliable conclusions.
- 3- The heat capacities computed from the DFT frequencies are consistently lower than those predicted by the BFM, with the largest deviations observed around 150 K.
- 4- The differences in heat capacities imply that the instantaneous temperature reached by small nanoclusters upon absorbing UV radiation would be 35 – 80 K larger than previously estimated.
- 5- The discrepancy in the heat capacities and temperature increase between BFM and DFT-PBE0 calculations are larger for pyroxenic than olivinic grains. This is especially clear in the fittings of low temperature heat capacities.

5.4 References

- ¹ Kim, Sang-Hee and Martin, P. G. The size distribution of interstellar dust particles as determined from polarization: Spheroids. *Astrophysical Journal*, Part 1. **1995**, 444(1), 293-305.
- ² Mathis, John S.; Rumpl, William and Nordsieck, Kenneth H. The size distribution of interstellar grains. *Astrophysical Journal*. **1977**, 217, 425-433.
- ³ Greenberg, J. M. In *Stars and Stellar Systems*; Middlehurst, B. M., Aller, L. H., Eds.: Univ. Chicago Press: Chicago, IL, 1968; Vol. 7, p 221.
- ⁴ Duley, W. W. Fluctuations in interstellar grain temperatures. *Astrophys. Space Sci.* 1973, 23, 43–50
- ⁵ Draine, B. T. and Anderson, N. Temperature fluctuations and infrared emission from interstellar grains. *Astrophysical Journal*. **1985**, 292, 494-499.
- ⁶ Cuppen, H. M.; Morata, O. and Herbst, E. Monte Carlo simulations of H₂ formation on stochastically heated grains. *Mon. Not. R. Astron. Soc.* **2006**, 367, 1757–1765.
- ⁷ Chen, L.-F.; Chang, Q.; Xi, H.-W. Effect of stochastic grain heating on cold dense clouds chemistry. *Mon. Not. R. Astron. Soc.* **2018**, 479, 2988–3001.
- ⁸ Camps, P.; Misselt, K.; Bianchi, S.; Lunttila, T.; Pinte, C.; Natale, G.; Juvela, M.; Fischera, J.; Fitzgerald, M. P.; Gordon, K.; Baes, M. and Steinacker, J. Benchmarking the calculation of stochastic heating and emissivity of dust grains in the context of radiative transfers simulations. *Astronomy & Astrophysics*. **2015**, 580, A87.
- ⁹ Draine, B. T.; Li, A. Infrared Emission from Interstellar Dust. I. Stochastic Heating of Small Grains. *Astrophys. J.* **2001**, 551, 807–824.
- ¹⁰ Zhukovska, Svitlana; Henning, Thomas and Dobbs, Clare. Iron and silicate dust growth in the galactic interstellar medium: clues from element depletions. *The Astrophysical Journal*. **2018**, 857(2), 94.

¹¹ Li, A, and Draine, B. T. Infrared emission from interstellar dust. II. The diffuse interstellar medium. *The Astrophysical Journal*. **2001**, 554(2), 778.

¹² Henning, Thomas. Cosmic silicates. *Annual Review of Astronomy and Astrophysics*. **2010**, 48(1), 21-46.

¹³ Escatllar, A. M.; Lazaukas, T.; Woodley, S. M. and Bromley, S. T. Structure and properties of nanosilicates with olivine (Mg₂SiO₄)_N and pyroxene (MgSiO₃)_N compositions. *ACS Earth and Space Chemistry*. **2019**, 3(11), 2390-2403.

¹⁴ McQuarrie, D. A. and Simons, J. D. *Molecular Thermodynamics*; University Science Book, Sausalito, CA, 1999.

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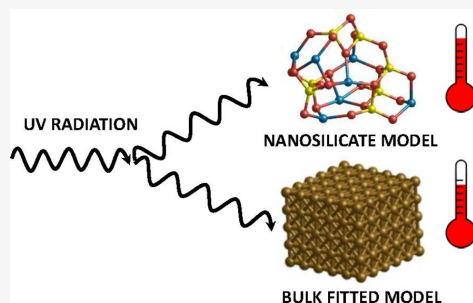


Article Recommendations



Supporting Information

ABSTRACT: Ultrasmall nanosized silicate grains are likely to be highly abundant in the interstellar medium. From sporadically absorbing energy from ultraviolet photons, these nanosilicates are subjected to significant instantaneous temperature fluctuations. These stochastically heated nanograins subsequently emit in the infrared. Previous estimates of the extent of the heating and emission have relied on empirical fits to bulk silicate heat capacities. The heat capacity of a system depends on the range of available vibrational modes, which for nanosized solids is dramatically affected by the constraints of finite size. Although experimental vibrational spectra of nanosilicates is not yet available, we directly take these finite size effects into account by using accurate vibrational spectra of low-energy nanosilicate structures from quantum chemical density functional theory calculations. Our results indicate that the heat capacities of ultrasmall nanosilicates are smaller than previously estimated, which would lead to a higher temperature and more intense infrared emission during stochastic heating. Specifically, we find that stochastically heated grains ultrasmall nanosilicates could be up to 35–80 K hotter than previously predicted. Our results could help to improve the understanding of infrared emission from ultrasmall nanosilicates in the ISM, which could be observed by the James Webb Space Telescope.



INTRODUCTION

Dust particles are prevalent throughout the interstellar medium (ISM), where they reveal themselves through their interaction with electromagnetic radiation.¹ Much of the dust mass in the ISM is carried by grains with a typical radius (r) of $\sim 0.1 \mu\text{m}$ (100 nm). However, the number of dust grains with respect to size approximately follows an inverse power law ($n_g(r) = cr^{-3.5}$),² which massively favors higher populations of smaller grains. It has long been realized that the low time-averaged temperature of very small grains in the ISM would not capture the large temperature fluctuations due to transient heating of such species when interacting with the radiation field of the ISM.³ The first calculations of this effect showed that dust grains with diameters of only a few nanometres are particularly susceptible to sporadic temperature spikes.⁴ This effect, now commonly referred to as stochastic heating, involves the relatively infrequent absorption of energy from ultraviolet (UV) photons, which leads to above average grain temperatures and a subsequently rapid readjustment to ambient ISM temperatures via emission in the infrared (IR). Stochastic heating is now appreciated to be an important mechanism for generating IR emission in a number of astrophysical environments. The temperature and emissivity of stochastically heated

nanograins on the rates of UV energy absorption and subsequent IR emission, which, in turn, is intimately linked to their specific heat capacity.^{5,6} Most modern calculations of stochastic heating follow the approach by Draine and Li, which used a statistical mechanical treatment.⁵ In this work the temperature dependent heat capacity, $C(T)$, of a nanosized dust grain is directly calculated from its distribution of available vibrational modes (for inducing temperature increase) with respect to their frequency (i.e., energy). We follow this approach and show how it can be enhanced for the smallest grain sizes by using vibrational modes evaluated from direct and accurate quantum chemical calculations using atomistically detailed stable nanograin structures.

Herein, we consider silicate dust, which is observed in a wide range of astronomical environments and typically has a magnesium-rich pyroxene (MgSiO_3) or olivine (Mg_2SiO_4)

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composition.⁷ Considering observations of IR emission in the ISM, it has been estimated that ultrasmall nanosilicates ($r \leq 1.5$ nm) could be highly abundant and account for $\sim 10\%$ of all silicon in the dust population.⁸ Nanosilicates can be formed from the processing of larger grains in the ISM,⁹ where they are a likely source of the anomalous microwave emission.^{10–12} and can assist in the formation of H_2 ^{13,14} and ices.¹⁵ With respect to the latter, studies have shown that stochastically heated silicate grains with $r \approx 0.005$ μm (5 nm) exhibit temperature fluctuations up to 20–40 K, which is predicted to have a significant impact on their role in astrochemical processes.^{16,17} For even smaller nanosilicates possessing only a few 10s of atoms (approximately with $r \leq 0.5$ nm), the fluctuations in temperature from stochastic heating have been estimated to be up to ~ 1000 K⁵ with, as yet, unknown consequences for astrochemistry.

In ref 5 the heat capacities of nanosilicate grains were estimated based on a bimodal distribution of harmonic vibrations, which was found to be reasonable for reproducing measured temperature-dependent heat capacities of bulk basalt, while providing a somewhat poorer fit to bulk SiO_2 . This bulk approximation (hereafter referred to as the “bulk fitted model”, BFM) has since been employed in other studies of stochastic heating of small silicate dust grains.^{16,17} For nanosilicates, their extreme small size and resultant non-bulk-like and noncrystalline structures leads to their vibrational spectra being quite unlike those of bulk silicates.¹⁸ Thus, although the general BFM approach represents a solid microscopic framework for calculating heat capacities of small silicate dust grains, the original implementation has a few shortcomings: (1) The reference bulk materials (i.e., basalt, obsidian, silica) are not compositionally good matches for the composition of Mg-rich silicate dust grains in the ISM; (2) The fit of the spectrum to the bulk $C(T)$ versus T curves is purely empirical and does not consider the direct physical origin of the vibrational modes in silicate dust grains; (3) The fit is with respect to the measured $C(T)$ of bulk samples (i.e., not nanosized grains). Herein, we address all these three issues using an accurate quantum chemical approach in which we directly calculate the vibrational modes in atomically detailed and energetically stable nanosilicates having Mg-rich olivine and pyroxene compositions. As heat capacities of nanosilicates are not yet experimentally available, our approach provides a direct and accurate alternative to relying on empirical fits to bulk heat capacity data. Our resulting calculated heat capacities and energy-dependent temperatures of ultrasmall nanosilicate grains are compared with those derived from the BFM approximation.

In previous work, we derived the atomistically detailed structures of low energy nanosilicate clusters for astronomically relevant Mg-rich pyroxene and olivine compositions.¹⁸ Therein, we confirmed that the IR vibrational spectra of these species, accurately obtained using quantum chemical density functional theory (DFT) based calculations, are quite distinct from those of bulk silicates. Herein, we use DFT-based calculations to obtain accurate full vibrational distributions of selected nanosilicate grains and use this data to directly derive temperature-dependent heat capacities. Our results show that BFM estimates of the distribution of vibrational modes tend to overestimate the heat capacity of nanosilicate grains, especially at temperatures around 50–300 K. As a result, for a typical range of energies for photon absorption, our refined heat capacity derivations predict that ultrasmall nanosilicates in the

ISM could be heated by 35–80 K more than previously expected.

Until now it has been impossible to directly confirm the presence of ultrasmall nanosilicates in the ISM. However, the James Webb Space Telescope (JWST) now has highly sensitive instruments covering an ideal range of wavelengths to observe nanosilicate IR emission in the ISM.¹⁹ Our results should allow for more accurate predictions of the IR emission characteristics of stochastically heated nanosilicate grains and could thus be important for accurately interpreting upcoming JWST observations of the ISM.

■ COMPUTATIONAL METHODOLOGY

Optimized nanosilicate structures and their harmonic vibrational spectra were obtained using DFT calculations with an all-electron light-tier 1 numerical atom-centered orbital basis set employing the Fritz Haber Institute ab initio molecular simulations package (FHI-AIMS).²⁰ In previous studies it has been shown that this basis set has a quality comparable to valence triple- ζ plus a polarization Gaussian-type orbital basis set.^{21,22} The PBE0²³ exchange-correlation functional was used in all the calculations. Previous works have shown that this functional is able to accurately reproduce the IR spectra of bulk crystalline olivine²⁴ (forsterite) and pyroxene²⁵ (enstatite), and the IR spectra of both pyroxene and olivine monomers.²⁶

Once the vibrational modes have been calculated for each nanosilicate, we assume that the grain is in thermal equilibrium at a given temperature, T , and use standard statistical mechanics²⁷ to obtain the average energy, $\bar{E}(T)$, from

$$\bar{E}(T) = \sum_{j=1}^N \frac{h\nu_j}{\exp\left(\frac{h\nu_j}{k_B T}\right) - 1} \quad (1)$$

where N is the number of vibrational frequencies of the grain, ν_j are the vibrational frequencies, and k_B is the Boltzmann constant. By differentiating the expression for average energy in (eq 1) with respect to T , one can then obtain the heat capacity of the grain:

$$C(T) = \frac{d\bar{E}}{dT} = k_B \sum_{j=1}^N \exp\left(\frac{-h\nu_j}{k_B T}\right) \cdot \left[\frac{h\nu_j}{1 - \exp\left(\frac{-h\nu_j}{k_B T}\right)} \right]^2 \quad (2)$$

In this work we study three sizes of ultrasmall silicate grains: (a) dimers of pyroxene (i.e., $(\text{MgSiO}_3)_2$ with 10 atoms) and olivine (i.e., $(\text{Mg}_2\text{SiO}_4)_2$ with 14 atoms), (b) 35-atom nanograins of pyroxene (i.e., $(\text{MgSiO}_3)_7$) and olivine (i.e., $(\text{Mg}_2\text{SiO}_4)_5$), and (c) 70-atom nanograins of pyroxene (i.e., $(\text{MgSiO}_3)_{14}$) and olivine (i.e., $(\text{Mg}_2\text{SiO}_4)_{10}$). The structures of all nanosilicate clusters were found by dedicated global optimization searches following the approach described in our previous work.¹⁸ Specifically, for the 35-atom and 70-atom nanosilicates, we used the lowest energy structure from these searches. For the pyroxene and olivine dimer species, we employed both the previously reported global minima and also the next two higher energy isomers in each case. We note that the low energy 70-atom pyroxene structure and the metastable dimer species were not reported previously, and their structures are provided in the Supporting Information.

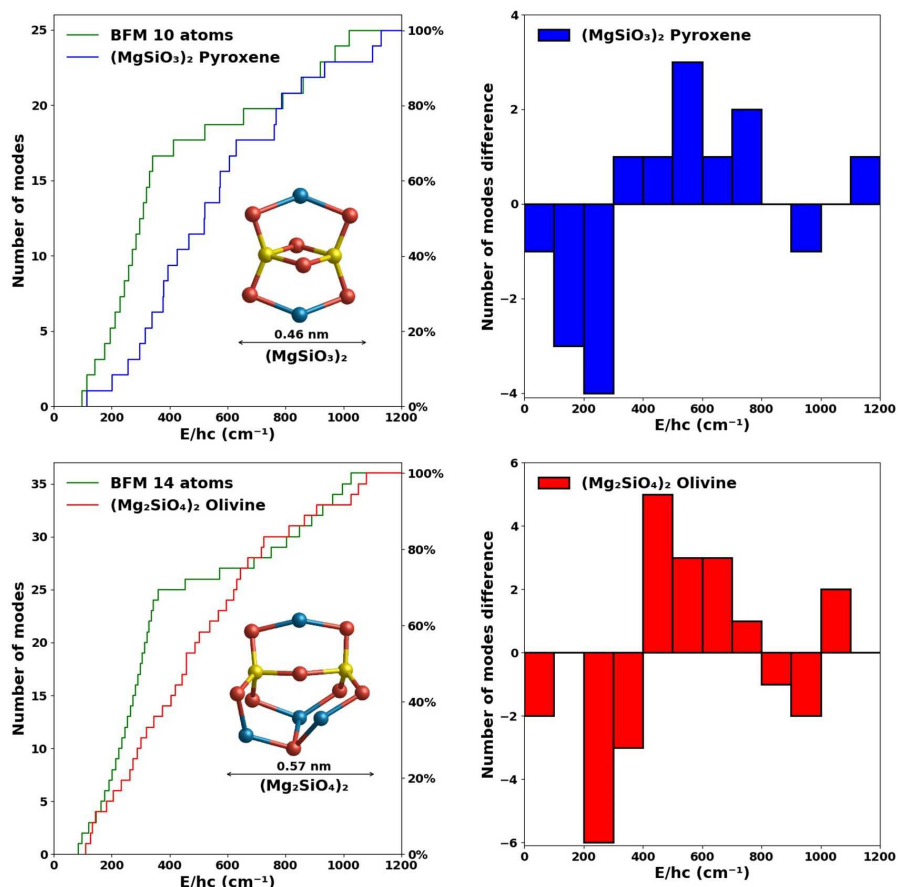


Figure 1. Left: Comparison of the cumulative vibrational mode spectra of pyroxene (blue, upper) and olivine (red, lower) dimers with respect to the corresponding BFM silicate vibrational spectra (green). Right: Differences in number of modes between the DFT and BFM spectra with respect to binned frequency in ranges of 100 cm^{-1} . Positive (negative) differences indicate that the DFT-derived spectra have more (fewer) vibrational modes in that bin. Atom color code: red, oxygen; blue, magnesium; yellow, silicon.

RESULTS AND DISCUSSION

Vibrational Mode Spectra. In Figure 1 we compare our DFT-calculated vibrational mode spectrum of the lowest energy pyroxene and olivine dimers with that derived from the BFM. In Figure 2 we can clearly see that the BFM spectra overestimates the number of vibrational modes that are found at lower frequencies (approximately $200\text{--}600 \text{ cm}^{-1}$) with respect to our more realistic model, in which the vibrations are more evenly distributed throughout the whole frequency range. This effect is observed in both pyroxene and olivine dimers, but is more noticeable in the case of pyroxene. In both cases, around 66% of the vibrational modes are found between 0 and 400 cm^{-1} in the BFM spectra. However, in our directly calculated spectra, we do not reach 66% of the modes until a frequency of $\sim 700 \text{ cm}^{-1}$. This difference can be more explicitly seen by summing the number of frequencies found in regular bins of 100 cm^{-1} and comparing the number of frequencies in each bin for each spectrum. From the resulting histograms (see Figure 1, right), we can see that the number of vibrations in the BFM spectra are relatively overestimated in the region between

0 and $300\text{--}400 \text{ cm}^{-1}$ and underestimated in the region between 400 and 800 cm^{-1} . For higher frequencies, all spectra converge and the differences are small.

We note that in our previous work we established that increasing the temperature of silicate dimers led to small shifts in the vibrational frequencies as compared to the 0 K harmonic frequencies.²⁶ Relatively elevated temperatures ($\sim 800 \text{ K}$) can induce small conformational structural changes in such ultrasmall silicate species.^{26,13} Higher temperatures will lead to a more significant structural isomerization and eventually total melting. To estimate the effect of isomerization, we compare the vibrational spectra of the global minima silicate dimers (i.e., those from Figure 1) with vibrational spectra derived from averaging the number of vibrational modes from a set of three low energy isomers for both pyroxene and olivine dimers. To obtain the average of the spectra, we divide each spectrum into bins of 100 cm^{-1} and average the total number of vibrational modes per isomer in each bin (see Figures 2 and 3).

The comparisons in Figures 2 and 3 show that the resulting vibrational spectra do not change significantly when consid-

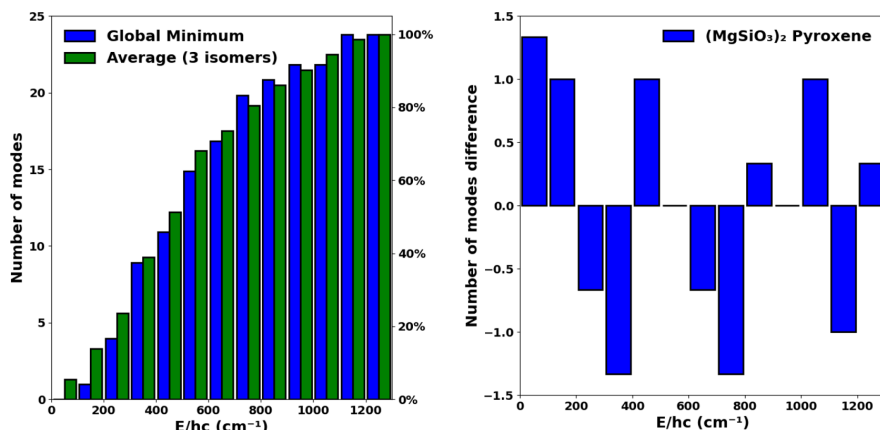


Figure 2. Left: Comparison between the cumulative vibrational spectra of the global minimum pyroxene dimer (blue) and the averaged spectra of three pyroxene dimer isomers (green). Right: The respective difference in the number of modes in each bin (i.e., global minimum vs average). A positive (negative) number of modes difference indicates that the averaged spectrum has more (fewer) vibrational modes in that bin.

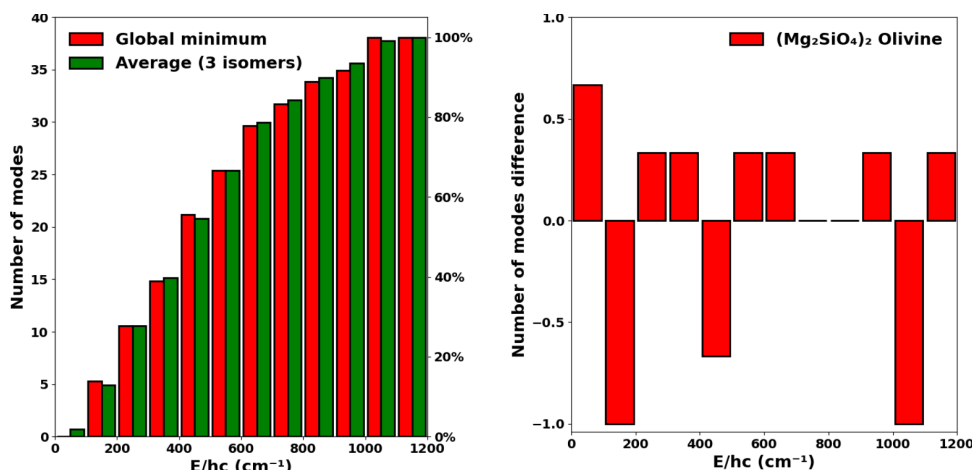


Figure 3. Left: Comparison between the cumulative vibrational spectra of the global minimum olivine dimer (red) and the averaged spectra of three olivine dimer isomers (green). Right: The respective difference in the number of modes in each bin (i.e., global minimum vs average). A positive (negative) number of modes difference indicates that the averaged spectrum has relatively more (fewer) vibrational modes in that bin.

ering either the lowest energy nanosilicate structure or multiple low energy isomers for either silicate stoichiometries. Specifically, in any 100 cm^{-1} bin, the maximum difference in the number of modes between the two spectra is always found to be less than two. Considering this result, in the rest of the study we shall only consider the spectra obtained from the lowest energy nanosilicate structure for each size and stoichiometry considered.

So far, we have considered only extremely small molecular silicate species. With increasing size, it may be expected that our bottom-up calculated vibrational spectra would better match the BFM vibrational spectra. To begin to answer this question, we obtain the vibrational spectra of larger nanosilicates containing 35 and 70 atoms with both pyroxene and olivine compositions.

From Figure 4 (left), we see that the vibrational spectra for 35-atom and 70-atom nanosilicates follow a very similar

tendency as found for the case of the silicate dimers. For both sizes considered, the increase in the number of modes with respect to frequency for both pyroxene and olivine follows a very similar tendency up to $\sim 700 \text{ cm}^{-1}$, where they show the greatest difference with the fitted spectra. In the BFM spectra 66% of the vibrational modes are found between 0 and 400 cm^{-1} , whereas in our bottom-up calculated spectra we need to reach 700 cm^{-1} before the same proportion of modes are found. In Figure 4 (right) we show the binned difference in the number of vibrational modes between the bulk-fitted spectra and our calculated spectra. As for the dimers, we can again observe that the BFM spectra begin with an overestimation of the number of vibrational modes, followed by an intermediate region in which the vibrational modes are underestimated with respect to our calculated spectra. For the higher frequency region ($>700 \text{ cm}^{-1}$), our calculated spectra, for all nanosilicate sizes, and the BFM spectra match quite well. Olivine species

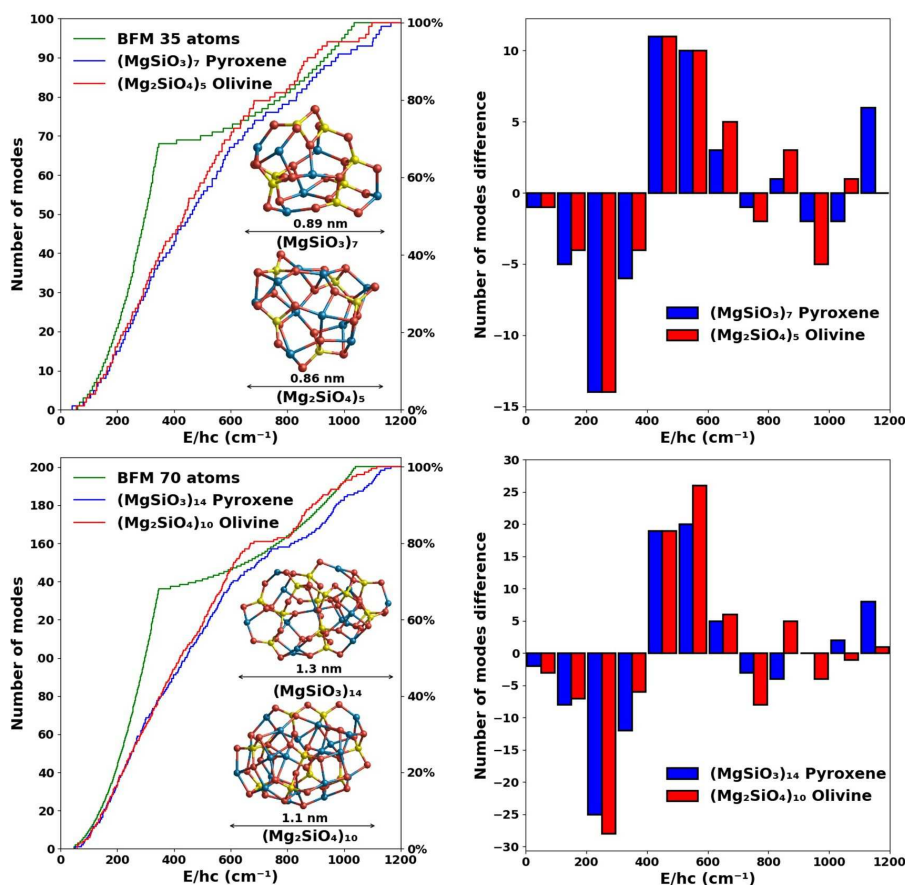


Figure 4. Left: Comparison of the cumulative vibrational mode spectra of pyroxene (blue) and olivine (red) nanosilicates containing 35 (upper) and 70 atoms (lower) with respect to the corresponding BFM vibrational spectra (green). Right: Differences in number of modes between the DFT and BFM spectra with respect to binned frequency ranges of 100 cm^{-1} . Positive (negative) differences indicate that the DFT-derived spectra have more (fewer) vibrational modes in that bin. Atom color code as in Figure 1.

show a tendency to have slightly more modes at lower frequencies (approximately $<700 \text{ cm}^{-1}$) than the pyroxene species of the same size and vice versa at higher frequencies. However, both pyroxene and olivine nanosilicates have a significantly lower number of modes in this frequency range than the BFM spectra.

Generally, our calculated vibrational mode spectra for all pyroxene and olivine nanosilicates show a relatively smooth monotonic increase in the number of modes with increasing frequency. In particular, none of our nanosilicates display a clear two-phase pattern to their cumulative vibrational spectra, with an abrupt change at $\sim 300 \text{ cm}^{-1}$, as used in the BFM spectra. It is of note, however, that for the largest size of 70 atoms ($r \approx 0.5/0.6 \text{ nm}$), we observe some indications of an emerging change in slope of the cumulative vibrational spectra near to 700 cm^{-1} ($12.5 \mu\text{m}$). We speculate that this may be linked to the emergence of the separate 10 and $18 \mu\text{m}$ IR vibrational bands observed in larger silicate dust particles.⁷

Finally, we note that all our vibrational spectra are derived using the harmonic approximation. Any vibrational modes

exhibiting anharmonicity tend to shift to slightly lower frequencies (with respect to purely harmonic modes) with increasing temperature. We have previously found that this effect is small in nanosilicates and only becomes apparent above at approximately 400 K .²⁶ Assuming a relatively large anharmonic downshift of all our harmonic frequencies by 5%, we find that our final results regarding the stochastic heating are essentially unchanged (see SI for details).

Heat Capacity. The heat capacity, $C(T)$, of a grain can be derived from the spectrum of its vibrational modes as described above (see eq 2). As we have seen, there are significant differences between our DFT-calculated vibrational mode spectra and those from the BFM, which will thus influence the corresponding $C(T)$ values. As this vibrational difference is especially notable in the low frequency region, we expect that the corresponding largest $C(T)$ differences would be at lower temperatures. In Figure 5 we show the $C(T)$ curves derived from the vibrational spectra shown in Figure 1 for the silicate dimer species. We see that the heat capacity derived from our vibrational modes for the pyroxene and olivine

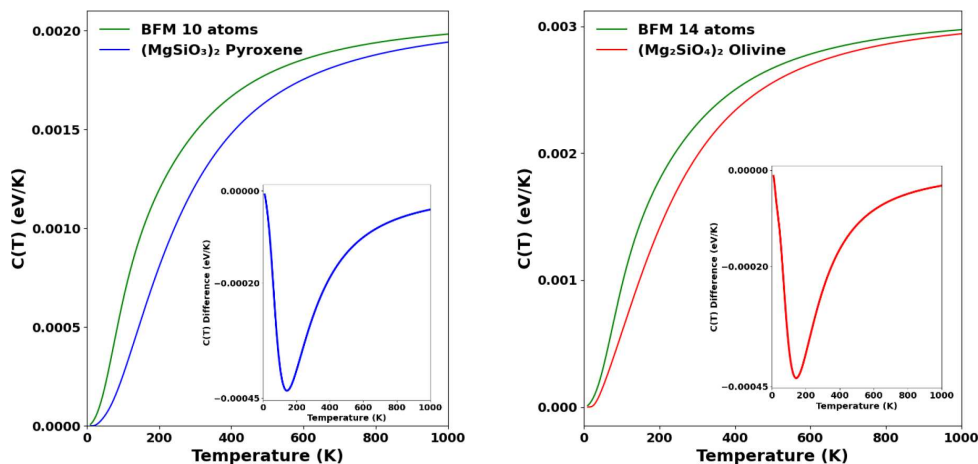


Figure 5. Specific heat capacity for pyroxene (left) and olivine (right) dimers compared with BFM (green). Inset plots show the heat capacity difference between the two respective $C(T)$ curves.

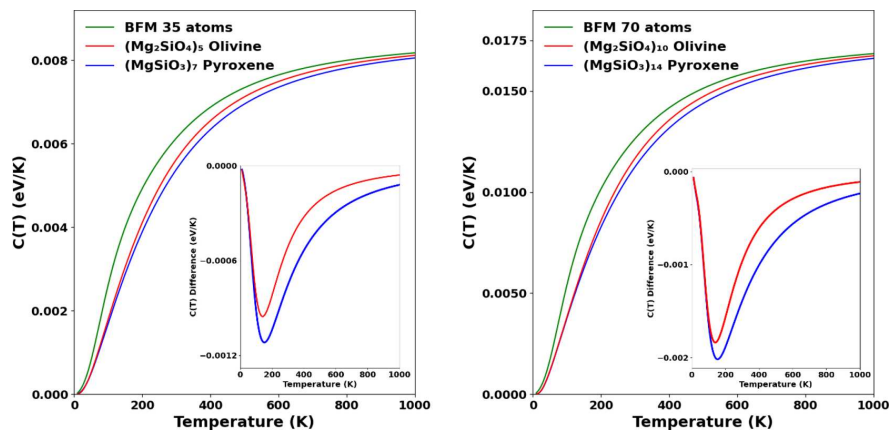


Figure 6. Specific heat capacity for pyroxene (blue) and olivine (red) nanosilicates with 35 (left) and 70 atoms (right) compared with BFM (green). Inset plots show the difference between the two respective $C(T)$ curves.

dimers is generally lower than the BFM heat capacity. This difference has its maximum around 150 K and is larger for the pyroxene stoichiometry. In Figure 6 we show the $C(T)$ curves for 35-atom and 70-atom nanosilicates, where we also observe the corresponding differences with the BFM as found in the case of the dimers.

The differences between the calculated specific heat capacities in Figures 5 and 6 can be simply explained from the corresponding differences in the vibrational mode spectra in each case. Above, we noted that the BFM vibrational spectra always overestimates the number of modes in the lower frequency region with respect to our DFT-calculated vibrational spectra. For nanosilicates having the same number of atoms, those with more modes at lower frequencies are able to distribute modest energy increases throughout more degrees of freedom, thus, resulting in a relatively lower temperature increase (i.e., a larger heat capacity).

The heat capacity plays an important role in calculating how these ultrasmall silicates absorb and emit radiation in the ISM

and thus how they are affected by stochastic heating.^{5,16,17,6} Our results show that the BFM vibrational spectra lead to overestimates of $C(T)$ with respect to heat capacities derived from accurate directly computed vibrational spectra for ultrasmall silicates. For such species, the immediate temperature rise induced by absorbing a UV photon in the ISM can be calculated using eq 1. In Figure 7 we show temperature versus average energy plots for nanosilicates for a range of nanosilicate stoichiometries and sizes. The energy axes in each case in Figure 7 cover the energies of typical UV photons in the ISM. We truncate the plots at a temperature at 1500 K, which is likely to be near the melting temperature of the largest nanosized silicate grains considered. We note that even the smallest nanosilicate species can withstand 800 K without fully melting.^{13,26}

The plots in Figure 7 show that the smallest silicate dimers would be readily heated to close to 1000 K by relatively low energy visible photons ($\sim 1.5 \times 10^4 \text{ cm}^{-1} \sim 1.2 \text{ eV}$). In such a scenario, our results show that BFM-based calculations

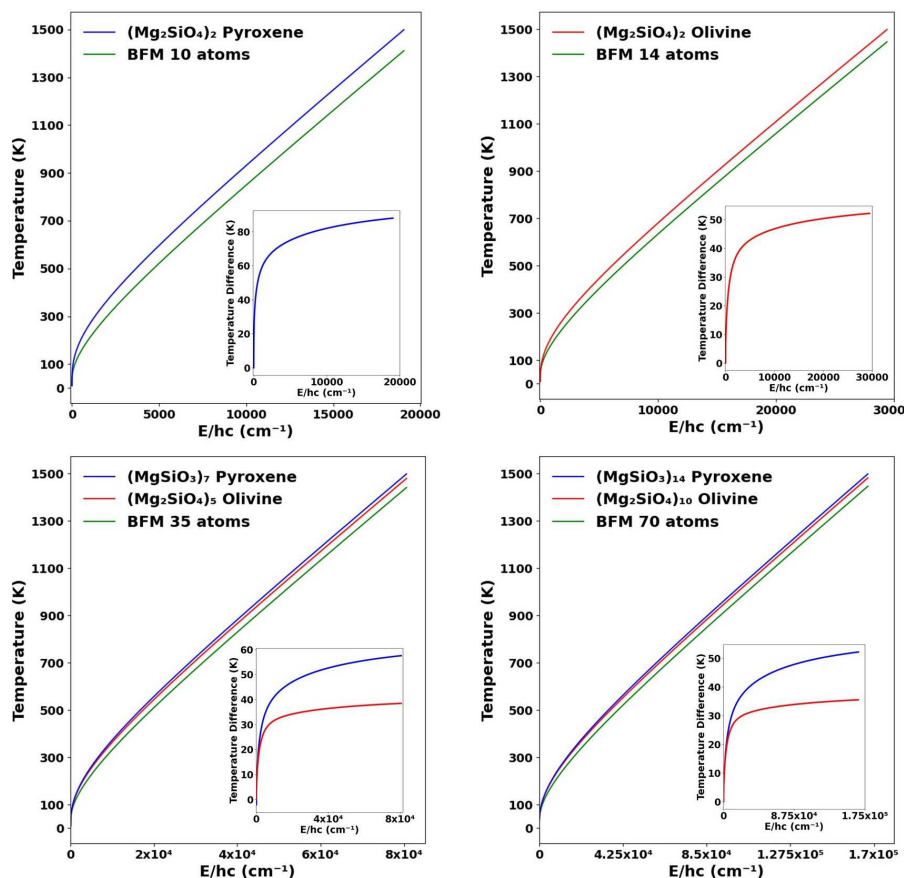


Figure 7. Temperature vs average energy plots for nanosilicates derived from DFT-calculated vibrational spectra (pyroxenes, blue; olivines, red) and from the BFM vibrational spectra (green) for different sizes. Insets show the difference between the DFT-derived values and the BFM-derived values (pyroxenes, blue; olivines, red).

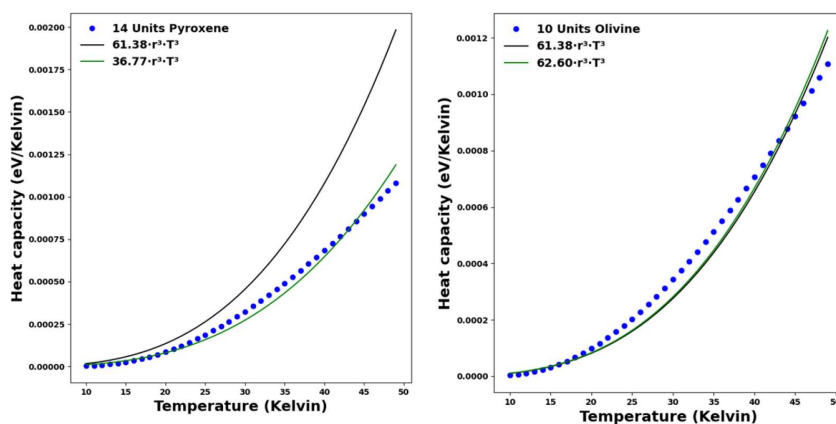


Figure 8. Comparison of the low-temperature BFM-like fitted $C(T)$ used in refs¹⁶ and ¹⁷ (black solid line) and our DFT-derived $C(T)$ values for 70-atom pyroxene (left) and olivine (right) nanosilicates (blue data points). We include an approximate fit to our data (green solid line) for comparison with the BFM-like fit.

underestimate the photon-induced instantaneous temperature increase by 50–80 K (see insets in the upper two plots in Figure 7). For larger nanosilicate grains with 35–70 atoms, higher energy UV photons are required to achieve a similar ~1000 K heating. In such cases, the BFM underestimation is ~35 K for olivine and ~55 K for pyroxene nanosilicates (see insets in the lower two plots in Figure 7). For small grains the interval between successive visible/UV photon absorption is relatively long compared with the time for IR emission,^{5,16} and stochastically heated ultrasmall nanosilicates will spend most of their time close to that of their ISM environment. However, considering that the total spectral flux is proportional to T^4 , these temperature corrections could lead to noticeable blue shifting in the emission spectra of the, presumably, very high population of ultrasmall nanosilicates in the ISM.

Finally, we note that for larger nanograins with radii of a few nanometers, stochastic heating is predicted to produce relatively milder heating of a few 10s of Kelvin.^{5,16,17} Such predictions are typically made on the basis of low temperature (0–50 K) approximations to the BFM-derived $C(T)$.^{16,17} In Figure 8 we compare our DFT-derived $C(T)$ data with the low temperature BFM-like fitted $C(T)$ used in refs 16 and 17 for 70-atom nanosilicates. Fitting our data with an Ar^3T^3 expression, we find that for olivines there is a good match between our data and the low temperature fit. However, for pyroxenes, the fit to our data is significantly different to the low temperature BFM-like fit. Although the studies in refs 16 and 17 relate to larger nanosilicates than we consider, these results clearly show that there is a limit to the size-dependent applicability of the low-temperature limiting fit of $C(T)$ for nanopyroxenes. Perhaps surprisingly, however, this fitted expression appears to hold for very low temperature stochastic heating of even ultrasmall olivine nanosilicates.

CONCLUSIONS

We calculate accurate vibrational spectra for ultrasmall nanosilicates (10–70 atoms) with stable low energy structures and with both Mg-rich pyroxene and olivine stoichiometries using quantum chemical DFT calculations. Such spectra are known to be significantly affected by the extreme small size of these species and quite distinct from the vibrational spectra of bulk silicates. Comparing our data with vibrational mode spectra that were empirically fitted to reproduce bulk-like $C(T)$ curves for bulk silicates (BFM), for example, we find significant differences, especially at low frequencies ($\leq 700\text{ cm}^{-1}$). Using our ab initio vibrational spectra, we also compute heat capacities of a range of nanosilicates from standard statistical mechanics. Generally, our $C(T)$ values are found to be lower than those derived using the BFM, especially around 150 K. These differences imply that the instantaneous photon-induced temperatures of relatively hot stochastically heated small nanograins in the ISM would be 35–80 K higher than previously expected. Our accurately derived $C(T)$ values could also have implications for relatively low-temperature stochastic heating of larger nanosilicate grains. Generally, our study shows the power of an accurate bottom-up quantum chemical approach for directly calculating the properties of nanoscale dust grains. Our results may provide useful insights for improving the modeling of the IR emission of the likely high population of ultrasmall nanosilicates in the ISM, which hopefully will be confirmed by upcoming JWST observations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.2c02199>.

Estimated maximal effect of anharmonicity on calculated $C(T)$; Cartesian coordinates of metastable silicate dimers (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Draine, B. T. Interstellar Dust Grains. *Annu. Rev. Astron. Astrophys.* **2003**, *41*, 241–289.
- (2) Mathis, J. S.; Rumpl, W.; Nordsieck, K. H. The size distribution of interstellar grains. *ApJ*. **1977**, *217*, 425.
- (3) Greenberg, J. M. In *Stars and Stellar Systems*; Middlehurst, B. M., Aller, L. H., Eds.; Univ. Chicago Press: Chicago, IL, 1968; Vol. 7, p 221.
- (4) Duley, W. W. Fluctuations in interstellar grain temperatures. *Astrophys. Space Sci.* **1973**, *23*, 43–50.
- (5) Draine, B. T.; Li, A. Infrared Emission from Interstellar Dust. I. Stochastic Heating of Small Grains. *Astrophys. J.* **2001**, *551*, 807–824.
- (6) Camps, P.; Misselt, K.; Bianchi, S.; Lunttila, T.; Pinte, C.; Natale, G.; Juvela, M.; Fischera, J.; Fitzgerald, M. P.; Gordon, K.; Baes, M.; Steinacker, J. Benchmarking the calculation of stochastic heating and emissivity of dust grains in the context of radiative transfers simulations. *A&A* **2015**, *580*, A87.
- (7) Henning, T. Cosmic Silicates. *Annu. Rev. Astron. Astrophys.* **2010**, *48*, 21–46.
- (8) Li, A.; Draine, B. T. On Ultrasmall Silicate Grains in the Diffuse Interstellar Medium. *Astrophys. J.* **2001**, *550*, L213–L217.
- (9) Hirashita, H.; Kobayashi, H. Evolution of dust grain size distribution by shattering in the interstellar medium: Robustness and uncertainty. *Earth Planets Space*. **2013**, *65*, 1083–1094.

- (10) Escatlar, A. M.; Bromley, S. T. Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study. *Astron. Astrophys.* **2020**, 634, A77.
- (11) Hensley, B. S.; Draine, B. T. Modeling the Anomalous Microwave Emission with Spinning Nanoparticles: No PAHs Required. *Astrophys. J.* **2017**, 836 (2), 179–192.
- (12) Hoang, T.; Vinh, N.-A.; Lan, N. Q. Spinning Dust Emission from Ultra-Small Silicates: Emissivity and Polarization Spectrum. *Astrophys. J.* **2016**, 824, 18–28.
- (13) Oueslati, I.; Kerkeni, B.; Bromley, S. T. Trends in the adsorption and reactivity of hydrogen on magnesium silicate nanoclusters. *Phys. Chem. Chem. Phys.* **2015**, 17 (14), 8951–8963.
- (14) Kerkeni, B.; Bromley, S. T. Competing mechanisms of catalytic H₂ formation and dissociation on ultrasmall silicate nanocluster dust grains. *Mon. Not. R. Astron. Soc.* **2013**, 435 (2), 1486–1492.
- (15) Kerkeni, B.; Bacchus-Montabonel, M.-C.; Bromley, S. T. How hydroxylation affects hydrogen adsorption and formation on nanosilicates. *Molecular Astrophys.* **2017**, 7, 1–8.
- (16) Cuppen, H. M.; Morata, O.; Herbst, E. Monte Carlo simulations of H₂ formation on stochastically heated grains. *Mon. Not. R. Astron. Soc.* **2006**, 367, 1757–1765.
- (17) Chen, L.-F.; Chang, Q.; Xi, H.-W. Effect of stochastic grain heating on cold dense clouds chemistry. *Mon. Not. R. Astron. Soc.* **2018**, 479, 2988–3001.
- (18) Escatlar, A. M.; Lazaukas, T.; Woodley, S. M.; Bromley, S. T. Structure and Properties of Nanosilicates with Olivine (Mg₂SiO₄)_N and Pyroxene (MgSiO₃)_N Compositions. *ACS Earth Sp. Chem.* **2019**, 3, 2390–2403.
- (19) Zeegers, S.; et al. Illuminating the dust properties in the diffuse ISM with JWST. *JWST Proposal. Cycle 1* **2021**, 2183.
- (20) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. Ab initio molecular simulations with numeric atom-centered orbitals. *Comput. Phys. Commun.* **2009**, 180, 2175–2196.
- (21) Lamiel-Garcia, O.; Ko, K. C.; Lee, J. Y.; Bromley, S. T.; Illas, F. When Anatase Nanoparticles Become Bulklike: Properties of Realistic TiO₂ Nanoparticles in the 1–6 nm Size Range from All Electron Relativistic Density Functional Theory Based Calculations. *J. Chem. Theory Comput.* **2017**, 13, 1785–1793.
- (22) Jensen, S. R.; Saha, S.; Flores-Livas, J. A.; Huhn, W.; Blum, V.; Goedecker, S.; Frediani, L. The Elephant in the Room of Density Functional Theory Calculations. *J. Phys. Chem. Lett.* **2017**, 8, 1449–1457.
- (23) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, 110, 6158–6170.
- (24) de la Pierre, M.; Orlando, R.; Maschio, L.; Doll, K.; Ugliengo, P.; Dovesi, R. Performance of Six Functionals (LDA, PBE, PBESOL, B3LYP, PBE0, and WC1LYP) in the Simulation of Vibrational and Dielectric Properties of Crystalline Compounds. The Case of Forsterite Mg₂SiO₄. *J. Comput. Chem.* **2011**, 32, 1775–1784.
- (25) Demichelis, R.; Suto, H.; Noel, Y.; Sogawa, H.; Naoi, T.; Koike, C.; Chihara, H.; Shimobayashi, N.; Ferrabone, M.; Dovesi, R. The infrared spectrum of ortho-enstatite from reflectance experiments and first-principle simulations. *Mon. Not. R. Astron. Soc.* **2012**, 420, 147–154.
- (26) Guiu, J. M.; Escatlar, A. M.; Bromley, S. T. How Does Temperature Affect the Infrared Vibrational Spectra of Nanosized Silicate Dust? *ACS Earth Space Chem.* **2021**, 5 (4), 812–823.
- (27) McQuarrie, D. A.; Simons, J. D. *Molecular Thermodynamics*; University Science Book, Sausalito, CA, 1999.

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CHAPTER 6

Does Processing or Formation of Water Ice Mantles Affect the Capacity of Nanosilicates to Be the Source of Anomalous Microwave Emission?

6.1 Introduction

Anomalous microwave emission (AME) is a foreground feature detected in various astronomical environments, including MCs¹ and the diffuse ISM². This feature is observed in the range between 10 and 60 GHz range with a peak between 20 and 30 GHz³. Small spinning dust grains are considered the primary candidate for carrying AME due to the strong spatial correlation between AME and IR dust emission⁴. Although multiple mechanisms have been proposed to explain AME^{5,6}, the prevailing consensus is that rapidly spinning dipolar nanoclusters are the most likely source.³

For the rotational emission of these grains to fall inside the observed AME frequency range, they must rotate at extremely high velocities and therefore be very small. Consequently, studies have focused on grains with diameters smaller than 1 nm.⁷ In principle, any small spinning grain with a sufficiently large dipole moment could contribute to AME⁸. In previous work, the magnitude of the required dipole moment was studied using the following parameter:

$$\beta = \frac{\mu}{\sqrt{N}} \quad 1$$

where μ is the magnitude of the dipole moment, in Debye, and N is the number of atoms in the grain.

It has been found that ultrasmall silicate grains can be viable carriers of the AME if $\beta > 0.3$, assuming that a small fraction of the interstellar silicon mass is locked in these grains^{9,10}. However, other small grains, such as PAHs may also contribute to AME.

However, the lack of observational correlation between AME and the IR intensities associated with PAHs has ruled them out as the main source of AME¹¹. Additionally, the intrinsically low dipole moments associated with covalently bonded carbonaceous dust also tends to exclude it as a viable source of AME.

Recent computational modelling of small nanosilicate clusters, has shown that, with just 1% of the silicon mass present in the ISM being locked in such grains with diameters of less than 1 nm, they could explain AME¹². The modelling in this work was based on bare nanosilicates. However, the potential of these grains to carry the AME once they are hydroxylated or water ice forms on them remains unexplored.

Once silicate grains are ejected into the ISM after their formation in evolved stars, they undergo processing (*e.g.* ion irradiation). One consequence of this processing in the ISM is the formation of hydroxyl groups on the grain's surfaces from interactions with high energy protons.¹³ In denser regions of the ISM such as MCs, the shielding from the UV field also allows water molecules to accrete onto silicate grains, leading to the formation of ices. The formation of water is recognized to be primarily driven by surface chemical reactions¹⁴ on silicate grains, with multiple proposed pathways.¹⁵

In this chapter we present the work carried out, in collaboration with Dr. Stefano Ferrero and Dr. Albert Rimola, to explore the impact of hydroxylation and molecular water interactions on small nanosilicates. Specifically, we focused on how the water affected the dipole moments of the grains, and consequently, their potential as AME carriers.

We focused on Mg-rich pyroxene nanosilicate grains with $(\text{MgSiO}_3)_6$ composition and modelled their hydroxylation (*i.e.* chemisorbed water) and molecular hydration (*i.e.* physisorbed water). The author's contribution to this work involved performing the necessary calculations to study the hydroxylation of the nanosilicate grains, as well as the analysis of their results and drawing conclusions regarding their potential role as AME carriers.

6.2 Results

The initial $(\text{MgSiO}_3)_6$ bare nanosilicate structures used in this work were obtained from global optimization searches in a previous study.¹⁶ Since our goal is to analyse the effects of water addition, both in molecular and dissociated forms, on the dipole moments of nanosilicates, we examined two different initial isomers. The first isomer, which has a low dipole moment, corresponds to the lowest energy isomer found in a previous study. The second isomer, with a slightly higher energy (+1.11 eV) exhibits a significant larger dipole moment. The structure of these two isomers is shown in Figure 1.

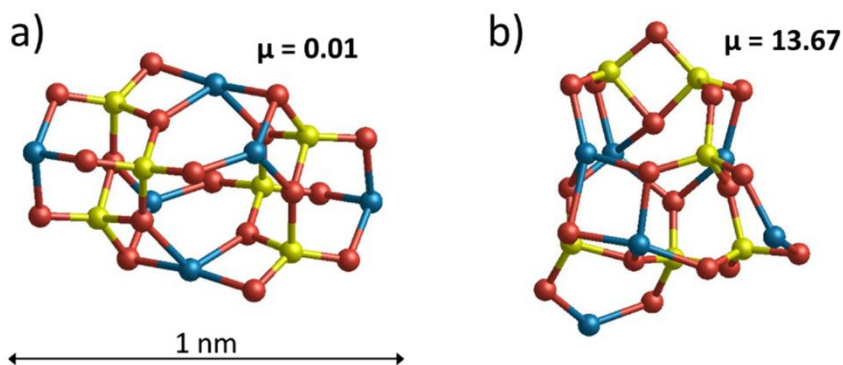


Figure 1: Bare $(\text{MgSiO}_3)_6$ nanosilicate isomers used in this work. **(A)** Global minimum structure with low dipole. **(B)** Higher energy isomer (+1.11 eV) with significantly larger dipole moment. Mg, Si, and O atoms are depicted as blue, yellow, and red spheres, respectively.

To model the dissociation of water on the surface of bare nanosilicates and the subsequent formation of hydroxyl groups, we considered three different levels of hydroxylation. These levels correspond to the addition of one, two or three water molecules, each undergoing full dissociation upon adsorption.

To model relevant nanosilicate structures containing dissociated water molecules, we performed global optimization searches to generate a set of low energy structures for each hydroxylation level. This process consisted of two steps. First, we conducted multiple MCBH searches using a polarizable classical FF. After these global optimization searches, we selected a subset of the lowest energy structures and further refined them using DFT based optimisations to improve the accuracy of their energetic ordering and to determine their dipole moments.

The lowest energy isomers found for each level of hydroxylation are shown in Figure 2.

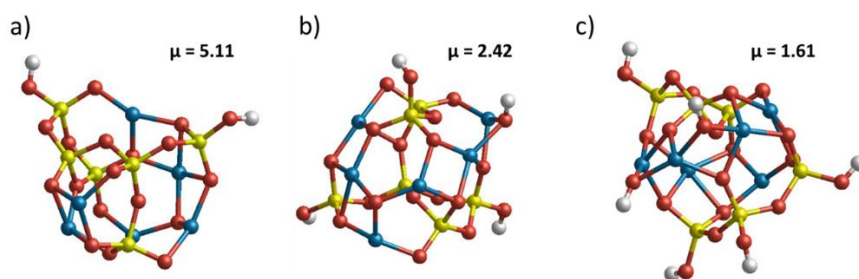


Figure 2: Lowest energy hydroxylated $(\text{MgSiO}_3)_6$ nanosilicate isomers found containing **a)** one, **b)** two, and **c)** three water molecules, and their dipole moments in Debyes. Mg, Si, O and H atoms are depicted as blue, yellow, red and white spheres, respectively.

The preferential formation of hydroxylation isomers among the lowest energy isomers indicates that water dissociated is more favourable than molecular water adsorption. As the number of added water molecules increases, further dissociation and formation of surface-bound OH^- groups on the surface is expected. Once the grain surface is saturated, additional water molecules are expected to be physisorbed onto the hydroxylated surface.

Additionally, the lowest energy isomers identified for each degree of hydroxylation exhibit significant dipole moment, although these values decrease with each successive water addition. These dipoles contrast with the negligible dipole moment of the global minimum $(\text{MgSiO}_3)_6$ bare cluster, which is due to its high symmetry.

A direct analysis of these three lowest energy isomers reveals that the first two possess sufficiently large dipole moments, with β values of 0.89 and 0.40 respectively. However, the third isomer falls slightly below the

threshold with $\beta = 0.26$. For a more accurate assessment of the potential of these grains to contribute to AME, it is essential to bear in mind that in the ISM, due to dust processing, nanosilicate dust populations are likely to contain a diverse range of isomers with varying energetic stabilities.

Consequently, from an astronomical perspective, it is more relevant to draw conclusions based on the dipole moments of a population of grains rather than individual isomers. A clear example of this can be seen in the analysis of $(\text{MgSiO}_3)_6$ dipoles presented in reference 12. While the lowest energy isomer has an almost negligible dipole moment (see Figure 1), considering a set of the 100 lowest energy isomers results in an average dipole of 7.7 Debyes, indicating the capability of a population of these grains to carry AME.

To follow the same approach and obtain a more realistic dipole moment for $(\text{MgSiO}_3)_6$ populations, we incorporated data from all the isomers identified in the global optimization searches (~ 100 isomers for each degree of hydroxylation). Figure 3 presents the relative energetic stability and the corresponding dipole moments for all the studied isomers.

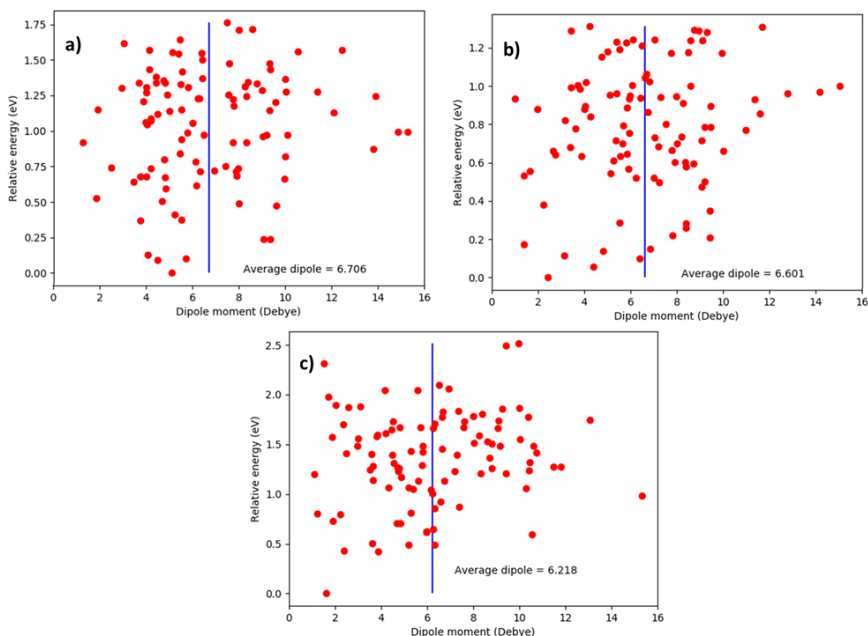


Figure 3: Relative energy vs dipole moment for hydroxylated $(\text{MgSiO}_3)_6$ nanosilicates containing **a)** one, **b)** two, and **c)** three water molecules. The vertical blue line indicates the average dipole moment of the corresponding set of isomers.

The average dipole moment of these populations is sufficiently large to yield β values above the minimum threshold required for AME carriers (see Table 1 for a quantitative analysis of the dipole moments).

These average results also confirm the trend observed in the lowest-energy isomers, where the average dipole moment decreases with increasing water addition (see Figure 2).

Additionally, it is important to highlight that although not all isomers in the populations exhibit dipole moments high enough to contribute to AME, the vast majority do meet the minimum required threshold (~ 1.7 Debye for one water, ~ 1.8 Debye for two and ~ 1.9 Debye for three water additions).

The study of molecular hydration was carried out by our collaborators, who modelled the addition of 1-3 water molecules without dissociation. In their approach water adsorption was considered on both low and high dipole silicate isomers (see Figure 1). A detailed discussion of these results is provided in the accompanying research article. A summary of these results is also presented in Table 1.

Water addition process	Bare cluster dipole / β	Average dipole / β (+ H ₂ O)	Average dipole / β (+ 2 H ₂ O)	Average dipole / β (+ 3 H ₂ O)
Hydroxylation	7.7 ^a / 1.41	6.71 / 1.17	6.60 / 1.1	6.22 / 1.04
Molecular adsorption	0.01 ^b / 0.002	2.87 / 0.50	3.323 / 0.55	3.30 / 0.55
Molecular adsorption	13.67 ^c / 2.50	14.40 / 2.51	11.97 / 2.00	12.65 / 2.12

Table 1: Evolution of the total dipole moments in Debyes of (MgSiO₃)₆ nanosilicates with increasing hydration via hydroxylation and molecular adsorption.

^a Average dipole moment from a set of 180 (MgSiO₃)₆ structures from reference 12.

^b Dipole moment of low dipole global minimum (MgSiO₃)₆ isomer Figure 1 a)

^c Dipole moment of high dipole (MgSiO₃)₆ isomer Figure 1 b)

6.3 Conclusions

These findings, combined with the additional data and analysis provided in the accompanying research article, support the following conclusions:

- 1- The lowest energy globally optimized structures of $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_N$ nanoclusters, with water dissociation, have large enough dipole to significantly contribute to AME in the cases with $N = 1$ and $N = 2$, but not when a third water is added.
- 2- The addition of the first dissociated water molecule on a globally optimized $(\text{MgSiO}_3)_6$ isomer increases its dipole moment, but each subsequent addition reduces the dipole moment. This dipole moment evolution is also observed when a population of different grains is considered.
- 3- Populations of ~ 100 distinct $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_N$ isomers have an average dipole moment that is large enough to contribute to the AME for all degrees of hydroxylation considered. Additionally, the majority of individual grains in all the populations have also large enough dipole to be carriers of the AME.
- 4- The modelling of molecular water addition gives rise to similar results as for the hydroxylated nanosilicates, although the dipole moments are larger than in hydroxylated grains.
- 5- Overall, the results strongly indicate that nanosilicates are plausible carriers of AME under a modest degree of hydration, broadening the potential species that could produce AME signals.

6.4 References

- ¹ Watson, R.A.; Rebollo, R.; Rubiño-Martín, J. A.; Hildebrandt, S.; Gutiérrez, C. M.; Fernández-Cerezo, S.; Hoyland, R. J. and Battistelli, E. S. Detection of anomalous microwave emission in the Perseus molecular cloud with the COSMOSOMAS experiment. *The Astrophysical Journal*. **2005**, 624(2), L89.
- ² Hildebrandt, S. R.; Rebolo, R.; Rubiño-Martín, J. A.; Watson, R. A.; Gutiérrez, C. M.; Hoyland, R. J. and Battistelli, E. S. COSMOSOMAS observations of the cosmic microwave background and Galactic foregrounds at 11 GHz: evidence for anomalous microwave emission at high Galactic latitude. *Monthly Notices of the Royal Astronomical Society*. **2007**, 382(2), 594-608.
- ³ Dickinson, C.; Ali-Haïmoud, Y.; Barr, A.; Battistelli, E. S.; Bell, A.; Bernstein, L.; Casassus, S.; Cleary, F.; Draine, B. T.; Génova-Santos, R.; Harper, S. E.; Hensley, B.; Hill-Valler, J.; Hoang, T.; Israel, F. P.; Jew, L.; Lazarian, A.; Leahy, J. P.; Leech, J.; López-Caraballo, C. H.; McDonald, I.; Murphy, E. J.; Onaka, T.; Paladini, R.; Peel, M. W.; Perrott, Y.; Poidevin, F.; Readhead, A. C. S.; Rubiño-Martín, J. A.; Taylor, A. C.; Tibbs, C. T.; Todorovic, M. and Vidal, M. The state-of-play of anomalous microwave emission (AME) research. *New Astronomy Reviews*. **2018**, 80, 1-28.
- ⁴ Casassus, S.; Cabrera, G. F.; Förster, F.; Pearson, T. J.; Readhead, A. C. S. and Dickinson, C. Morphological analysis of the centimeter-wave continuum in the dark cloud LDN 1622. *The Astrophysical Journal*. **2006**, 639(2), 951.
- ⁵ Drain, B. T. and Lazarian, A. Magnetic dipole microwave emission from dust grains. *The Astrophysical Journal*. **1999**, 512(2), 740.
- ⁶ Agladze, N. I.; Sievers, A. J.; Jones, S. A.; Burlitch, J. M. and Beckwith, S. V. W. Laboratory results on millimeter-wave absorption in silicate grain materials at cryogenic temperatures. *Astrophysical Journal*. **1996**, 462, 1026.
- ⁷ Draine, B. T. and Lazarian, A. Electric dipole radiation from spinning dust grains. *The Astrophysical Journal*. **1998**, 508(1), 157.

- ⁸ Ali-Haïmoud, Y. Spinning dust radiation: a review of the theory. *Advances in Astronomy*. **2013**, 2013(1), 462697.
- ⁹ Hensley, B. S. and Draine, B. T. Modeling the anomalous microwave emission with spinning nanoparticles: no PAHs required. *The Astrophysical Journal*. **2017**, 836(2), 179.
- ¹⁰ Hoang, T.; Vinh, N.-A. and Lan, N. Q. Spinning dust emission from ultra-small silicates: emissivity and polarization spectrum. *The Astrophysical Journal*. **2016**, 824(1), 18.
- ¹¹ Hensley, B.; Murphy, E. and Staguhn, J. Characterizing extragalactic anomalous microwave emission in NGC 6946 with CARMA. *Monthly Notices of the Royal Astronomical Society*. **2015**, 449(1), 809-819.
- ¹² Escatllar, A. M. and Bromley, S. T. Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study. *Astronomy & Astrophysics*. **2020**, 634, A77.
- ¹³ Zeller, E. J.; Ronca, L. B. and Levy, P. W. Proton-induced hydroxyl formation on the lunar surface. *Journal of Geophysical Research*. **1966**, 71(20), 4855-4860.
- ¹⁴ Van Dishoeck, E. F. Herbst, E. and Neufeld, D. A. Interstellar water chemistry: from laboratory to observations. *Chemical Reviews*. **2013**, 113(12), 9043-9085.
- ¹⁵ Molpeceres, G.; Rimola, A.; Ceccarelli, C.; Käsner, J.; Ugliengo, P. and Maté, B. Silicate-mediated interstellar water formation: A theoretical study. *Monthly Notices of the Royal Astronomical Society*. **2019**, 482(4), 5389-5400.
- ¹⁶ Escatllar, A. M.; Lazaukas, T.; Woodley, S. M. and Bromley, S. T. Structure and properties of nanosilicates with olivine (Mg_2SiO_4) N and pyroxene (MgSiO_3) N compositions. *ACS Earth and Space Chemistry*. **2019**, 3(11), 2390-2403.



Does Processing or Formation of Water Ice Mantles Affect the Capacity of Nanosilicates to Be the Source of Anomalous Microwave Emission?

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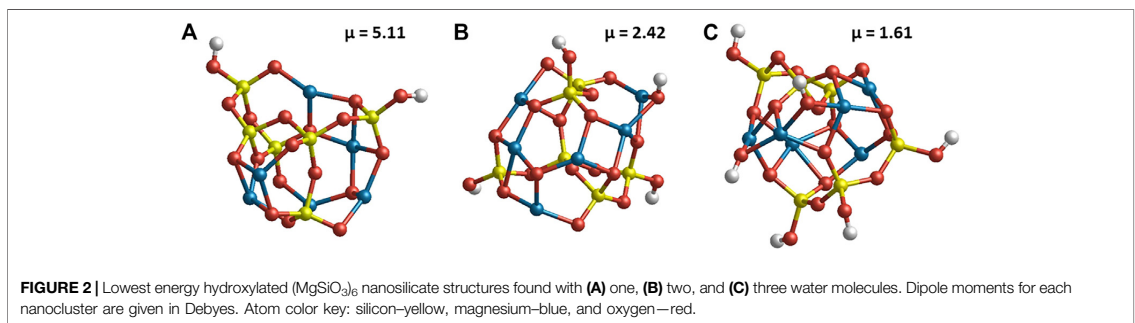
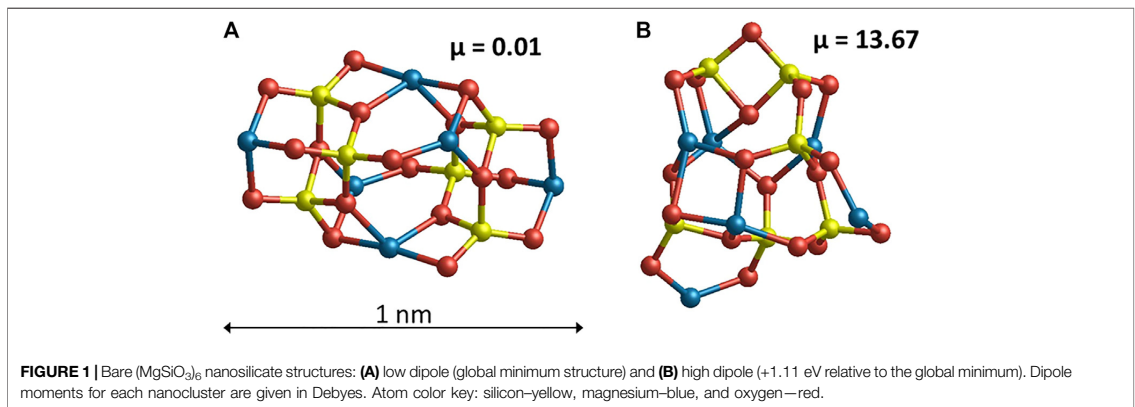
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Anomalous microwave emission (AME) is detected in many astrophysical environments as a foreground feature typically peaking between 20–30 GHz and extending over a 10–60 GHz range. One of the leading candidates for the source of AME is small spinning dust grains. Such grains should be very small (approx. ≤ 1 nm diameter) in order for the rotational emission to fall within the observed frequency range. In addition, these nanosized grains should possess a significant dipole moment to account for the observed emissivities. These constraints have been shown to be compatible with spinning bare nanosilicate clusters, assuming that $\sim 1\%$ of the total Si mass budget is held in these ultrasmall grains. Silicate dust can be hydroxylated by processing in the interstellar medium and is generally known to provide seeds for molecular water ice nucleation in denser regions. Herein, we use quantum chemical calculations to investigate how the dipole moment of Mg-rich pyroxenic (MgSiO_3) nanoclusters is affected by both accretion of molecular water and dissociative hydration. Our work thus provides an indication of how the formation of water ice mantles is likely to affect the capacity of nanosilicates to generate AME.

Keywords: anomalous microwave emission, dust grains, nanosilicates, water ices, interstellar medium, grain processing, hydroxylation, density functional theory

INTRODUCTION

Silicate dust is ubiquitously found in a wide range of astrophysical environments (Henning, 2010). Chemical nucleation and growth in the circumstellar envelopes of oxygen-rich evolved stars is an important source of silicate dust (Goumans and Bromley, 2012; Gobrecht et al., 2016). From infrared (IR) emission observations, it is inferred that most of these newly formed silicate grains are Mg-rich and have sizes of the order $0.1 \mu\text{m}$ (diameter) (Norris et al., 2012). Interactions between the dust and the stellar radiation field cause the grains to be ejected into the interstellar medium (ISM). Supernova shocks in the ISM induce grain–grain collisions which shatter the dust into smaller components (Jones et al., 1996). A typical shock is thought to result in 5–15% of the original grain mass ending up in the form of ultrasmall nanosilicates (< 3 nm diameter). Nanograin production from larger grains is also predicted to occur close to sources of intense radiation (e.g., massive stars and supernovae) via rotational disruption of dust grains by radiative torques (Hoang et al., 2019). These models of dust

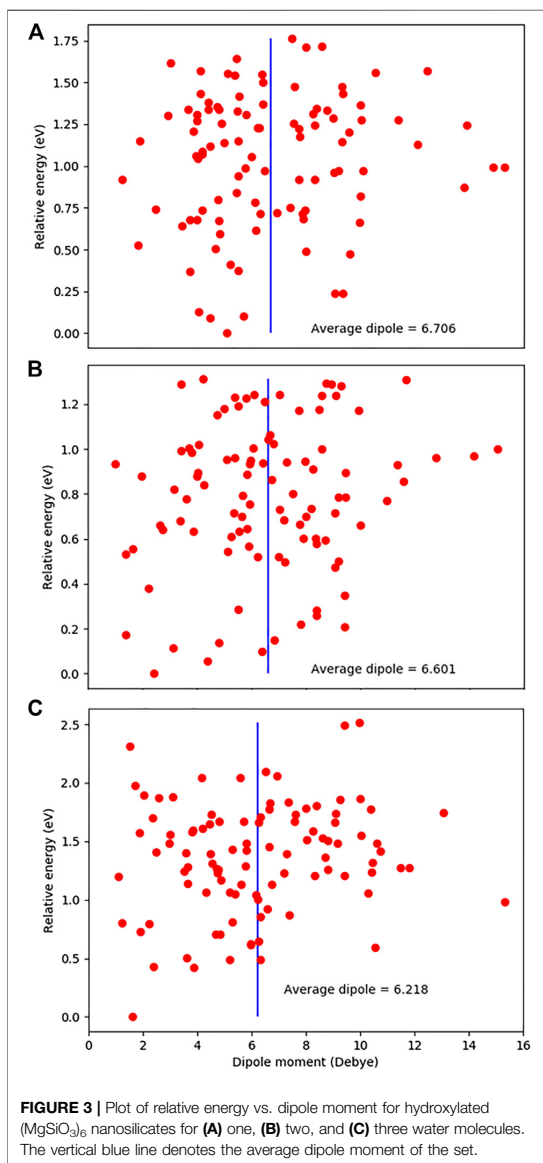


processing are compatible with estimates that approximately 10% of the Si in the ISM could be held in ≤ 3 nm diameter nanosilicate grains (Li and Draine, 2001) without violating observational constraints.

Via gas–grain collisions and interactions with radiation, small nanosilicate grains will be rotationally excited. Such spinning nanosilicate grains have been proposed as the main carrier of anomalous microwave emission (AME) – a microwave foreground feature which typically peaks between 20–30 GHz and extends over a 10–60 GHz range (Macià Escatllar and Bromley, 2020; Hoang et al., 2016; Hensley and Draine, 2017). AME is observed in a number of astrophysical environments including molecular clouds (Watson et al., 2005) and the diffuse ISM (Hildebrandt et al., 2007). As smaller grains can be spun up to larger frequencies than larger grains in any given astronomical environment, proportionally they emit more power, and thus the smallest grains are expected to dominate the spinning dust microwave spectrum. For a grain to emit in the microwave region associated with AME via rotational emission, its size should be of the order of ~ 1 nm in diameter (Draine and Lazarian, 1998a; Draine and Lazarian, 1998b). In principle, contributions to the AME from the spinning of such nanograins could occur from any type of nanograin if it is sufficiently abundant and has a large enough dipole moment

(Ali-Haïmoud, 2013; Dickinson et al., 2018). Observational evidence has tended to rule out small spinning organic dust species (i.e., polycyclic aromatic hydrocarbons—PAHs) as the most important source of AME (Hensley et al., 2016). The atomistically detailed structures and physical properties of nanosilicates with Mg-rich olivinic $(\text{Mg}_2\text{SiO}_4)_N$ and pyroxenic $(\text{MgSiO}_3)_N$ compositions with diameters ≤ 1 nm have recently been determined by quantum chemical modeling (Macià Escatllar et al., 2019). These accurate calculations clearly show how the ionic chemical bonding in nanosilicates intrinsically tends to lead to grains with significant dipoles. Based on those structures, it has been shown that the AME can be explained if only 1% of the Si in the ISM were held in ultrasmall (i.e., ≤ 1 nm diameter) nanosilicate grains (Macià Escatllar and Bromley, 2020). Although the dipoles possessed by these bare nanosilicates are more than sufficient to account for the observed AME, it is not clear if these results can be extended to nanosilicates, which become hydroxylated by processing and/or upon which water ice forms.

Silicate grains emerging from the outflows of evolved stars are processed from ion irradiation (e.g., protons, He^+) from supernovae shocks in the ISM. From laboratory studies of the effect of the solar wind on lunar surface silicate material, proton irradiation was found to cause two important intertwined



chemical processes: 1) hydroxyl formation (Zeller et al., 1966) and 2) Mg cation depletion by preferential sputtering (Keller and McKay, 1997). Analysis of interplanetary dust has provided direct evidence of such grain processing (Bradley, 1994). Such processes would tend to transform Mg-rich nano-olivine dust grains into hydroxylated nano-pyroxene grains. Relatively elevated levels of pyroxene (with respect to the initial dominance of olivine) are consistent with the pyroxene-rich environments of protostars (Demyk et al., 1999) and the estimated fraction of amorphous pyroxene grains in the ISM (Kemper et al., 2004).

In denser regions of the ISM such as molecular clouds, the ultraviolet radiation field is shielded and molecular water can accrete on silicate grain surfaces. This marks the beginning of the formation of water ice-dominated mantles on silicate grains. Water is one of the most abundant molecules in the universe in the solid phase (Gibb et al., 2004; Boogert et al., 2008). Interstellar water ices are thought to present an amorphous structural state because of the similarities of their IR features with those of amorphous solid water measured in terrestrial laboratories (Watanabe and Kouchi, 2008). Gas-phase reactions based on low-temperature ion-neutral and high-temperature neutral-neutral processes allow for the explaining of the abundance of water as a gaseous component, but they cannot justify the large abundance of water ice in interstellar and protostellar clouds (Hollenbach and McKee, 1989; van Dishoeck et al., 2013). Accordingly, reaction routes based on surface chemical processes have long been recognized to be the major channel for the formation of water ice (Tielens and Hagen, 1982; van Dishoeck et al., 2013). Therefore, water ice, rather than being formed by successive adsorption of water molecules coming from the gas phase, is formed *in situ* on the surfaces of dust grains. Different reactive channels leading to the formation of interstellar water on the surfaces of grains are hydrogenation of atomic O (e.g., Dulieu et al., 2010), of molecular O₂ (e.g., Ioppolo et al., 2008), and even of O₃ (e.g., Mokrane et al., 2009), among others. We refer to the work of Molpeceres et al. (2019) for a complete list of postulated reactions leading to water formation on interstellar grains.

Herein, we perform a systematic quantum chemical study of the effect of both hydroxylation and molecular water interactions on ultrasmall (~1 nm diameter) Mg-rich pyroxenic nanosilicates with a (MgSiO₃)₆ composition. We specifically focus on how the dipole moments of the original bare P-6 nanosilicates are affected by these chemical changes. If we focus on the dipole moments of the most energetically stable grains in a population, we find that both processes can significantly affect the dipole moment of these selected grains. However, when considering a more realistic population of nanosilicate grains, our results suggest that neither hydroxylation nor molecular hydration has a significant effect on the average magnitude of the dipole moment. Our results thus suggest that the capacity of nanosilicates to be the source of AME should not be significantly diminished by processing and/or initial water ice mantle formation.

METHODS

The initial bare (MgSiO₃)₆ isomer structures were obtained in a previous work (Macià Escatllar et al., 2019). We chose to compare two distinct isomers: 1) the lowest energy (global minimum) cluster structure with a very low dipole and 2) a slightly energetically metastable cluster structure with a high dipole. These bare (MgSiO₃)₆ structures are shown in Figure 1.

In the case of hydroxylated bare nanosilicate clusters, we carried out global optimization calculations to find the 50 lower energy isomers of (MgSiO₃)₆ after dissociative

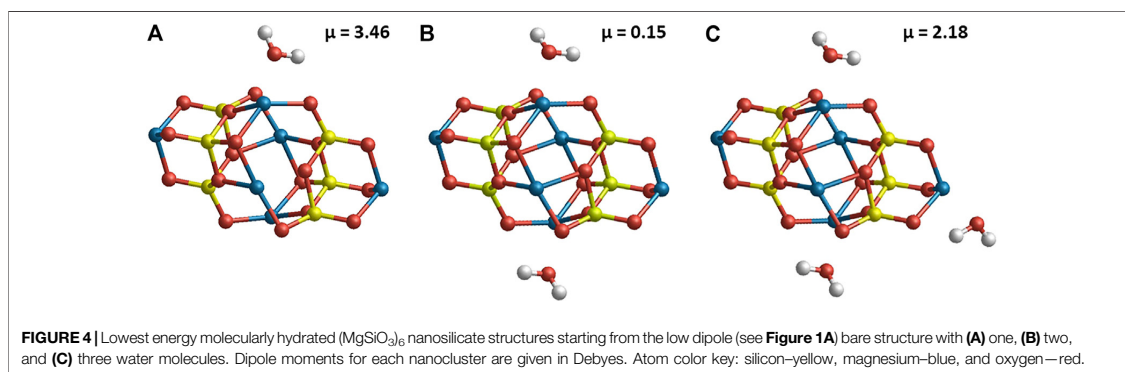
TABLE 1 | Evolution of total dipole moments (μ) in Debyes of $(\text{MgSiO}_3)_6$ nanosilicates with increasing hydration via hydroxylation (chemisorption) and molecular water adsorption (physisorption). The average dipoles of the hydrated nanosilicates are based on the data obtained herein and shown in **Figures 2–4**. Values of β are calculated as $\beta = \mu / \sqrt{N_{\text{atoms}}}$.

Water addition process	Dipole moment of initial bare nanosilicates/ β	Average dipole moment/ β (+ 1 $\times$ H_2O)	Average dipole moment/ β (+ 2 $\times$ H_2O)	Average dipole moment/ β (+ 3 $\times$ H_2O)
Hydroxylation (chemisorption)	7.7 ^a /1.41	6.71/1.17	6.60/1.1	6.22/1.04
Molecular adsorption (physisorption)	0.01 ^b /0.002	2.87/0.50	3.32/0.55	3.30/0.55
Molecular adsorption (physisorption)	13.67 ^c /2.50	14.40/2.51	11.97/2.00	12.65/2.12

^aAverage value of dipole moment calculated from a set of 180 $(\text{MgSiO}_3)_6$ structures—see Macià Escatllar and Bromley (2020).

^bDipole moment of low dipole global minimum $(\text{MgSiO}_3)_6$ structure—see Macià Escatllar et al. (2019) and **Figure 1A**.

^cDipole moment of high dipole $(\text{MgSiO}_3)_6$ structure (+1.1 eV with respect to the global minimum)—see **Figure 1B**.

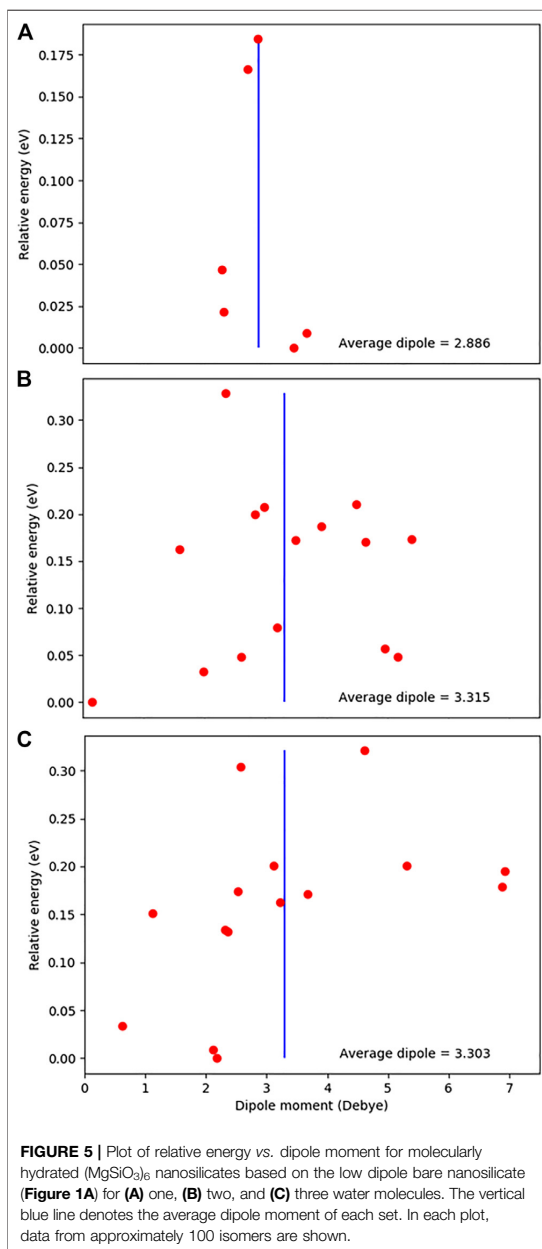


interaction of one, two, and three water molecules, respectively. The global optimization calculations were split into two steps. First, we used the Monte Carlo basin hopping (MCBH) algorithm (Wales and Doye, 1997), employing previously developed polarizable classical interatomic potentials (IPs) (Macià Escatllar et al., 2019), to explore the potential energy surface (PES), followed by the structural configurations of the hydroxylated clusters. Previous studies have shown that the MCBH method is an efficient method for exploring the low energy PES of nanoclusters and for finding the global minimum (Wales and Doye, 1997). The standard MCBH algorithm uses random atomic displacements at each step to explore the PES. In addition, we also allowed that 0.5% of the steps attempt an $\text{Mg} \leftrightarrow \text{Si}$ cation exchange move assist in this exploration. To run the MCBH calculations, we employed a previously developed cascade MCBH code (Cuko et al., 2017), which uses the General Utility Lattice Package (GULP) (Gale and Rohl, 2003) to locally optimize the cluster structures at each step. To avoid problems with the local optimization of distorted structures containing polarized ions, we preoptimize each cluster structure with an IP with polarizable shells removed before optimizing using the IP with shells. We note that, in principle, an MCBH global optimization search only depends on the chemical composition of the system and should be independent of the initial hydroxylated cluster structure. In practice, the exploration of the PES can be somewhat biased by the initial structure and thus, to help

ensure that our searches were not biased, for each addition of water, we ran the MCBH searches a total of 20 times with different starting structures. Each MCBH run consisted of 10,000 steps.

After this global optimization procedure, we selected 100 distinct lowest energy nanocluster structures for each degree of hydroxylation for further refinement. The selected cluster structures were optimized using density functional theory (DFT)-based calculations using the PBE functional (Perdew et al., 1996) with a light-tier one numerical atom-centered orbital (NAO) basis set. Previous studies on oxide nanoparticles have shown that this basis set has a similar quality to valence triple- ζ plus polarization Gaussian-type Orbital basis sets (Lamiel-Garcia et al., 2017). These DFT-based calculations employed the Fritz Haber Institute Ab Initio Molecular Simulation package (FHI-AIMS) (Blum et al., 2009).

In the case of the molecularly hydrated $(\text{MgSiO}_3)_6$ clusters, the initial positions of the physisorbed water molecules on both bare cluster isomers (**Figure 1**) were prepared using an electrostatic compatibility criterion. Specifically, the negatively charged oxygen atom of each water molecule was placed at a distance 2 Å above each positively charged magnesium cation of the silicate cluster. Subsequently, for each water + cluster combination, the whole system structure was locally optimized. All optimizations were carried out using DFT-based calculations using the PBE functional and a def-2-



TZVPP (i.e., valence triple- ζ plus polarization) basis set (Weigend and Ahlrichs, 2005). This process was repeated for sampling all the Mg sites and all distinct combinations of adsorption sites when using two and three water molecules. The ORCA code (Neese et al., 2020) was used for these calculations.

RESULTS AND DISCUSSION

In the following subsections, we describe our findings for both hydroxylation and molecular interaction with water for bare $(\text{MgSiO}_3)_6$ nanosilicate clusters (see Figure 1). Note that these bare nanosilicates contain 30 atoms and have a typical maximum diameter of ~ 1 nm. The hydrated $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_n$ nanosilicates we consider have up to 39 atoms, which induces only a minor increase in the average diameter. Although the chemical compositions of the hydrated nanosilicate systems considered in each case (i.e., hydroxylation and molecular interactions) are identical, astronomically each relate to distinct processes and regions of the ISM. As such, we discuss the two considered modes of nanosilicate hydration separately with relation to their astronomical context.

Dissociative Hydration

As discussed above, hydroxylation of silicate dust can occur through high energy processing by supernovae shocks in the diffuse ISM. Hydroxylation is also the natural chemical result of dissociative chemisorption of water molecules on dust grain surfaces. However, as water molecules are quickly photodissociated by high-energy ultraviolet (UV) photons in the diffuse ISM, chemical routes to hydroxylated nanosilicate dust would more likely occur via reactions with other species (e.g., O and H atoms). We note that the explicit modeling of these reactions and how the resulting hydroxylation affects subsequent H_2 formation reactions were investigated in previous works on a $(\text{MgSiO}_3)_4$ nanopyroxene cluster (Goumans and Bromley, 2011; Kerkeni et al., 2017; Kerkeni et al., 2019). Generally, hydroxylation of silicate grain surfaces is the most plausible mechanism by which hydration of silicates can occur in the diffuse ISM.

We consider hydroxylated nanopyroxene clusters with chemical compositions $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_n$, with $n = 1-3$. After finding the low-energy minima of these systems using the MCBH global optimization method, although some of the higher energy isomers displayed physisorbed water molecules, most clusters exhibited $2n$ hydroxyls. First, this shows that hydroxylation is energetically more favorable than molecular water adsorption. The lowest energy (i.e., candidate global minima) hydroxylated isomers found for each n are shown in Figure 2. By only considering the lowest energy isomers, we can follow the evolution of the dipole moment from the bare $(\text{MgSiO}_3)_6$ with increasing hydroxylation (see Figure 2). Second, we note that the global minimum bare $(\text{MgSiO}_3)_6$ nanosilicate isomer has a negligible dipole moment, due to its high symmetry. However, all lowest energy hydroxylated nanosilicates have a significant dipole moment and correspondingly low symmetry structures. Based on this relatively small change in the degree of hydroxylation for the lowest energy isomers, the initial relatively large increase in the dipole moment going from a bare cluster to one with two hydroxyls (+5.1 Debye) is then dampened with further hydroxylation increase.

In the ISM, due to energetic processing, the population of nanosilicates is likely to exhibit a range of isomeric structures and compositions with a corresponding range of energetic stabilities.

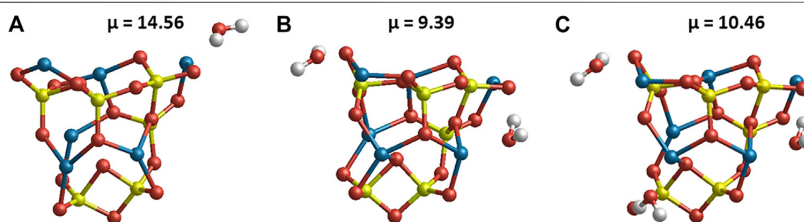


FIGURE 6 | Lowest energy molecularly hydrated $(\text{MgSiO}_3)_6$ nanosilicate structures starting from the high dipole (see **Figure 1B**) bare structure with **(A)** one, **(B)** two, and **(C)** three water molecules. Dipole moments for each nanocluster are given in Debyes. Atom color key: silicon—yellow, magnesium—blue, and oxygen—red.

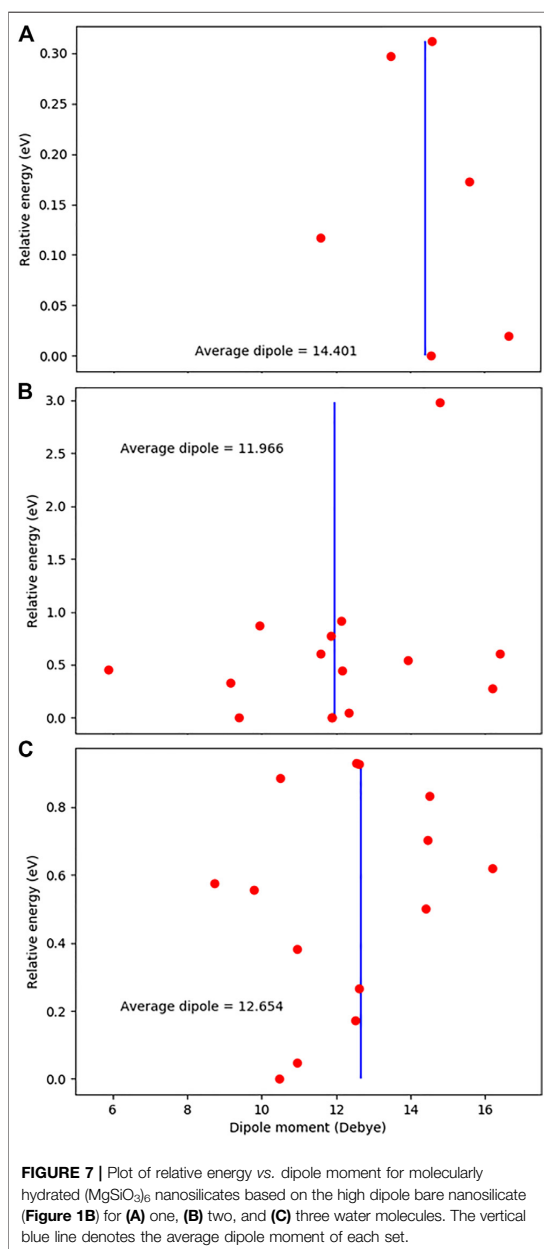
From an astronomical perspective, it is thus more relevant to extract average properties of grain populations. From this more general perspective, it has previously been shown that the high symmetry of the global minimum bare $(\text{MgSiO}_3)_6$ nanosilicate is not typical of the majority of isomers. In fact, the average dipole moment of $(\text{MgSiO}_3)_6$ isomers, considering over 100 lowest energy structures, is found to be 7.7 Debyes (Macià Escatllar and Bromley, 2020). In the case of the hydroxylated nanosilicates considered herein, our global optimization searches also produce a large number of low-energy isomer structures from which to obtain the average dipole moments. In **Figure 3**, we show the relative energetic stability and corresponding dipole moments for approximately 100 distinct nanocluster isomers for each degree of hydroxylation (i.e., $n = 1-3$) considered. In **Table 1**, we report the average dipole moments of all hydroxylated $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_n$ nanoclusters based on these data. It has been shown that for a dipolar nanocluster species to contribute to AME, it should possess a sufficiently large size-normalized dipole moment ($\beta = \mu / \sqrt{N_{\text{atoms}}}$) such that $\beta > 0.3$ (Hoang et al., 2016; Hensley and Draine, 2017). In **Table 1**, we also reported values of β based on the average dipole moments on our sets of hydroxylated nanosilicate clusters. We note that although there is a very slight decrease in the average dipole moment with increasing hydroxylation, the value of β is always over three times the size required according to the above AME constraint. These data clearly show that in all cases, a population of hydroxylated $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_n$ nanoclusters could significantly contribute to the observed AME.

Molecular Hydration

Hydroxylation via shock-induced processing or suitable chemical reactions is initially very energetically favorable for bare grains, but, with increasing hydroxylation, the surface sites for the hydroxylation to take place quickly become occupied. As such, nanosized grains can only maintain a limited number of hydroxyls on their surfaces before they become too energetically favorable for any formed water to interact with the hydroxylated grain in a molecular physisorbed manner (Kerker and Bromley, 2013). As mentioned above, the main mechanism through which water ice forms and grows on the core grains (e.g., silicates) is by cumulative water formation on the same grain surface, where it remains firmly attached. Here, to check how the presence of interacting water molecules affects the dipole moment of the bare nanograin, we assume that water formation has already taken place on the binding sites where the water molecules are molecularly adsorbed.

Following our results for hydroxylation, we also consider the initial stages of molecular hydration in $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_n$ species for $n = 1-3$. Note that unlike in the energetic process of hydroxylation in the ISM, in protected molecular cloud environments, each molecular hydration is a low-energy event in which we assume that the bare nanocluster structure is unaffected. We take the two nanocluster structures in **Figure 1** as seeds for studying the initial stages of molecular physisorption. First, we consider the global minimum low dipole nanocluster (see **Figure 1A**) which has a negligible dipole due to its very symmetric structure. In **Figure 4**, we show the lowest energy $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_n$ structures that we obtained for the addition of 1–3 water molecules. Upon nucleation of the first water molecule, the symmetry of the cluster is broken, resulting in a dramatic increase in the dipole moment. Conversely, with two water molecules, the lowest energy structure is highly symmetric, leading to a very low dipole moment. Finally, with three water molecules, the symmetry is once again broken and the lowest energy system is found to exhibit a high dipole moment. As in the case of the hydroxylated clusters, in astronomical environments there is likely to be a range of isomers for each degree of hydration, and the average effect of molecular hydration is of more interest. In this case, due to the limited number of distinct binding sites, we have fewer possibilities for each water addition than in the case of hydroxylated nanocluster isomers. Specifically, for the nucleation of one water molecule, we find six distinct adsorption sites, and for two and three water molecules, we consider 15 distinct adsorption sites. The relative energies and dipole moments of all these systems are shown in **Figure 5**. The corresponding average dipole moments (see **Table 1**) are all close to 3 Debyes, showing that molecular water adsorption can induce an average increase in the dipole moment, even for bare nanoclusters with negligible dipole moments. The corresponding values of β are all close to 0.5, which is more than sufficient for such hydrated nanoclusters to contribute to AME.

In the case of molecular nucleation of a bare cluster with an initial large dipole moment (see **Figure 1B**), we show the lowest energy $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_n$ structures that we obtained in our searches in **Figure 6**. For these specific low-energy structures, we see that the dipole moment stays high (>9 Debyes) for each water addition. More generally, we consider a similar range of hydrated structures as in the low dipole moment case to obtain averages. In **Figure 7**, we show the relative energies and dipole moments of all considered systems. Here, we also see that the



average dipole moments (see also **Table 1**) for each degree of hydration also stay high. Correspondingly, the values of β obtained from these average dipole moment values are also high (>2 Debyes), meaning that they would be strong emitters of microwave radiation.

CONCLUSION

We use searches based on global optimization and electrostatic considerations to obtain a range of structures for hydroxylated and molecularly hydrated nanoclusters, respectively, with a $(\text{MgSiO}_3)_6(\text{H}_2\text{O})_n$ composition ($n = 1-3$). These hydrated nanoproxenes could be relevant for nanosilicate grain processing in the ISM or initial water ice mantle formation in molecular clouds. We have used accurate quantum chemical DFT calculations to calculate the dipole moments of all hydrated pyroxene nanoclusters. We find that both hydroxylation and molecular hydration, irrespective of the initial dipole moment of the bare nanocluster, induce and/or maintain systems with dipole moments that are sufficiently high to significantly contribute to AME. These results thus strongly indicate that the validity of previous reports showing that nanosilicates are very plausible carriers of AME is not affected by a modest degree of nanosilicate hydration. Overall, this study broadens the range of potential nanosilicate species and types of astrophysical environments that could produce AME signatures.

DATA AVAILABILITY STATEMENT

The data supporting the findings of this study are available on reasonable request from the corresponding authors.

AUTHOR CONTRIBUTIONS

The original idea for the study was proposed by SB. All authors participated in the initial conception and planning of the study and in the discussion of the results. JMG and SF performed the calculations. SB and AR participated in the writing and editing of the manuscript and coordinated the project.

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REFERENCES

- Ali-Haïmoud, Y. (2013). Spinning Dust Radiation: A Review of the Theory. *Adv. Astron.* 2013, 462697. doi:10.1155/2013/462697
- Blum, V., Gehrke, R., Hanke, F., Havu, P., Havu, V., Ren, X., et al. (2009). Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals. *Comput. Phys. Commun.* 180, 2175–2196. doi:10.1016/j.cpc.2009.06.022
- Boogert, A. C. A., Pontoppidan, K. M., Knez, C., Lahuis, F., Kessler-Silacci, J., van Dishoeck, E. F., et al. (2008). The c2dSpitzerSpectroscopic Survey of Ices Around Low-Mass Young Stellar Objects. I. H₂O and the 5–8 μ m Bands 1,2. *ApJ* 678, 985–1004. doi:10.1086/533425
- Bradley, J. P. (1994). Chemically Anomalous, Preaccretionally Irradiated Grains in Interplanetary Dust from Comets. *Science* 265, 925–929. doi:10.1126/science.265.5174.925
- Cuko, A., Macià, A., Calatayud, M., and Bromley, S. T. (2017). Global Optimisation of Hydroxylated Silica Clusters: A Cascade Monte Carlo Basin Hopping Approach. *Comput. Theor. Chem.* 1102, 38–43. doi:10.1016/j.comptc.2016.12.030
- Demyk, K., Jones, A. P., Dartois, E., Cox, P., and d'Hendecourt, L. (1999). The Chemical Composition of the Silicate Dust Around RAFGL7009S and IRAS 19110+1045. *Astron. Astrophys.* 349, 267–275.
- Dickinson, C., Ali-Haïmoud, Y., Barr, A., Battistelli, E. S., Bell, A., Bernstein, L., et al. (2018). The State-Of-Play of Anomalous Microwave Emission (AME) Research. *New Astron. Rev.* 80, 1–28. doi:10.1016/j.newar.2018.02.001
- Draine, B. T., and Lazarian, A. (1998a). Electric Dipole Radiation from Spinning Dust Grains. *ApJ* 508, 157–179. doi:10.1086/306387
- Draine, B. T., and Lazarian, A. (1998b). Diffuse Galactic Emission from Spinning Dust Grains. *Astrophys. J.* 494, L19–L22. doi:10.1086/311167
- Dulieu, F., Amiaud, L., Congiu, E., Fillion, J.-H., Matar, E., Momeni, A., et al. (2010). Experimental Evidence for Water Formation on Interstellar Dust Grains by Hydrogen and Oxygen Atoms. *Astron. Astrophys.* 512, A30. doi:10.1051/0004-6361/200912079
- Gale, J. D., and Rohl, A. L. (2003). The General Utility Lattice Program (GULP). *Mol. Simul.* 29, 291–341. doi:10.1080/0892702031000104887
- Gibb, E. L., Whittet, D. C. B., Boogert, A. C. A., and Tielens, A. G. G. M. (2004). Interstellar Ice: The Infrared Space Observatory Legacy. *Astrophys. J. Suppl. S* 151, 35–73. doi:10.1086/381182
- Gobrecht, D., Cherchneff, I., Sarangi, A., Bromley, S. T., and Bromley, S. T. (2016). Dust Formation in the Oxygen-Rich AGB Star Iκ Tauri. *A&A* 585, A6. doi:10.1051/0004-6361/201425363
- Goumans, T. P. M., and Bromley, S. T. (2011). Hydrogen and Oxygen Adsorption on a Nanosilicate - a Quantum Chemical Study. *Mon. Not. R. Astron. Soc.* 414, 1285–1291. doi:10.1111/j.1365-2966.2011.18463.x
- Goumans, T. P. M., and Bromley, S. T. (2012). Efficient Nucleation of Stardust Silicates via Heteromolecular Homogeneous Condensation. *Mon. Not. R. Astron. Soc.* 420, 3344–3349. doi:10.1111/j.1365-2966.2011.20255.x
- Henning, T. (2010). Cosmic Silicates. *Annu. Rev. Astron. Astrophys.* 48, 21–46. doi:10.1146/annurev-astro-081309-130815
- Hensley, B. S., and Draine, B. T. (2017). Modeling the Anomalous Microwave Emission with Spinning Nanoparticles: No PAHs Required. *ApJ* 836, 179. doi:10.3847/1538-4357/aa5c37
- Hensley, B. S., Draine, B. T., and Meisner, A. M. (2016). A Case against Spinning PAHs as the Source of the Anomalous Microwave Emission. *ApJ* 827, 45. doi:10.3847/0004-637x/827/1/45
- Hildebrandt, S. R., Rebolo, R., Rubiño-Martín, J. A., Watson, R. A., Gutiérrez, C. M., Hoyland, R. J., et al. (2007). COSMOSMAS Observations of the Cosmic Microwave Background and Galactic Foregrounds at 11 GHz: Evidence for Anomalous Microwave Emission at High Galactic Latitude. *Mon. Not. R. Astron. Soc.* 382, 594–608. doi:10.1111/j.1365-2966.2007.12380.x
- Hoang, T., Vinh, N.-A., and Lan, N. Q. (2016). Spinning Dust Emission from Ultra-small Silicates: Emissivity and Polarization Spectrum. *ApJ* 824, 18. doi:10.3847/0004-637x/824/1/18
- Hoang, T., Tram, L. N., Lee, H., and Ahn, S.-H. (2019). Rotational Disruption of Dust Grains by Radiative Torques in Strong Radiation Fields. *Nat. Astron.* 3, 766–775. doi:10.1038/s41550-019-0763-6
- Hollenbach, D., and McKee, C. F. (1989). Molecule Formation and Infrared Emission in Fast Interstellar Shocks. III - Results for J Shocks in Molecular Clouds. *ApJ* 342, 306. doi:10.1086/167595
- Ioppolo, S., Cuppen, H. M., Romanzin, C., van Dishoeck, E. F., and Linnartz, H. (2008). Laboratory Evidence for Efficient Water Formation in Interstellar Ices. *Astrophys. J.* 686, 1474–1479. doi:10.1086/591506
- Jones, A. P., Tielens, A. G. G. M., and Hollenbach, D. J. (1996). Grain Shattering in Shocks: The Interstellar Grain Size Distribution. *ApJ* 469, 740. doi:10.1086/177823
- Keller, L. P., and McKay, D. S. (1997). The Nature and Origin of Rims on Lunar Soil Grains. *Geochim. Cosmochim. Acta* 61, 2331–2341. doi:10.1016/s0016-7037(97)00085-9
- Kemper, F., Vriend, W. J., and Tielens, A. G. G. M. (2004). The Absence of Crystalline Silicates in the Diffuse Interstellar Medium. *ApJ* 609, 826–837. doi:10.1086/421339
- Kerkeni, B., and Bromley, S. T. (2013). Competing Mechanisms of Catalytic H₂ Formation and Dissociation on Ultrasmall Silicate Nanocluster Dust Grains. *Mon. Not. R. Astron. Soc.* 435, 1486–1492. doi:10.1093/mnras/stt1389
- Kerkeni, B., Bacchus-Montabonel, M.-C., and Bromley, S. T. (2017). How Hydroxylation Affects Hydrogen Adsorption and Formation on Nanosilicates. *Mol. Astrophys.* 7, 1–8. doi:10.1016/j.molap.2017.04.001
- Kerkeni, B., Bacchus-Montabonel, M.-C., Shan, X., and Bromley, S. T. (2019). Understanding H₂ Formation on Hydroxylated Pyroxene Nanoclusters: Ab Initio Study of the Reaction Energetics and Kinetics. *J. Phys. Chem. A* 123, 9282–9291. doi:10.1021/acs.jpca.9b06713
- Lamiel-Garcia, O., Ko, K. C., Lee, J. Y., Bromley, S. T., and Illas, F. (2017). When Anatase Nanoparticles Become Bulklike: Properties of Realistic TiO₂ Nanoparticles in the 1–6 nm Size Range from All Electron Relativistic Density Functional Theory Based Calculations. *J. Chem. Theor. Comput* 13, 1785–1793. doi:10.1021/acs.jctc.7b00085
- Li, A., and Draine, B. T. (2001). On Ultrasmall Silicate Grains in the Diffuse Interstellar Medium. *Astrophys. J. Lett.* 550, L213–L217. doi:10.1086/319640
- Macià Escatllar, A., and Bromley, S. T. (2020). Assessing the Viability of Silicate Nanoclusters as Carriers of the Anomalous Microwave Emission: a Quantum Mechanical Study. *Astronom. Astrophys.* 634, A77. doi:10.1051/0004-6361/201936419
- Macià Escatllar, A., Lazaukas, T., Woodley, S. M., and Bromley, S. T. (2019). Structure and Properties of Nanosilicates with Olivine (Mg₂SiO₄) N and Pyroxene (MgSiO₃) N Compositions. *ACS Earth Sp. Chem.* 3, 2390–2403. doi:10.1021/acsearthspacechem.9b00139
- Mokrane, H., Chaabouni, H., Accolla, M., Congiu, E., Dulieu, F., Chehrouri, M., et al. (2009). Experimental Evidence for Water Formation via Ozone Hydrogenation on Dust Grains at 10 K. *ApJ* 705, L195–L198. doi:10.1088/0004-637x/705/2/l195
- Molpeceres, G., Rimola, A., Ceccarelli, C., Kästner, J., Ugliengo, P., and Maté, B. (2019). Silicate-mediated Interstellar Water Formation: A Theoretical Study. *Mon. Not. R. Astron. Soc.* 482, 5389–5400. doi:10.1093/mnras/sty3024
- Neese, F., Wennmohs, F., Becker, U., and Riplinger, C. (2020). The ORCA Quantum Chemistry Program Package. *J. Chem. Phys.* 152, 224108. doi:10.1063/5.0004608
- Norris, B. R. M., Tuthill, P. G., Ireland, M. J., Lacour, S., Zijlstra, A. A., Lykou, F., et al. (2012). A Close Halo of Large Transparent Grains Around Extreme Red Giant Stars. *Nature* 484, 220–222. doi:10.1038/nature10935
- Perdew, J. P., Burke, K., and Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 77, 3865–3868. doi:10.1103/physrevlett.77.3865
- Tielens, A. G. G. M., and Hagen, W. (1982). Model Calculations of the Molecular Composition of Interstellar Grain Mantles. *Astron. Astrophys.* 114, 245
- van Dishoeck, E. F., Herbst, E., and Neufeld, D. A. (2013). Interstellar Water Chemistry: From Laboratory to Observations. *Chem. Rev.* 113, 9043–9085. doi:10.1021/cr4003177
- Wales, D. J., and Doye, J. P. K. (1997). Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms. *J. Phys. Chem. A* 101, 5111–5116. doi:10.1021/jp970948n
- Watanabe, N., and Kouchi, A. (2008). Ice Surface Reactions: A Key to Chemical Evolution in Space. *Prog. Surf. Sci.* 83, 439–489. doi:10.1016/j.progsurf.2008.10.001

- Watson, R. A., Rebolo, R., Rubiño-Martín, J. A., Hildebrandt, S., Gutiérrez, C. M., Fernández-Cerezo, S., et al. (2005). Detection of Anomalous Microwave Emission in the Perseus Molecular Cloud with the COSMOSOMAS Experiment. *ApJ* 624, L89–L92. doi:10.1086/430519
- Weigend, F., and Ahlrichs, R. (2005). Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* 7, 3297. doi:10.1039/b508541a
- Zeller, E. J., Ronca, L. B., and Levy, P. W. (1966). Proton-induced Hydroxyl Formation on the Lunar Surface. *J. Geophys. Res.* 71, 4855–4860. doi:10.1029/jz071i020p04855

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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CHAPTER 7

Predicting Observable Infrared Signatures of Nanosilicates in the Diffuse Interstellar Medium

7.1 Introduction

In the previous chapters of this thesis, the crucial role of silicate dust in astrochemistry has been discussed. We have also noted that high-energy processes in the ISM are likely to generate a large population of nano-sized silicate grains¹⁻³. However, despite their predicted abundance, the presence of nanosilicates has not yet been confirmed through direct astronomical observations. In principle, high resolution IR spectroscopy should be ideal for identifying the presence of nanosilicates due to their characteristic Si-O stretching and O-Si-O bending vibrational modes⁴.

Computational modelling techniques have been already used in previous studies to predict the characteristic IR signals of globally optimised nanosilicates⁵. These studies have shown that the 10-micron Si-O stretching feature associated with nanosilicates experiences a downshift with respect to the same mode in bulk silicates. A shift of the 18-micron O-Si-O bending mode towards 15 microns is also predicted for nanosilicates. Additionally, a specific nanosilicate feature centred at 11.5 microns is observed. However, no analysis of the IR intensities of these signals have been conducted to determine whether nanosilicates produce sufficiently intense signals to be detected in astronomical observations.

IR-based observational information regarding the mineralogy and composition of interstellar dust is typically obtained from sightlines with high column densities of dust, which provide sufficient signal-to-noise ratios for this analysis. However, these sightlines present significant observational challenges, as they encompass both the diffuse ISM and denser regions. The advent of JWST offers an unprecedented opportunity to study silicate dust properties in the diffuse ISM, thanks to the highly sensitive spectrometers of the mid-IR instrument (MIRI). This increased sensitivity could potentially allow for the direct detection of nanosilicates for the first time.

In this chapter, we present the work carried out in collaboration with Dr. Sascha Zeegers, Prof. Francisca Kemper and Dr. Jonathan Marshall. We combined DFT calculated IR spectra with models of the observational performance of JWST to predict potential IR signatures that could be used to confirm the presence and abundance of nanosilicate grains in the ISM.

The contribution of the author of this thesis to the work consisted in building the set of nanosilicates obtained using global minimum searches using MCBH⁶ and a genetic algorithm⁷, and computing their harmonic IR spectra using DFT calculations. The resulting computed IR spectra were then used by our collaborators to convert the computed intensities to cross sections^{8,9} which were then used in the observational modelling.

7.2 Results

For the computational modelling side of this work, we prepared an IR spectral library of nanosilicates with Mg-rich olivine (*i.e.* $(\text{Mg}_2\text{SiO}_4)_N$) and pyroxene (*i.e.* $(\text{MgSiO}_3)_N$) compositions with a range of sizes $N = 1 - 10$. For each size and composition, we identified the structures of the 50 most energetically stable isomers through global optimization searches using FFs. These structures were subsequently reoptimized using DFT for a more accurate energetic ordering of the nanosilicates. From the reoptimized set, we selected the five lowest energy isomers of each size and stoichiometry (except for the monomers) and computed their IR spectra to create a library of 96 IR spectra. In Figure 1, the three lowest energy structures used for the 10 units olivine $(\text{Mg}_2\text{SiO}_4)_{10}$ are shown as an example.

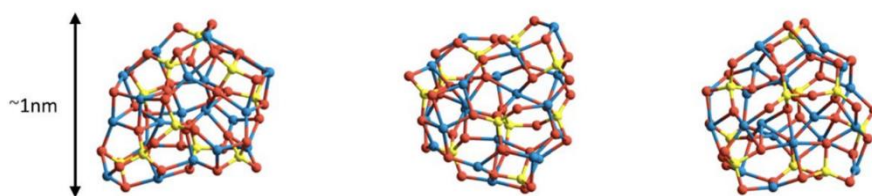


Figure 1: Structures of the three lowest energy isomers corresponding to the 10 units olivine stoichiometry $(\text{Mg}_2\text{SiO}_4)_N$. Oxygen, magnesium and silicon atoms are depicted as red, blue and yellow spheres respectively.

Once the library of computed IR spectra was built, we generated characteristic spectra representative of nanosilicate populations in the ISM. Since we have populated the library with nanosilicates with pure pyroxenic or olivinic grains, the most straightforward spectra that can be obtained are those of populations formed solely of pyroxenic or olivinic grains. These spectra were obtained by equally weighting all the nanosilicates in each respective stoichiometrically pure population. The resulting characteristic spectra are shown in Figure 2.

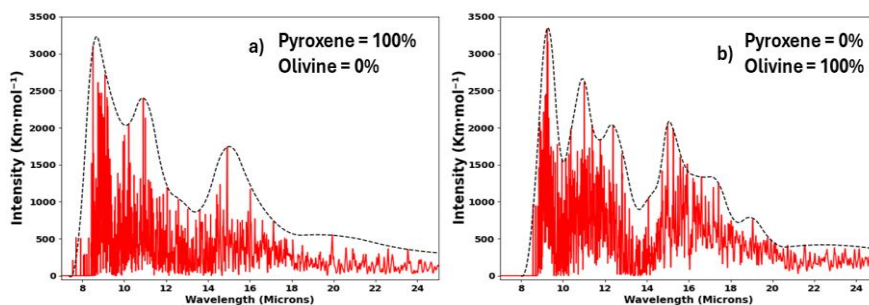


Figure 2: Calculated IR spectra of nanosilicates populations containing 46 pyroxene nanoclusters (left) and 46 olivine nanoclusters (right). Each red line in the spectra corresponds to an individual vibrational mode. Dashed lines indicate approximations to the overall spectral shape expected for larger nanosilicate populations.

The spectra shown in Figure 2 reveal, as anticipated from previous work⁵, that the nanosilicate spectra, of either pyroxenic or olivinic nature, exhibit significant differences compared to those of bulk amorphous silicate grains. First, nanosilicate spectra do not display the characteristic 18-micron O-Si-O bending mode signal observed in bulk silicates. Instead, this signal is downshifted to the 15 - 16-micron region for both stoichiometries, although it appears broader and more intense for olivinic grains.

Differences are also observed in the 10-micron region, where the nanosilicate spectra do not present a single peak at 10 microns. Instead, the bulk-like signal is split into two components, a more intense feature around 9 microns and another one around 11 microns.

The study of these two nanosilicate populations has revealed several differences with the typical IR signals assigned to silicates in the ISM. However, these two purely stoichiometric populations are unlikely to be representative of the real population found in the ISM. Although, when first formed, silicate dust tends to have a more olivinic composition,¹⁰ the sputtering in the diffuse ISM depletes Mg cations¹¹ which increases the fraction of pyroxenic dust¹². To better approximate the real ISM nanosilicate population, we generated the spectra of nanosilicate populations with mixed-stoichiometries by combining the pure spectra in Figure 2 in different proportions. The resulting spectra for various pyroxene:olivine ratios are presented in Figure 3.

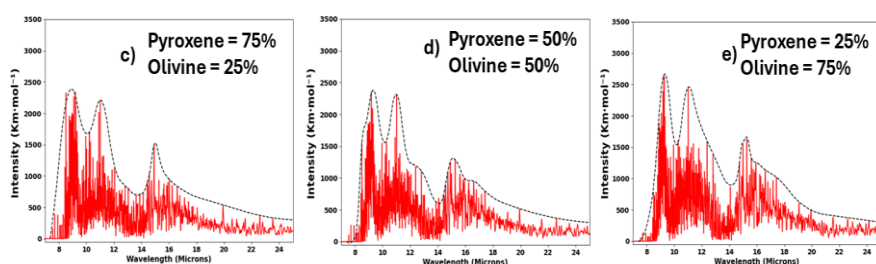


Figure 3: Calculated IR spectra of nanosilicate populations obtained from mixing the spectra in Figure 2 in different pyroxene:olivine ratios. Dashed line indicates approximations to the overall spectral shape expected for larger nanosilicate populations.

The spectra in Figure 3 are in line with those presented in Figure 2, displaying the same general differences with respect to bulk silicates IR, with minor variations depending on the pyroxene to olivine ratio.

The different computed nanosilicates IR were afterwards used, by our collaborators, in the observational modelling to assess the potential observation of their features by JWST. For this purpose, it was estimated that 3-10% of the mass of silicon in silicates present in the ISM resides in grains with diameters smaller than 1 nm, in line with those in the computed populations. The rest of the silicates considered were assumed to consist of larger particles with radius of 0.1 μm .

Two different scenarios were explored in the observational modelling. The first scenario involved the observation of the nearby diffuse ISM, modelled using a main sequence O star as background source, with bulk matter (grains with radius of $0.1 \mu\text{m}$) assumed to have Mg-rich pyroxene composition. This choice was based on the predicted dominance of pyroxene in diffuse ISM due to destruction events¹². The results of this modelling, shown in Figure 4, indicate that nanosilicates are distinguishable from amorphous bulk matter even when considering just 3% of Si mass in nanosilicates along the line of sight, although the distinction is naturally easier when considering a 10% of Si mass locked in nanosilicate grains. This is evidenced by the nanosilicate features being larger than the JWST noise.

Based on these results, the characteristic signals of nanosilicates are expected to be observable mainly as intensity enhancement below the main 10-micron signal, probably as a shoulder in the IR spectrum, along with an extra signal or shoulder in the region around 11 microns. Furthermore, nanosilicate features are also expected to be observable in the region around 16 microns although with greater difficulty due to the higher JWST noise levels in this region of the spectrum.

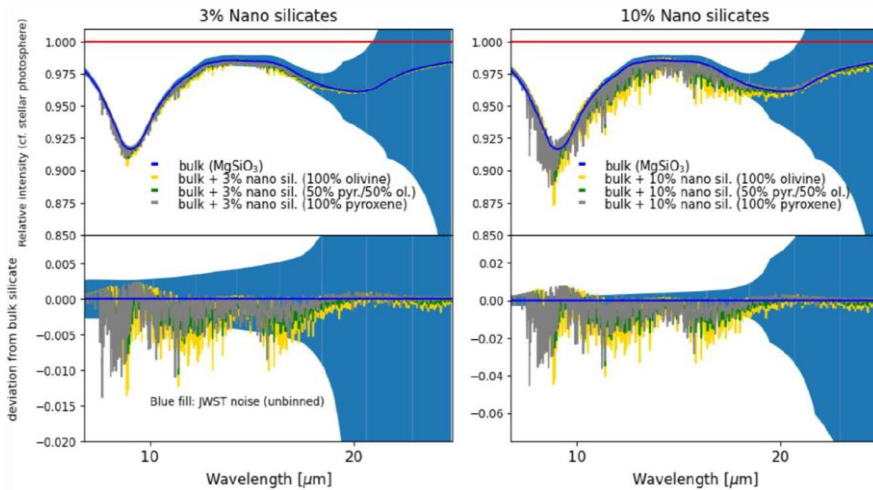


Figure 4: Observational modelling results for the nearby diffuse ISM considering that 3% (left) or 10% (right) of the available Si mass is in nanosilicates along the line of sight. Top panels show the absorption by dust and lower panels the deviation from the bulk matter. Blue line shows the contribution of 100% of bulk matter. Three different nanosilicates populations IR with 100% olivinic composition (yellow), 50% olivine and 50% pyroxene (green) and 100% pyroxene composition (grey) are also shown. Blue area indicates the JWST noise level.

We also modelled the possibility of detecting nanosilicates in the dense ISM. In this case, a carbon-rich Wolf-Rayet star was used as the background source, and the bulk material characterized by amorphous olivine grains. As shown in Figure 5, the results reveal both similarities and differences compared to the diffuse ISM modelling. With respect to the differences, dense ISM models exhibit deeper silicate features (see y-axis value of top plots in Figures 4 and 5) and larger signal-to-noise ratio, which makes it easier to observe nanosilicate signals on top of bulk material. These differences can be attributed to the variation in density between the two environments. Regarding the potential observation of nanosilicates, the conclusions that can be extracted are similar to those for the diffuse ISM, *i.e.* the nanosilicate features should be observed as a shoulder of the 10-micron feature, and as new features at ~ 11 and 16 microns. In this case, the signal around 16 microns should be more easily observed thanks to the larger densities as explained above.

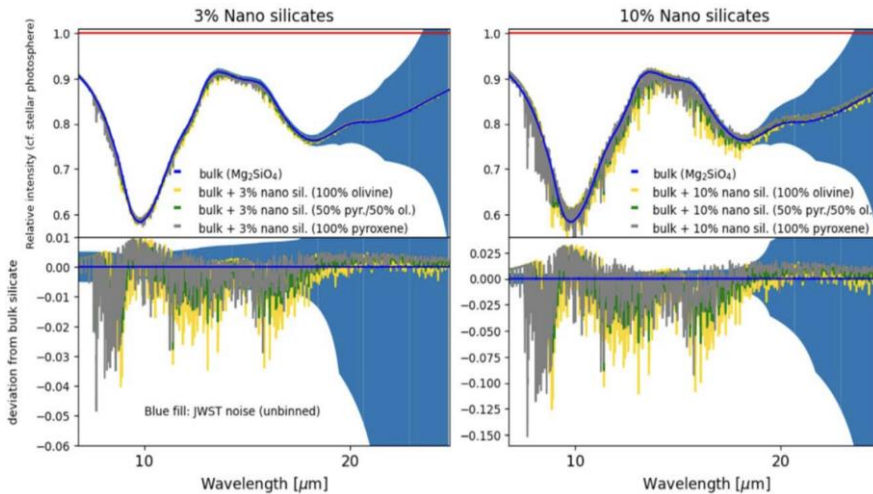


Figure 5: Observational modelling results for the dense ISM considering the presence of 3% (left) or 10% (right) of nanosilicates along the line of sight. Top panels show the absorption by dust and lower panels the deviation from the bulk matter. Blue line shows the contribution of 100% of bulk matter. Three different nanosilicates populations IR with 100% olivine composition (yellow), 50% olivine and 50% pyroxene (green) and 100% pyroxene composition (grey) are also shown. Blue area indicates the JWST noise level.

It is important to highlight that previous observations have already shown intensity excess in the observation of dusty sightlines, in the range between 10 and 20 microns, with the Spitzer Space Telescope, showing that this part of the spectrum cannot be entirely fitted with existing silicate models¹³. Additionally, studies based on the observation of the 10-micron feature, concluded that although the best fitting of this feature is obtained considering dust of Mg-rich olivine composition, it is not capable of explaining the shift of the signal to shorter wavelengths¹⁴, exactly where pyroxenic nanosilicates show distinguishable features.

7.3 Conclusions

These findings, combined with the additional data and analysis provided in the accompanying research article, support the following conclusions:

- 1- We have built an IR spectral library containing the computed harmonic IR spectra of the five lowest energy isomers of nanosilicates with pure Mg-rich pyroxene and olivine composition across a wide range of sizes. The resulting library contains 92 different IR spectra.
- 2- The characteristic IR spectra of different nanosilicate populations have been modelled by combining the individual spectra from the library in various ways. The resulting spectra exhibit distinctive features that differ significantly from those of bulk silicates. Notably, the nanosilicate spectra lack the 18-micron signal typically observed in bulk silicates, showing instead a downshifted feature around the 15–16-micron region. Additionally, the 10-micron feature is split into two separate signals: one downshifted around 9 microns and the other upshifted to approximately 11 microns.
- 3- The predictive modelling of JWST observations of the diffuse ISM has demonstrated that nanosilicate features could, in principle, be detected on top of bulk IR spectra in these regions, even when only a 3% of the available Si mass in a nanosilicate grain population.
- 4- The predictive modelling of JWST observations of the dense ISM has revealed that nanosilicate features could also be observed along these sightlines. Detection in these regions is facilitated by the presence of larger amounts of matter, enhancing the visibility of specific nanosilicate IR signatures.

7.4 References

- ¹ Li, A. and Draine, B. T. On ultrasmall silicate grains in the diffuse interstellar medium. *The Astrophysical Journal*. **2001**, 550(2), L213.
- ² Bringa, E. M.; Kucheyev, S. O.; Loeffler, M. J.; Baragiola, R. A.; Tielens, A. G. G. M.; Dai, Z. R.; Graham, G.; Bajt, S.; Bradley, J. P.; Dukes, C. A.; Felter, T. E.; Torres, D. F. and Van Breugel, W. Energetic processing of interstellar silicate grains by cosmic rays. *The Astrophysical Journal*. **2007**, 662(1), 372.
- ³ Jones, A. P.; Tielens, A. G. G. M. and Hollenbach, D. J. Grain shattering in shocks: The interstellar grain size distribution. *Astrophysical Journal*. **1996**, 469, 740.
- ⁴ Henning, T. Cosmic silicates. *Annual Review of Astronomy and Astrophysics*. **2010**, 48(1), 21-46.
- ⁵ Escatllar, A. M.; Lazaukas, T.; Woodley, S. M. and Bromley, S. T. Structure and properties of nanosilicates with olivine (Mg₂SiO₄)_N and pyroxene (MgSiO₃)_N compositions. *ACS Earth and Space Chemistry*. **2019**, 3(11), 2390-2403.
- ⁶ Wales, D. and Doye, J. P. K. Global Optimization by Basin Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms, *J. Phys. Chem. A*, **1997**, 101(97), 5111–5116
- ⁷ Lazauskas, T.; Sokol, A. A. and Woodley, S. M, An Efficient Genetic Algorithm for Structure Prediction at the Nanoscale, *Nanoscale*. **2017**, 9(11), 3850–3864.
- ⁸ Bauschlicher, C. W.; Boersma, C.; Ricca, A.; Mattioda, A. L.; Cami, J.; Peeters, E.; Sánchez de Armas, F.; Saborido, G. P.; Hudgins, D. M. and Allamandola, L. J. The NASA Ames polycyclic aromatic hydrocarbon infrared spectroscopic database: the computed spectra. *The Astrophysical Journal Supplement Series*. **2010**, 189(2), 341.
- ⁹ Boersma, C.; Bauschlicher, C. W.; Ricca, A.; Mattioda, A. L.; Cami, J.; Peeters, E.; Sánchez de Armas, F.; Saborido, G. P.; Hudgins, D. M.; Allamandola, L. J. The Nasa Ames Pah Ir Spectroscopic Database Version 2.00: Updated Content, Website And On/Offline Tools, *Astrophys. J. Suppl.*, **2014**, 211(1), 8.

¹⁰ Dorschner, J.; Begemann, B.; Henning, T.; Jäger, C. and Mutschke, H. Steps toward interstellar silicate mineralogy. II. Study of Mg-Fe-silicate glasses of variable composition, *Astronomy and Astrophysics*. **1995**, 300, 503–520.

¹¹ Bradley, J. P. Chemically anomalous, preaccretionally irradiated grains in interplanetary dust from comets, *Science*. **1994**, 265, 925.

¹² Kemper, F.; Vriend, W. J. and Tielens, A. The absence of crystalline silicates in the diffuse interstellar medium, *The Astrophysical Journal*. **2004**, 609, 826.

¹³ Fogerty, S.; Forrest, W.; Watson, D. M.; Sargent, B. A. and Koch, I. Silicate Composition of the Interstellar Medium, *The Astrophysical Journal*. **2016**, 830, 71.

¹⁴ Van Breemen, J. M. The 9.7 and 18 mm silicate absorption profiles towards diffuse and molecular cloud lines-of-sight, *Astronomy and Astrophysics*. **2011**, 526, A152.

PAPER

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Predicting observable infrared signatures of nanosilicates in the diffuse interstellar medium

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The destruction time scale of dust in the diffuse interstellar medium is estimated to be an order of magnitude shorter than its residence time. Nevertheless, dust is observed in the interstellar medium, leading to the conclusion that reformation and grain growth must take place. Direct observations of nanometre-sized silicate grains, the main constituent of interstellar dust, would provide a smoking gun for the occurrence of grain condensation in the diffuse interstellar medium. Here we employ quantum chemical calculations to obtain the mid-infrared (IR) optical properties of a library of Mg-end member silicate nanoparticles with olivine (Mg_2SiO_4) and pyroxene (MgSiO_3) stoichiometries. We use this library as an input for a foreground-screen model to predict the spectral appearance of the absorption profile due to mixtures of bulk and nanoparticle silicates towards bright background sources. The mid-IR spectrum observed towards an O8V star or a carbon-rich Wolf–Rayet star starts to change when $\sim 3\%$ of the silicate mass is in the form of nanosilicates. We predict that a 3–10% nanosilicate fraction can be detected with the James Webb Space Telescope (JWST) using the mid-IR instrument (MIRI). With our upcoming JWST observations using MIRI, we will be able to detect or place limits on the nanosilicate content in the diffuse interstellar medium, and thus potentially directly confirm interstellar dust formation.

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Introduction

Observations of the nearby universe are significantly affected by the presence of dust in the interstellar medium (ISM). The formation of most dust is thought to occur during high-temperature nucleation processes around dying stars^{1,2} after which it is ejected into the diffuse ISM as small dust grains. Dust grains tend to be either carbonaceous or siliceous in nature, with the latter being more common.³ In the diffuse ISM the nascent grains are subject to energetic processing by supernovae shockwaves, cosmic rays⁴ and ultraviolet (UV) radiation which lead to sputtering, shattering and ionization.^{5,6} Dust grain processing in the ISM is predicted to create a huge population of nano-sized silicate grains⁷ which could be astrochemically relevant for formation/dissociation of H₂,^{8,9} and water molecules,^{10,11} and are a prime candidate for being the source of the anomalous microwave emission (AME).^{12–14} Due to the dominance of photoelectric electron ejection over recombination in very small grains in the ISM, nano-silicates are also likely to be positively ionized¹⁵ enhancing their role as seed species for dust (re)nucleation.¹⁶ Ionised nanosilicates could also act as sinks for oxygen depletion – potentially contributing to the unresolved problem of the “missing” oxygen in the ISM.^{17,18}

Silicate dust is mainly thought to be Mg-rich and of olivine (Mg₂SiO₄) or pyroxene (MgSiO₃) composition¹⁹ and originally more olivinic when first formed.²⁰ However, sputtering in the diffuse ISM leads to depletion of Mg cations^{21,22} tending to relatively increase the fraction of pyroxenic dust.²³ Generally, the chemical composition of interstellar silicate dust is thus the result of a combination of production and destruction processes and varies considerably with the type of astrophysical environment. It is estimated that the rate of dust destruction by supernova shocks in the ISM is far in excess of the stardust production rate.^{6,24} As such, we do not yet understand the observed abundance of dust in the ISM.

Infrared (IR) spectroscopy is ideal for identifying and quantifying the composition and structure of interstellar dust. Diagnostic bands for silicates fall almost exclusively in the near- and mid-IR region between 8 and 25 μm where features due to Si–O stretching (~10 μm) and O–Si–O bending (~18–20 μm) modes are dominant.¹⁹ Until recently, only sightlines with high column densities of dust against bright background sources, including towards the Galactic Center (GC), provided sufficient signal-to-noise to study the dust composition and mineralogy. Indeed, much of our current information about dust composition is obtained from such sightlines. However, our understanding of these sightlines is complicated because they include both the diffuse ISM and denser molecular regions, for instance the GC sightline includes the Galactic *Central Molecular Zone* and three intervening spiral arms. Dense molecular clouds typically shield the dust grains from dust destruction processes, and they also facilitate grain growth, so a larger typical grain size is expected in the denser regions of the ISM. The highly sensitive spectrometers of the mid-IR instrument (MIRI) on the James Webb Space Telescope (JWST) allow for a detailed study of the characteristics of dust in the diffuse ISM, including the opportunity to detect silicate nanoclusters for the first time. Thus far, interpretations of silicate dust grain observations have employed laboratory-based measurements on bulk silicate samples.²⁰

Nanosilicates, however, are known to have specific non-bulk-like structures with associated distinct infrared features,²⁵ which should be taken into account when interpreting IR observations.

In this work we use a combination of accurate quantum chemical calculations and models of the observational performance of JWST to predict potential IR signatures that could be used to determine the presence, abundance and composition of nanosilicate dust in the ISM. Observations of dust along the line of sight of twelve O and B stars in the diffuse ISM with JWST MIRI are already planned.²⁶ Here we present our modelled predictions for the diffuse ISM using an O8V star and for the dense ISM on a longer sightline using a carbon-rich Wolf-Rayet star.

Methodology

Computational chemistry calculations

We populated our spectral library using calculated IR spectra from nanoclusters of olivine ($(\text{Mg}_2\text{SiO}_4)_N$) and pyroxene ($(\text{MgSiO}_3)_N$) stoichiometry, with sizes $N = 1$ –10. The structures of the nanosilicates were obtained from systematic global optimization searches using the Monte Carlo Basin-Hopping (MCBH) algorithm²⁷ and a genetic algorithm.²⁸ Full details on this procedure can be found in previous work.²⁹ As an example, the three lowest energy structures used for $(\text{Mg}_2\text{SiO}_4)_{10}$ are shown in Fig. 1. We determined the energies and structures of the 50 most stable nanosilicates from the global optimisation searches for each stoichiometry and size employing density functional theory (DFT) calculations using the hybrid PBE0 exchange and correlation functional³⁰ with a tier1/light numerical atom-centered orbital (NAO) basis set. This basis set has a quality similar to a valence triple- ζ plus polarization Gaussian-type orbital basis set.³¹ For the DFT optimizations we used the all-electron, full potential Fritz Haber Institute *Ab Initio* Molecular Simulation package (FHI-AIMS).³² For both nanosilicate stoichiometries and for each N , we then calculated the IR spectra for the five lowest energy isomers, except for the monomers (*i.e.* $N = 1$) for which we only included the lowest energy isomer. The resulting nanosilicate spectral library thus contains 92 distinct IR spectra (*i.e.* 46 from nano-pyroxenes and 46 from nano-olivines).

The harmonic IR spectra of 96 nanosilicates were obtained using the same DFT specification described above. We note that DFT-calculated IR vibrational frequencies using this approach agree very well with those obtained from high level quantum chemical calculations³³ and experimental data.³⁴ By summing all the as-calculated spectra for each stoichiometry separately, we obtain two stoichiometrically pure spectra which we take to be characteristic of pyroxene

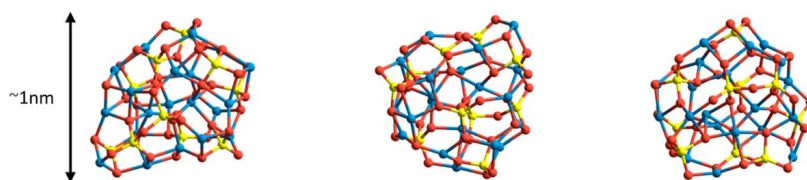


Fig. 1 Examples of optimized low energy nanosilicate structures with an olivine ($(\text{Mg}_2\text{SiO}_4)_{10}$) chemical composition. Atom colour key: Si – yellow, Mg – blue, O – red.

nanosilicates and olivine nanosilicates (see Fig. 2a and b). Using these two pure spectra we can then create characteristic spectra for nanosilicate populations with mixed-stoichiometries by proportionally combining these pure spectra. In Fig. 2c–e we show the mixed stoichiometry nanosilicate spectra for three different pyroxene : olivine ratios. Note that we assume that there is no particular preference for size and/or energetic stability in producing these spectra, and all individual spectra have an equal weighting.

Observational modelling

In order to use the calculated nanosilicate spectra in astronomical extinction models, the intensities of nanosilicate IR spectra in kilometers per mole (km mol^{-1}) are converted to cross sections integrated over the frequency. The conversion is described in detail in paragraph 2.2 of Mattioda *et al.*,³⁵ who use the same conversion for polycyclic aromatic hydrocarbons (PAHs) from the NASA AMES PAH database.^{36,37} Below, we summarize the conversion process.

The intensities of the spectral lines are designated as *A*-values (in km mol^{-1}), not to be confused with Einstein *A* coefficients. The cross section is related to the *A*-values in the following way:

$$\sigma_{\nu,\text{int}} = \int_{\nu} \sigma(\nu) d\nu = 10^5 \frac{c \cdot A\text{-value}}{N_A}.$$

Here, the cross section is indicated by σ , which is expressed as integrated over the frequency ν (cm^{-1}), c is the speed of light and N_A is Avogadro's number.

For this study, we estimate that 3–10% of the silicates in the ISM have ≤ 1 nm diameter (as characterised by our set of nanosilicates – see Fig. 1). Although the amount of nanosilicates may vary for different sightlines depending on grain

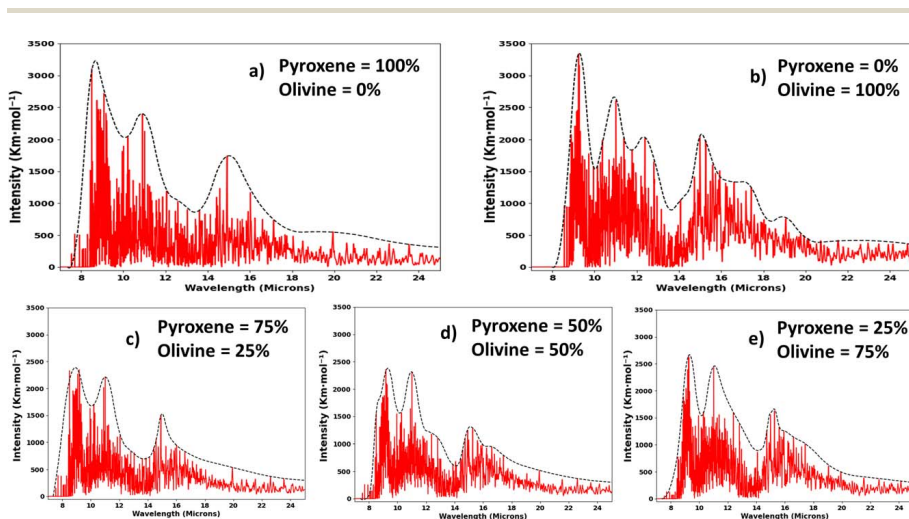


Fig. 2 Calculated IR spectra for nanosilicates where each red line corresponds to an individual vibrational mode. Top: pure stoichiometric nanosilicate IR spectra corresponding to: (a) 46 pyroxene nanosilicates and (b) 46 olivine nanosilicates. Bottom: mixed stoichiometric nanosilicate IR spectra for which the pyroxene : olivine ratio is varied as: (c) 3 : 1, (d) 1.1, (e) 1 : 3. The dashed lines indicate tentative approximations to the limiting overall spectral shape for more realistic larger nanosilicate populations.

destruction processes in the environment, we assume here that in both the dense and diffuse ISM this value may range between 3 and 10%. These percentages have been derived assuming an MRN size distribution,³⁸ which considers a size range 0.005–0.25 μm . We extended this distribution to the smallest nanosilicates (*i.e.* $N = 1$). Draine and Li^{7,39} predict that similar quantities of nanosilicates could be present in the ISM. Based on IR emission spectra it is estimated that an upper limit mass fraction of $\sim 15\%$ of amorphous nanosilicates could have diameters of ≤ 1 nm. We note that all small nanosilicates in the size regime we consider are intrinsically non-crystalline (*i.e.* amorphous),²⁵ and so crystalline silicates are not relevant. The other 90–97% of the silicates modelled in this distribution consist of larger particles, which we refer to as bulk matter. For simplicity we assume that these grains are all 0.1 μm radii particles, which is the average size of grains in the ISM. These larger particles can have different shapes. We consider this using a continuous distribution of ellipsoids (CDE) model.⁴⁰

The reddening by dust along the line of sight can be expressed in visual extinctions, A_V . On average there is about two magnitudes of visual extinction per kiloparsec (kpc).⁴¹ The amount of extinction can be converted to an estimate of the column density of hydrogen particles along the line of sight toward a - background source: $\frac{N_H}{A_V} = 1.9 \times 10^{21} \text{ cm}^{-2} \text{ magn}^{-1}$.⁴² From the column density N_H we can derive the number of silicon atoms along the line of sight using the abundance of this element. A fraction of the silicon atoms will be present in the gas phase, but most of them are depleted in dust. In this study we assume that 98% of the silicates are locked up in dust particles.^{43,44} To calculate the extinction by dust along the line of sight we compute the optical depth from our modelling:

$$\frac{I}{I_0} = e^{-\tau} = e^{-N_d \cdot \sigma},$$

where I_0 is the intrinsic brightness of the source, I is the observed brightness, and τ is the optical depth. τ can be expressed as the column density of particles (N_d) times the extinction cross section (σ). We calculate the optical depth contribution for both the bulk silicates and the nanosilicate particles.

We model two scenarios:

- (1) The nearby diffuse ISM
- (2) The dense ISM in the Galactic Center area

Since we are observing the nanosilicates in extinction, we need to make use of a background source to observe the extinction by dust along the line of sight. For this study we selected sources that are featureless in the IR, because intrinsic features from the source may hinder the analysis of the nanosilicates. In the first scenario we use an O8V star. Main sequence O stars are bright in the IR and, most importantly, the stellar atmosphere can be easily modelled using stellar template models.^{45,46} To model the nearby diffuse ISM, we use a star located at a distance of 2 kpc. In the case of scenario 1 we model the extinction along the line of sight with $A_V = 4$. This degree of extinction allows for sufficiently deep silicate features, as can be seen in Fig. 3, and is common in the nearby diffuse ISM. We model the bulk matter with an amorphous pyroxene (MgSiO_3) model consisting of particles of radius 0.1 μm as indicated above.⁴⁷ The medium-resolution spectroscopy (MRS) observing mode for MIRI on JWST, enables us to obtain detailed spectroscopic data between 4.9 to 27.9 μm with a resolving power of ~ 3700 and 1300.⁴⁸ The modelled spectra are shown with the

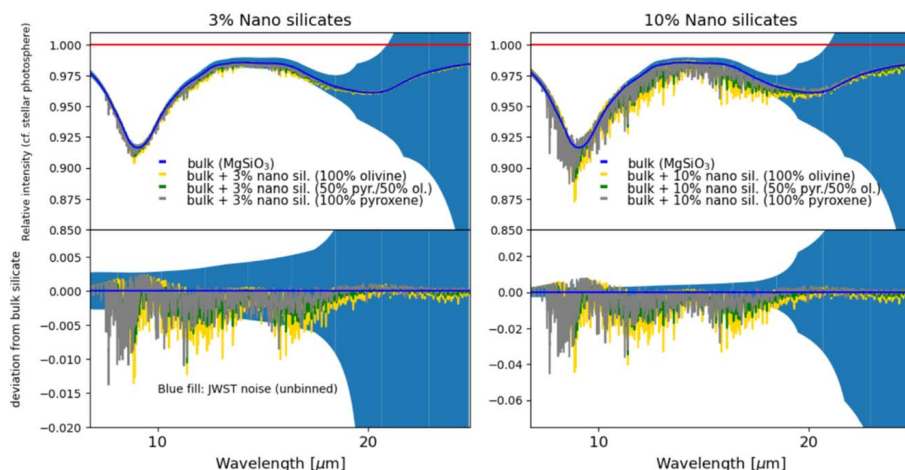


Fig. 3 Diffuse ISM: the upper two panels show absorption by dust relative to the photosphere of an O8V star (red line) for 3 and 10% nanosilicates along the line of sight. The blue line shows the contribution of 100% bulk matter modelled with MgSiO_3 . Three models with nanosilicates are shown in the native (unbinned) resolution of JWST, containing different compositions: yellow 100% olivine composition, green 50% pyroxene and 50% olivine composition and grey 100% pyroxene composition. The models are shown with the uncertainties in the unbinned data (with blue fill). The two lower panels show the same models but highlight the deviation from the bulk matter.

uncertainties from MIRI MRS in the unbinned data (with blue fill). Signal-to-noise values were obtained using the JWST exposure time calculator (ETC).^{49,50} The exposure time used in this modelling is 2220 seconds. We demonstrate the different nanosilicate compositions using three models from Fig. 2 – 100% olivine, 50% pyroxene + 50% olivine and 100% pyroxene. The silicate features are shown relative to the unabsorbed stellar continuum. The two different panels show the results for 3% and 10% of nanosilicates along the line of sight. In the case of the olivinic MgSiO_3 bulk silicate (blue line) we assume that 100% of the silicates are in the 0.1 μm particles.

In the second scenario we model the dense ISM along a more distant sightline of 8 kpc towards the Galactic Center area with an extinction of $A_V = 16$. In this case the source is a carbon-rich Wolf-Rayet star. This source is bright in the IR and we are able to observe these sources at high extinction.^{23,51} As a template we use a WC7 star from the PoWR database with an effective temperature $T = 50$ K and radius $\log R_t = 1.0$ in solar radii.⁵² Carbon rich Wolf-Rayet stars are assumed to be devoid of silicates. Therefore, we can assume that the silicate features around 10–20 μm belong entirely to interstellar dust. In this scenario, we model the dense ISM bulk matter using amorphous olivine (Mg_2SiO_4) with grain radii of 0.1 μm .⁴⁷ We also demonstrate the same three nanosilicate compositions as in scenario 1 in our modelling of this sightline. The modelling is shown in Fig. 4. The modelled exposure time is the same as in scenario 1.

Results and discussion

Fig. 3 and 4 show simulations of modelled JWST observations of two stars in different environments in the Galaxy. The difference in density between the two

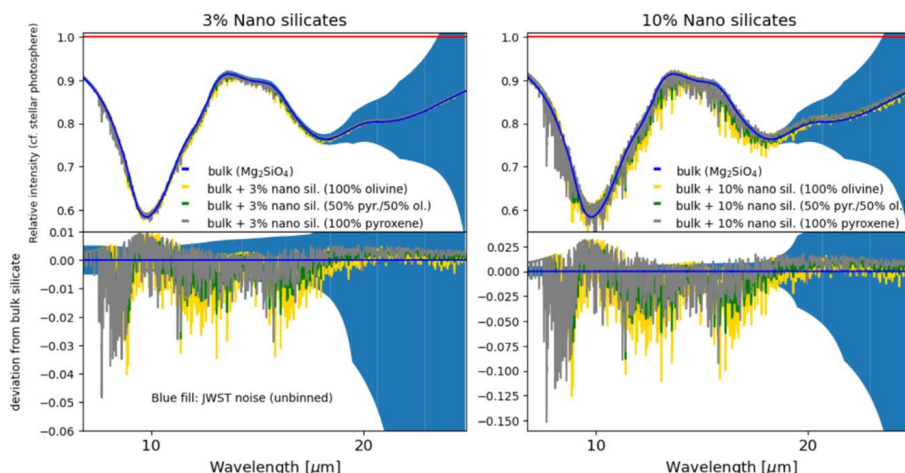


Fig. 4 Dense ISM: the upper two panels show absorption by dust relative to the photosphere of a Wolf–Rayet star (red line) for 3 and 10% nanosilicates along the line of sight. The blue line shows the contribution of 100% bulk matter modelled with Mg_2SiO_4 . Three models with nanosilicates are shown in the native (unbinned) resolution of JWST, containing different compositions: yellow 100% olivine composition, green 50% pyroxene and 50% olivine composition and grey 100% pyroxene composition. The models are shown with the uncertainties in the unbinned data (with blue fill). The two lower panels show the same models but highlight the deviation from the bulk matter.

environments can be observed in the depth of the silicate features. We also made a distinction between dust species selected for the bulk matter. We assume that the diffuse ISM contains pyroxene silicates and the dense ISM contains olivine silicates. This distinction, although exaggerated for this analysis, is based on the prediction that pyroxene dust is more dominant in the diffuse ISM due to destruction events.²³ Recent findings from X-ray spectroscopy provide observational support for this effect, since the dense sightlines in these studies are dominated by olivine type,^{53,54} whereas pyroxene is the dominant dust species along diffuse sightlines.⁵⁵

From the modelling of both sightlines, we can distinguish different types of nanosilicates from the amorphous bulk silicates along the line of sight of two modelled sources. In the case of 3% of nanosilicates along the line of sight this is more challenging. However, we do note that the uncertainties (shown by the blue filled lines) are smaller than the silicate features and that this is the native (unbinned) resolution of MRS using MIRI on JWST. Binning the data will decrease the errors further and will highlight the general effect of the nanosilicates. In the case of 10% nanosilicates along the line of sight, we can clearly distinguish the effect of these particles in both scenarios: the deviation from the bulk matter as well as their different spectral features. The effect of the nanosilicates is most prominent in the spectra between 10 and 20 μm . From observations of dusty sightlines with the Spitzer Space Telescope it is already clear that this part of the spectrum cannot be fitted entirely with the existing silicate models and that excess extinction is observed between 10 and 20 μm .⁵⁶ Furthermore, the 10 μm feature itself also cannot be fitted well with bulk matter models. Van Breemen *et al.* concluded that although the best fitting dust to the feature around 10 μm consists of magnesium rich olivine, this

does not explain the shift in the feature to shorter wavelength, which is exactly where the pyroxene nanosilicates dominate the spectrum.⁵⁷

Our simulations of detection of nanosilicates open the possibility to study grain formation and destruction along these sightlines. The amount of nanosilicates gives an indication of the processes at work in these environments. We can try to piece together the cycle of shattering, destruction, formation, and grain growth. So far, grain formation has been invoked, as the residence time of silicates in the ISM is about ten times longer than the destruction time scale, but it has been assumed that this process occurs in molecular clouds, and it has not been directly observed.⁵⁸ By sampling different sightlines with a variety of distances and magnitudes of extinction, we can probe differences in various environments of the Galaxy. Of course, the distance to the clouds of gas and dust in the ISM is degenerate since we do not know exactly where along the line of sight these clouds are situated from just these observations. This problem can be partly solved by comparing the observations with Galaxy dust maps.⁵⁹ If the nanosilicates are abundantly present in the spectra we may observe areas along the line of sight with active grain formation in the diffuse ISM.

Conclusions

We have modelled the IR spectral features associated with Mg-rich olivine and pyroxene nanosilicate dust grains (and a 50 : 50 mixture) based on a library of nanosilicate IR spectra calculated using an accurate quantum chemical based approach. We consider the impact of intervening nanosilicates on mid-IR spectra of background stars in two distinct astrophysical environments, namely the nearby diffuse ISM ($A_V = 4$) and the dense galactic centre ($A_V = 16$). We compare the features imprinted by nanosilicates with bulk material of the same compositions, finding distinctive features and deviations at the few per cent level across mid-IR wavelengths. Differentiation between the species is easier toward denser intervening material, but still possible for the diffuse ISM at high signal-to-noise ratios. These models demonstrate the feasibility of the detection of nanosilicates in already planned JWST MIRI observations for a selection of nearby O stars. Furthermore, these observations will potentially allow us to directly trace grain destruction and grain growth in the ISM for the first time.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- 1 H.-P. Gail and E. Sedlmayr, Inorganic dust formation in astrophysical environments, *Faraday Discuss.*, 1998, **109**, 303–319.
- 2 T. P. M. Goumans and S. T. Bromley, Efficient Nucleation of Stardust Silicates via Heteromolecular Homogeneous Condensation, *Mon. Not. R. Astron. Soc.*, 2012, **420**, 3344–3349.
- 3 A. G. G. M. Tielens, The Composition of Circumstellar and Interstellar Dust, *ASP Conf. Ser.*, 2001, **231**, 92.
- 4 E. M. Bringa, S. O. Kucheyev, R. A. Loeffler, *et al.*, Energetic Processing of Interstellar Silicate Grains by Cosmic Rays, *Adv. Pharm. J.*, 2007, **662**, 372.
- 5 A. P. Jones, A. G. G. M. Tielens and D. J. Hollenbach, Grain Shattering in Shocks: The Interstellar Grain Size Distribution, *Astrophys. J.*, 1996, **469**, 740.
- 6 A. P. Jones and J. A. Nuth III, Dust destruction in the ISM: a re-evaluation of dust lifetimes, *Astron. Astrophys.*, 2011, **530**, A44.
- 7 A. Li and B. T. Draine, On Ultrasmall Silicate Grains in the Diffuse Interstellar Medium, *Astrophys. J.*, 2001, **550**, L213–L217.
- 8 I. Oueslati, B. Kerkeni and S. T. Bromley, Trends in the adsorption and reactivity of hydrogen on magnesium silicate nanoclusters, *Phys. Chem. Chem. Phys.*, 2015, **17**, 8951–8963.
- 9 B. Kerkeni and S. T. Bromley, Competing mechanisms of catalytic H₂ formation and dissociation on ultrasmall silicate nanocluster dust grains, *Mon. Not. R. Astron. Soc.*, 2013, **435**(2), 1486–1492.
- 10 T. P. M. Goumans and S. T. Bromley, Hydrogen and oxygen adsorption on a nanosilicate – a quantum chemical study, *Mon. Not. R. Astron. Soc.*, 2011, **414**, 1285–1291.
- 11 B. Kerkeni, M.-C. Bacchus-Montabonel and S. T. Bromley, How hydroxylation affects hydrogen adsorption and formation on nanosilicates, *Mol. Astrophys.*, 2017, **7**, 1–8.
- 12 A. Macia Escatller and S. T. Bromley, Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study, *Astron. Astrophys.*, 2020, **634**, A77.
- 13 B. S. Hensley and B. T. Draine, Modeling the Anomalous Microwave Emission with Spinning Nanoparticles: No PAHs Required, *Astrophys. J.*, 2017, **836**, 179–192.
- 14 T. Hoang, N.-A. Vinh and N. Q. Lan, Spinning Dust Emission from Ultra-Small Silicates: Emissivity and Polarization Spectrum, *Astrophys. J.*, 2016, **824**, 18–28.
- 15 J. C. Weingartner and B. T. Draine, Photoelectric Emission from Interstellar Dust: Grain Charging and Gas Heating, *Astrophys. J. Suppl.*, 2001, **134**, 263.
- 16 S. Zhukovska, C. Dobbs, E. B. Jenkins and R. S. Klessen, Modeling Dust Evolution in Galaxies with a Multiphase, Inhomogeneous ISM, *Astrophys. J.*, 2016, **831**, 147.
- 17 D. C. B. Whittet, Oxygen Depletion in the Interstellar Medium: Implications for Grain Models and the Distribution of Elemental Oxygen, *Astrophys. J.*, 2010, **710**, 1009–1016.

- 18 J. Mariño-Guiu, B.-A. Ghejan, T. M. Bernhardt, J. M. Bakker, S. M. Lang and S. T. Bromley, Cluster Beam Study of $(\text{MgSiO}_3)^+$ -Based Monomeric Silicate Species and Their Interaction with Oxygen: Implications for Interstellar Astrochemistry, *ACS Earth Space Chem.*, 2022, **6**(10), 2465–2470.
- 19 T. Henning, Cosmic Silicates, *Annu. Rev. Astron. Astrophys.*, 2010, **48**, 21.
- 20 J. Dorschner, B. Begemann, Th. Henning, C. Jäger and H. Mutschke, Steps toward interstellar silicate mineralogy. II. Study of Mg-Fe-silicate glasses of variable composition, *Astron. Astrophys.*, 1995, **300**, 503–520.
- 21 L. P. Keller and D. S. McKay, The nature and origin of rims on lunar soil grains, *Geochim. Cosmochim. Acta*, 1997, **61**, 2331.
- 22 J. P. Bradley, Chemically anomalous, preaccretionally irradiated grains in interplanetary dust from comets, *Science*, 1994, **265**, 925.
- 23 F. Kemper, W. J. Vriend and A. Tielens, The absence of crystalline silicates in the diffuse interstellar medium, *Astrophys. J.*, 2004, **609**, 826.
- 24 J. D. Slavin, E. Dwek and A. P. Jones, Destruction of Interstellar Dust in Evolving Supernova Remnant Shock Waves, *Astrophys. J.*, 2015, **803**, 7.
- 25 A. Macia Escatller, T. Lazaukas, S. M. Woodley and S. T. Bromley, Structure and Properties of Nanosilicates with Olivine $(\text{Mg}_2\text{SiO}_4)_N$ and Pyroxene $(\text{MgSiO}_3)_N$ Compositions, *ACS Earth Space Chem.*, 2019, **3**, 2390.
- 26 Illuminating the dust properties in the diffuse ISM with JWST, Zeegers *et al.*, 2021, JWST Proposal. Cycle 1, ID. #2183.
- 27 D. Wales and J. P. K. Doye, Global Optimization by Basin Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms, *J. Phys. Chem. A*, 1997, **101**(97), 5111–5116.
- 28 T. Lazauskas, A. A. Sokol and S. M. Woodley, An Efficient Genetic Algorithm for Structure Prediction at the Nanoscale, *Nanoscale*, 2017, **9**(11), 3850–3864.
- 29 A. Macià Escatllar, T. Lazaukas, S. M. Woodley and S. T. Bromley, Structure and Properties of Nanosilicates with Olivine $(\text{Mg}_2\text{SiO}_4)_N$ and Pyroxene $(\text{MgSiO}_3)_N$ Compositions, *ACS Earth Space Chem.*, 2019, **3**, 2390–2403.
- 30 C. Adamo and V. Barone, Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
- 31 O. Lamiel-Garcia, K. C. Ko, J. Y. Lee, S. T. Bromley and F. Illas, When Anatase Nanoparticles Become Bulklike: Properties of Realistic TiO_2 Nanoparticles in the 1–6 nm Size Range from All Electron Relativistic Density Functional Theory Based Calculations, *J. Chem. Theory Comput.*, 2017, **13**, 1785–1793.
- 32 V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals, *Comput. Phys. Commun.*, 2009, **180**, 2175–2196.
- 33 J. Mariño-Guiu, A. M. Escatllar and S. T. Bromley, How does temperature affect the infrared vibrational spectra of nanosized silicate dust?, *ACS Earth Space Chem.*, 2021, **5**, 812–823.
- 34 J. Mariño-Guiu, B.-A. Ghejan, T. M. Bernhardt, J. M. Bakker, S. M. Lang and S. T. Bromley, *ACS Earth Space Chem.*, 2022, **6**(10), 2465–2470.
- 35 A. L. Mattioda, D. M. Hudgins, C. Boersma, A. Ricca, E. Peeters, J. Cami, F. Sánchez de Armas, G. Puerta Saborido, C. W. J. Bauschlicher and L. J. Allamandola, The Nasa Ames Psh Ir Spectroscopic Database: The Laboratory Spectra, *Astrophys. J., Suppl. Ser.*, 2020, **251**(22).

- 36 C. Boersma, C. W. Bauschlicher Jr, A. Ricca, A. L. Mattioda, J. Cami, E. Peeters, F. Sánchez de Armas, G. Puerta Saborido, D. M. Hudgins and L. J. Allamandola, The Nasa Ames Pah Ir Spectroscopic Database Version 2.00: Updated Content, Website And On/Offline Tools, *Astrophys. J. Suppl.*, 2014, **211**(1), 8.
- 37 <https://www.astrochem.org/pahdb/>.
- 38 J. S. Mathis, W. Ruml and K. H. Nordsieck, The size distribution of interstellar grains, *Astrophys. J.*, 1977, **217**, 425.
- 39 B. T. Draine and A. Li, Infrared Emission from Interstellar Dust. I. Stochastic Heating of Small Grains, *Astrophys. J.*, 2001, **551**, 807–824.
- 40 C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, New York, 1983.
- 41 A. Tielens, *The Physics and Chemistry of the Interstellar Medium*, Cambridge University Press, Cambridge, 2005.
- 42 R. C. Bohlin, B. D. Savage and J. F. Drake, A survey of interstellar H I from L-alpha absorption measurements. II, *Astrophys. J.*, 1978, **224**, 132–142.
- 43 J. Wilms, A. Allen and R. McCray, On the Absorption of X-Rays in the Interstellar Medium, *Astrophys. J.*, 2000, **542**, 914–924.
- 44 E. B. Jenkins, A Unified Representation of Gas-Phase Element Depletions in the Interstellar Medium, *Astrophys. J.*, 2009, **700**, 1299–1348.
- 45 Spanish virtual observatory, <https://svo2.cab.inta-csic.es/theory/newov2/index.php>.
- 46 F. Allard, D. Homeier and B. Freytag, *ASP Conference Series*, 2011, vol. 448, p. 91.
- 47 C. Jäger, J. Dorschner, H. Mutschke, T. Posch and T. Henning, Steps toward interstellar silicate mineralogy. VII. Spectral properties and crystallization behaviour of magnesium silicates produced by the sol-gel method, *Astron. Astrophys.*, 2003, **408**, 193–204.
- 48 <https://jwst-docs.stsci.edu/jwst-mid-infrared-instrument/miri-observing-modes/miri-medium-resolution-spectroscopy>.
- 49 K. M. Pontoppidan, T. E. Pickering, V. G. Laidler, *et al.*, *Proc. SPIE 9910, Observatory Operations: Strategies, Processes, and Systems VI*, 2016, p. 991016.
- 50 <https://jwst.etc.stsci.edu/>.
- 51 J. E. Chiar and A. G. G. M. Tielens, Pixie Dust: The Silicate Features in the Diffuse Interstellar Medium, *Astrophys. J.*, 2006, **637**, 774–785.
- 52 <https://www.astro.physik.uni-potsdam.de/%7Ewrh/PoWR/wc/>
- 53 S. T. Zeegers, Dust absorption and scattering in the silicon K-edge, *Astron. Astrophys.*, 2019, **627**, A16.
- 54 D. Rogantini, Magnesium and silicon in interstellar dust: X-ray overview, *Astron. Astrophys.*, 2020, **641**, A149.
- 55 I. Psaradaki, Oxygen and iron in interstellar dust: an X-ray investigation, *Astron. Astrophys.*, 2023, **670**, A30.
- 56 S. Fogerty, W. Forrest, D. M. Watson, B. A. Sargent and I. Koch, Silicate Composition of the Interstellar Medium, *Astrophys. J.*, 2016, **830**, 71.
- 57 J. M. van Breemen, The 9.7 and 18 μm silicate absorption profiles towards diffuse and molecular cloud lines-of-sight, *Astron. Astrophys.*, 2011, **526**, A152.
- 58 S. Zhukovska, C. Dobbs, E. B. Jenkins and R. S. Klessen, Modeling Dust Evolution in Galaxies with a Multiphase, Inhomogeneous ISM, *Astrophys. J.*, 2016, **831**, 147.
- 59 R. Lallement, Three-dimensional maps of interstellar dust in the Local Arm: using Gaia, 2MASS, and APOGEE-DR14, *Astron. Astrophys.*, 2018, **616**, A132.

CHAPTER 8

Cluster Beam Study of $(\text{MgSiO}_3)^+$ Based Monomeric Silicate Species and Their Interactions with Oxygen: Implications for Interstellar Astrochemistry

8.1 Introduction

Highly energetic processes acting on bulk silicate grains in the ISM are likely to create a large population of small nanosilicate grains¹⁻³, as discussed in previous chapters. All the work presented so far to assess the potential observability of these small grains in the IR has focused on modelling neutral nanosilicates. However, in the diffuse ISM, where photoelectric electron ejection can dominate over recombination in very small grains, nanosilicates, if present, are quite likely to be positively ionized^{4,5}. The presence of positively charged nanosilicates is also believed to enhance their role as seeds for nucleation through electrostatic focusing^{6,7}.

The analysis of the calculated IR vibrational modes presented so far in this thesis has been tested for accuracy against high-level quantum chemical calculations⁸ (see Chapter 3). However, a more direct comparison with the IR spectra of experimentally produced nanosilicates would be ideal to fully assess the accuracy of our computational modelling.

The experimental production of small nanoclusters via cluster beam experiments is a well established field. A typical technique to characterize the produced particles involves obtaining, on the fly, the IR spectra of the produced particles and determining their chemical composition by mass spectrometry. Afterwards, computational modelling is employed to obtain the lowest energy isomers of a given chemical composition and to compute their corresponding IR spectra, enabling the full characterization of the clusters. This methodology has been successfully applied in the past to characterize various inorganic nanoclusters⁹⁻¹¹. Moreover, it also allows computational modelling researchers to assess the accuracy of their models by directly comparing theoretical and experimental IR spectra.

In the present work the experimental synthesis of small cationic nanosilicates has been achieved using cluster beam experiments. The experimental set-up aimed to mimic silicate dust processing conditions by using laser ablation of a solid Si/Mg source material to produce thermally excited Mg and Si atoms/cations in the presence of oxygen. These species condense afterwards into small cationic clusters through collisional cooling with He. The produced nanoclusters were characterized by a combination of mass spectrometry and infrared multiple-photon dissociation (IR-MPD) recorded using the Free Electron Laser for Intra Cavity Experiments (FELICE).

The author's contribution to this collaborative work consisted of obtaining low energy candidate cluster isomers with the appropriate chemical composition using the MCBH global optimization algorithm. A selection of these isomers was subsequently optimized at DFT level and their vibrational frequencies computed employing the harmonic approximation. Finally, the author also participated in the analysis of the computed vibrational modes to understand the origin of the observed bands and in the comparison between the modelled and the experimental spectra.

8.2 Results

The production of silicate clusters was experimentally achieved through laser ablation of a binary Mg₂Si target in the presence of oxygen. The resulting clusters were characterized by a combination of mass spectrometry with isotopic labeling experiments (using ¹⁶O₂ and ¹⁸O₂) and IR-MPD spectroscopy. While the detailed experimental procedure lies beyond the scope of this thesis, further information can be found in the following research paper and in Appendix C. The most relevant result from the experimental point of view is the detection of various Mg_xSi_yO_z⁺ clusters with MgSiO₉⁺ having the most intense signal in the mass spectrum.

The IR-MPD spectrum of this MgSiO₉⁺ species provides valuable insights into the interaction between the nanosilicate and the oxygen molecules. Two bands observed in the 1500 cm⁻¹ region (see Appendix C) are characteristic of the O–O stretching mode of weakly bound O₂ molecules. The double peak structure indicates either the presence of an isomer with two differently bound oxygen molecules or the presence of two isomers with different bound oxygen molecules. The IR-MPD spectra of MgSi¹⁶O₉⁺ and MgSi¹⁸O₉⁺ are shown in the top panels of Figure 1.

To further characterize the silicate core formed in the experiment, low-energy MgSiO₉⁺ isomers were obtained using MCBH global optimization searches, considering the presence of at least one oxygen molecule bound to the silicate core. Previous studies have predicted that the neutral pyroxene monomer (MgSiO₃) exhibits a rhombus-like MgSiO₂ structure, with the remaining oxygen bound to the silicon atom¹². Based on this information we considered that the MgSiO₉⁺ would consist of a pyroxenic monomer core with weakly attached oxygen molecules. Some of the lower energy isomers found in these searches follow this idea (see isomers (1,1,9)-b and (1,1,9)-c in Figure 1).

However, we found that the lowest energy isomer silicate core exhibits a different silicate core, featuring an O₃ moiety forming a ring structure with the Si atom rather than a terminal O bound to Si (see isomers (1,1,9)-a and (1,1,9)-d in Figure 1). The remaining oxygen molecules weakly interact with the silicate core.

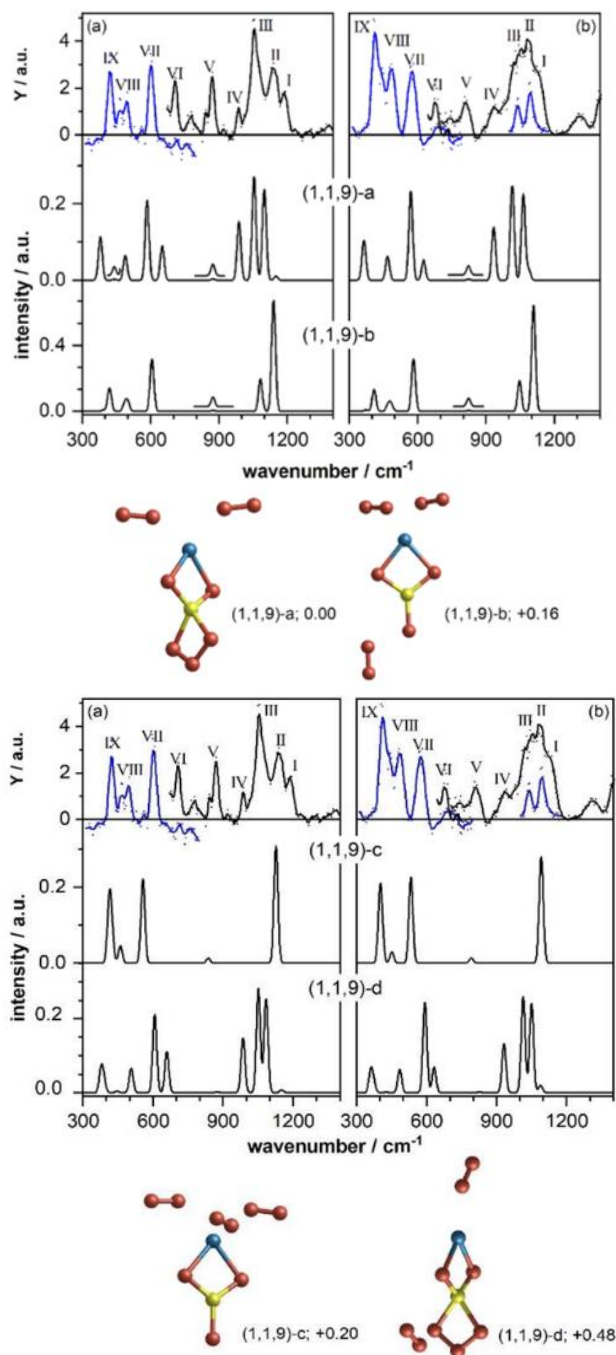


Figure 1: Top panels: IR-MPD spectra of $\text{MgSi}_{16}\text{O}_9^+$ (a) and $\text{MgSi}_{18}\text{O}_9^+$ (b). Lower panels: calculated harmonic DFT spectra of the four lowest energy isomers, with their structures shown below as well as their relative energies in eV. Labels (1,1,9) correspond to the nomenclature (x,y,z) for $\text{Mg}_x\text{Si}_y\text{O}_z^+$. Mg, Si and O atoms are depicted as blue, yellow and red spheres respectively.

Although the O_3 moiety resembles free singlet ozone, DFT structural and electronic analyses reveal some differences (see Figure 2) indicating a strong interaction between the O_3 and the silicate. This interaction is further supported by a binding energy of 4.3 eV for the O_3 interacting with MgSiO_2^+ .

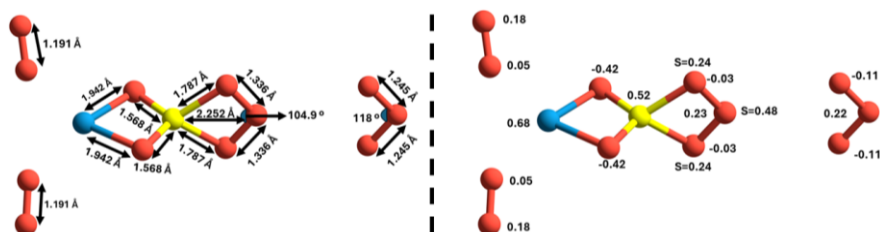


Figure 2: Left: Structure comparison between MgSiO_9^+ and free O_3 . Right: atomically partitioned charge population comparison between MgSiO_9^+ and free O_3 . Atomically partitioned spin populations (S) on the oxygen atoms of the O_3 moiety are also provided. Mg, Si and O atoms are depicted as blue, yellow and red spheres respectively.

All the spectra presented in Figure 1 are consistent with the IR-MPD spectra, as every computed frequency has a corresponding band in the IR-MPD spectrum. However, not all IR-MPD bands are reproduced in each of the computed spectra. Notably, the computed spectrum of the lowest energy isomer (1,1,9)-a successfully predicts the presence of all IR-MPD bands, although the relative intensities do not all match. The vibrational modes associated with the O_3 moiety correspond to experimental bands I, IV and V (see Table 1, for the complete band assignment). Particularly important is band IV, assigned to the O_3 asymmetric stretch, which is exclusively observed in isomers containing the O_3 moiety. This observation strongly suggests that at least one isomer with this silicate core is formed in the experiment. Additionally, the isomers (1,1,9)-b and (1,1,9)-c cannot be ruled out due to their relatively low energies and the presence of their computed signals in the experimental spectrum.

Experimental band	Experimental frequencies (cm^{-1})	(1,1,9)-a calculated frequencies (cm^{-1})	Vibrational mode ^(a)
I	1185	1149	O ₃ symmetric stretch
II	1137	1098	OSiO (of MgSiO ₂ ring) asymmetric stretch
III	1060	1053	OSiO (of MgSiO ₂ ring) symmetric stretch
IV	987	987	O ₃ asymmetric stretch
V	870	872	O ₃ bending
VI	706	651	OSiO (of MgSiO ₂ ring) bending
VII	602	585	OMgO symmetric stretch
VIII	493	489	OMgO asymmetric stretch
Shoulder of VIII	468	441	OSiO (Of SiO ₃ ring) asymmetric stretch
IX	423	380 ^(b)	MgSiO ₂ out of plane bending / MgSiO ₂ -SiO ₃ symmetric stretch

Table 1: Frequencies of $\text{MgSi}^{16}\text{O}_9^+$ IR-MPD spectrum bands, calculated frequencies for isomer (1,1,9)-a, and their vibrational mode description. ^(a) Contribution of the most prominent motions. ^(b) two modes with almost the same frequency.

Another intense peak observed in the mass spectrum corresponds to $\text{Mg}_2\text{SiO}_9^+$. The IR-MPD spectrum shows six well resolved bands, with $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$ displaying two additional signals (see Figure 3).

The core silicate structure is unlikely to adopt an olivine-like cluster due to the odd number of oxygen atoms. The olivine monomer has been previously reported to adopt a Mg_2SiO_3 ring structure with the fourth oxygen terminally bound to Si¹². This suggests that the core of $\text{Mg}_2\text{SiO}_9^+$ might adopt a similar ring structure. However, the lowest energy isomer found has the same pyroxenic monomer core as MgSiO_9^+ with an additional Mg bound to the terminal O.

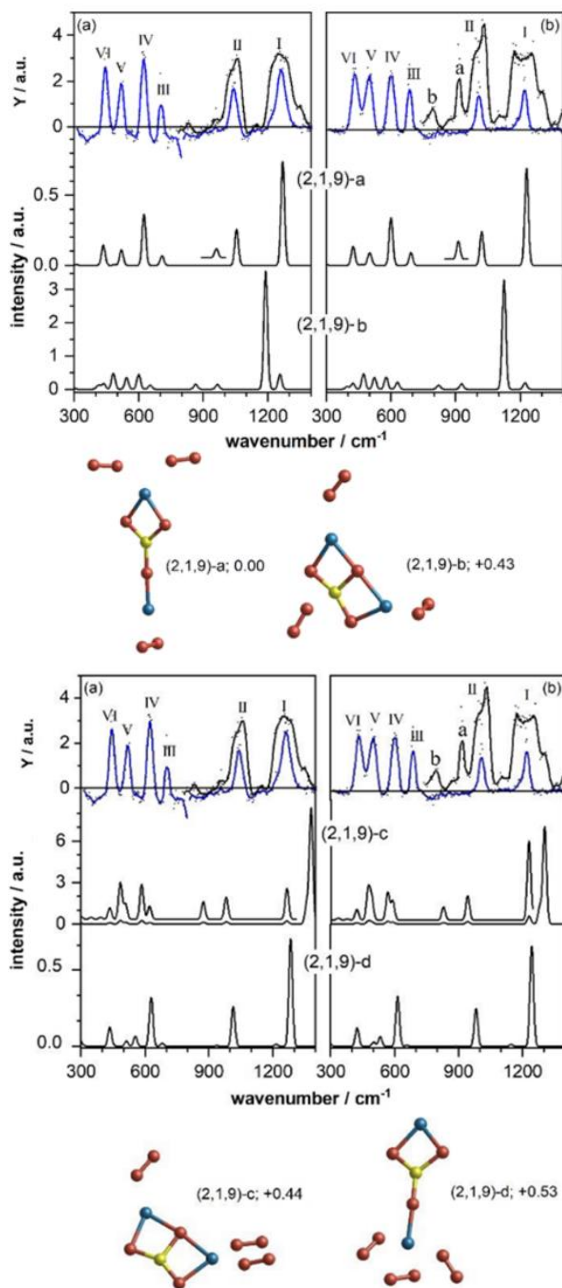


Figure 3: Top panels: IR-MPD spectra of $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ (a) and $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$ (b). Lower panels: DFT-calculated harmonic spectra of the four lowest energy isomers, with their structures shown below as well as their relative energies in eV. Labels (2,1,9) correspond to the nomenclature (x,y,z) for $\text{Mg}_x\text{Si}_y\text{O}_z^+$. Mg, Si and O atoms are depicted as blue, yellow and red spheres respectively.

Experimental band	Experimental frequencies (cm^{-1})	(1,1,9)-a calculated frequencies (cm^{-1})	Vibrational mode ^(a)
I	1261	1268	Si-O stretch
II	1041	1054	OSiO (of MgSiO_2 ring) asymmetric stretch
III	704	780	OSiO (of MgSiO_2 ring) + Mg-O ₂ symmetric stretch
IV	624	624	OMgO (of MgSiO_2 ring) + Mg-O ₂ symmetric stretch
V	518	521	OMgO (of MgSiO_2 ring) asymmetric stretch
VI	445	435	MgSiO_2 out of plane bend
a		960	OSiO (of MgSiO_2 ring) symmetric stretch

Table 2: Frequencies of $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ IR-MPD spectrum bands, calculated frequencies for isomer (1,1,9)-a, and their vibrational mode description. ^(a) Contribution of the most prominent motions.

8.3 Conclusions

These findings, combined with the additional data and analysis provided in the accompanying research article, support the following conclusions:

- 1- Small cationic silicate clusters have been produced through cluster beam experiments for the first time. The two most abundant clusters (MgSiO₉⁺ and Mg₂SiO₉⁺) have been characterized by a combination of IR-MPD spectroscopy and DFT calculations
- 2- The lowest energy isomers of both analyzed clusters exhibit a pyroxenic monomer-based (MgSiO₃⁺) core, which interacts strongly with oxygen molecules.
- 3- For the MgSiO₉⁺ cluster, the formation of an ozone-like unit bonded to the monomeric core is obtained as the most stable isomer. The presence of this bound O₃ moiety is essential to reproduce the experimental band IV.
- 4- The other low energy MgSiO₉⁺ isomers considered could also be formed in the experiment as their computed vibrational frequencies align with portions of the experimental spectrum.
- 5- In Mg₂SiO₉⁺ clusters, no low-energy structures containing an O₃ moiety are found. Instead, the remaining oxygen molecules can be either relatively weakly bound to the cationic core, or interact more strongly as superoxide-like species.
- 6- The computed spectrum of the lowest energy Mg₂Si¹⁶O₉⁺ isomer is in excellent agreement with the experiment, but it fails to reproduce some of the experimental bands obtained for Mg₂Si¹⁸O₉⁺. Higher energy isomers are unlikely to be formed, as vibrations ~1200 cm⁻¹ don't have an experimental counterpart band.

- 7- The strong capacity of these cationic species to adsorb oxygen, in contrast to bulk silicates, could contribute to solving the long-standing puzzle of oxygen depletion in the ISM ¹³ (see accompanying paper).
- 8- The binding of a Mg atom to the MgSiO_3 monomer to form $\text{Mg}_2\text{SiO}_9^+$ cluster can be considered as the initial step in silicate growth from a monomeric seed cluster, indicating the feasibility of this process in the ISM (see accompanying paper).

8.4 References

- ¹ Li, A. and Draine, B. T. On ultrasmall silicate grains in the diffuse interstellar medium. *The Astrophysical Journal*. **2001**, 550(2), L213.
- ² Jones, A. P.; Nuth, J. A., III Dust destruction in the ISM: a reevaluation of dust lifetimes. *Astron. Astrophys.* **2011**, 530, A44
- ³ Jones, A. P.; Tielens, A. G. G. M.; Hollenbach, D. J. Grain shattering in shocks: The interstellar grain size distribution. *Astrophysical Journal*. **1996**, 469, 740.
- ⁴ Weingartner, J. C. and Draine, B. T. Photoelectric emission from interstellar dust: Grain charging and gas heating. *The Astrophysical Journal Supplement Series*. **2001**, 134(2), 263.
- ⁵ Ibáñez-Mejía, J. C.; Walch, S.; Ivlev, A. V.; Clarke, S.; Caselli, P. and Joshi, P. R. Dust charge distribution in the interstellar medium. *Monthly Notices of the Royal Astronomical Society*. **2019**, 485(1), 1220-1247.
- ⁶ Zhukovska, S.; Henning, T. and Dobbs, C. Iron and silicate dust growth in the galactic interstellar medium: clues from element depletions. *The Astrophysical Journal*. **2018**, 857(2), 94.
- ⁷ Zhukovska, S.; Dobbs, C.; Jenkins, E. B. and Klessen, R. S. Modeling dust evolution in galaxies with a multiphase, inhomogeneous ISM. *The Astrophysical Journal*. **2016**, 831(2), 147.
- ⁸ Valencia, E. M.; Worth, C. J.; Fortenberry, R. C. Enstatite (MgSiO_3) and forsterite (Mg_2SiO_4) monomers and dimers: highly detectable infrared and radioastronomical molecular building blocks. *Mon. Not. R. Astron. Soc.* **2020**, 492, 276–282.
- ⁹ Haertelt, M.; Fielicke, A.; Meijer, G.; Kwapien, K.; Sierka, M. and Sauer, J. Structure determination of neutral MgO clusters—hexagonal nanotubes and cages. *Physical Chemistry Chemical Physics*. **2012**, 14(8), 2849-2856.
- ¹⁰ Asmis, K. R. and Sauer, J. Mass-selective vibrational spectroscopy of vanadium oxide cluster ions. *Mass spectrometry reviews*. **2007**, 26(4), 542-562.

- ¹¹ Fielicke, A.; Meijer, G. and Von Helden, G. Infrared spectroscopy of niobium oxide cluster cations in a molecular beam: identifying the cluster structures. *Journal of the American Chemical Society*. **2003**, 125(12) 3659-3667.
- ¹² Escatllar, A. M.; Lazaukas, T.; Woodley, S. M.; Bromley, S. T. Structure and Properties of Nanosilicates with Olivine (Mg₂SiO₄)_N and Pyroxene (MgSiO₃)_N Compositions. *ACS Earth Sp. Chem*. **2019**, 3, 2390–2403.
- ¹³ Whittet, D. C. B. Oxygen Depletion in the Interstellar Medium: Implications for Grain Models and the Distribution of Elemental Oxygen. *The Astrophysical Journal*. **2010**, 710, 1009–1016.

Cluster Beam Study of $(\text{MgSiO}_3)^+$ -Based Monomeric Silicate Species and Their Interaction with Oxygen: Implications for Interstellar Astrochemistry

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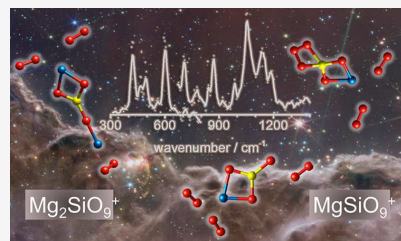
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ABSTRACT: Silicates are ubiquitously found as small dust grains throughout the universe. These particles are frequently subject to high-energy processes and subsequent condensation in the interstellar medium (ISM), where they are broken up into many ultrasmall silicate fragments. These abundant molecular-sized silicates likely play an important role in astrochemistry. By approximately mimicking silicate dust grain processing occurring in the diffuse ISM by ablation/cooling of a Mg/Si source material in the presence of O_2 , we observed the creation of stable clusters based on discrete pyroxene monomers $(\text{MgSiO}_3)^+$, which traditionally have only been considered possible as constituents of bulk silicate materials. Our study suggests that such pyroxene monomer-based clusters could be highly abundant in the ISM from the processing of larger silicate dust grains. A detailed analysis, by infrared multiple-photon dissociation (IR-MPD) spectroscopy and density functional theory (DFT) calculations, reveals the structures and properties of these monomeric silicate species. We find that the clusters interact strongly with oxygen, with some stable cluster isomers having a silicate monomeric core bound to an ozone-like moiety. The general high tendency of these monomeric silicate species to strongly adsorb O_2 molecules also suggests that they could be relevant to the observed and unexplained depletion of oxygen in the ISM. We further find clusters where a Mg atom is bound to the MgSiO_3 monomer core. These species can be considered as the simplest initial step in monomer-initiated nucleation, indicating that small ionized pyroxenic clusters could also assist in the reformation of larger silicate dust grains in the ISM.

KEYWORDS: magnesium silicates, interstellar dust, pyroxene monomer, gas phase clusters, infrared spectroscopy, DFT calculations, oxygen depletion, cosmic dust formation



1. INTRODUCTION

Silicates constitute the main solid components of the universe. Terrestrially, silicates make up over 90% of the Earth's crust and upper mantle and are also commonly found in rocky bodies throughout the Solar system and beyond. The formation of most silicates is thought to occur during high-temperature nucleation processes around dying stars,^{1,2} after which, they are ejected into the cold interstellar medium (ISM) as small dust grains. Generally, cosmic dust is thought to be hugely important for providing surface sites for astrochemical reactions, especially, but not only, when grains arrive in relatively denser and protected regions of the ISM.^{3,4} In the diffuse ISM, the nascent grains are subject to sporadic energetic processing by supernovae shockwaves, high-energy cosmic rays, and strong UV radiation, which lead to sputtering, shattering, and ionization before cooling again.^{5,6} Dust grain processing in the ISM is likely to create a huge population of nanosized silicate grains,⁷ which could be astrochemically relevant for formation/dissociation of H_2 ^{8,9} and water molecules,^{10,11} and are a likely candidate for the source of

the ubiquitous anomalous microwave emission.^{12–14} Silicate dust is mainly thought to be Mg-rich and of olivine (Mg_2SiO_4) or pyroxene (MgSiO_3) composition¹⁵ and originally more olivinic when first formed.¹⁶ However, sputtering in the diffuse ISM leads to depletion of Mg cations,^{17,18} tending to relatively increase the fraction of pyroxenic dust.¹⁹ Due to the dominance of photoelectric electron ejection over recombination in very small grains in the diffuse ISM, nanosilicates are also likely to be positively ionized,²⁰ which could enhance their role as seed species for nucleation.²¹

Here, we use laser ablation of a solid Si/Mg source material to produce thermally excited Mg and Si atomic/cationic species in the presence of O_2 , which then condense into small,

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ionized silicate clusters at lower temperature by collisional cooling with helium. In this way, we approximately mimic silicate dust grain processing conditions in the ISM. Our study identifies the detailed structures and infrared spectral characteristics of the produced cationic silicate clusters by comparing experimental infrared multiple-photon dissociation (IR-MPD) spectra with accurate quantum chemical calculations. We mainly focus on two distinct clusters, which we structurally determine to be based on the same cationic pyroxene monomer, MgSiO_3^+ .

Studies of silicate cosmic dust nucleation have traditionally assumed that silicate monomers are only conceptually valid within bulk silicates and that they do not exist as stable discrete species.²² This assumption is based on considerations of molecular chemical stability in high-temperature ($\text{SiO}/\text{Mg}/\text{H}_2\text{O}$)-based circumstellar silicate nucleation.^{1,2} Such a scenario is quite different from those of the ISM, where nanosilicates formed from dust processing events would be quickly cooled. Our work shows that cationic pyroxene monomers are structurally robust individual clusters that are readily produced in an ablation/cooling process. We further confirm that these species strongly interact with both oxygen and metal atoms/ions and thus could be chemically important species in astronomical environments.

2. RESULTS AND DISCUSSION

2.1. IR-MPD Spectroscopy and Structure of MgSiO_9^+

Cationic magnesium silicate clusters were produced by pulsed laser ablation of a binary Mg_2Si target in the presence of a 1% O_2/He gas mixture that is subsequently expanded into vacuum. Mass spectrometric characterization of the formed clusters showed predominantly oxygen-rich clusters, $\text{Mg}_x\text{Si}_y\text{O}_z^+$ with $z > x + y$. Using isotopic labeling experiments with $^{16}\text{O}_2$ and $^{18}\text{O}_2$ and simulated isotopic distributions based on the natural abundance of Mg and Si, a series of magnesium oxides $\text{MgO}_{6,8,10}^+$ and $\text{Mg}_2\text{O}_{7,9}^+$ as well as the magnesium silicates $\text{MgSiO}_{5,7,9,11}^+$ and $\text{Mg}_2\text{SiO}_{7,9,11}^+$ were identified. Interestingly, no pure silicon oxide clusters Si_yO_z^+ were observed, potentially due to the high magnesium content of the target (details on the experiment, mass spectra, and their analysis are given in Section S1).

One of the most intense signals in the mass spectrum is observed at mass 196 amu, corresponding to $\text{MgSi}^{16}\text{O}_9^+$ (cf. Section S2.1). Its infrared multiple-photon dissociation (IR-MPD) spectrum, recorded using the Free Electron Laser for Intra Cavity Experiments (FELICE),^{23,24} is shown in Figure 1a. The experimental spectrum shows nine bands in the 300–1400 cm^{-1} spectral region (labeled I–IX in Figure 1a, black spectrum). The IR-MPD spectrum for its $\text{MgSi}^{18}\text{O}_9^+$ isotopologue (cf. Figure 1b) is very similar, although here bands I–III are less resolved. When irradiating this species at lower laser intensity, two well-separated bands remain (blue spectrum). Further bands observed are a doublet at 1585/1515 cm^{-1} ($\text{MgSi}^{16}\text{O}_9^+$) and 1490/1430 cm^{-1} ($\text{MgSi}^{18}\text{O}_9^+$), respectively, and one between 1900 and 2000 cm^{-1} (cf. Figure S7). The doublet is characteristic for the O–O stretch motion of weakly bound and rather unperturbed O_2 units (compared to 1580 cm^{-1} for free $^{16}\text{O}_2$),²⁵ whereas the higher-frequency band is most likely a combination band. For clarity of comparison between the experimental and calculated spectra for the silicate cluster bands, we focus on the 300–1400 cm^{-1} spectral region in Figure 1.

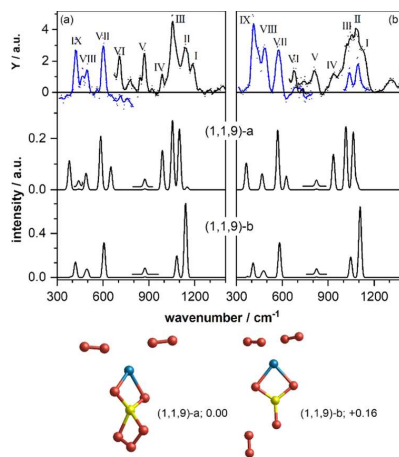


Figure 1. Top panels: IR-MPD spectra of (a) $\text{MgSi}^{16}\text{O}_9^+$ and (b) $\text{MgSi}^{18}\text{O}_9^+$. The dots represent the average of typically four to five spectra, and the solid lines represent a five-point average. The spectra in blue have been obtained at reduced IR macropulse intensity. Lower panels: calculated harmonic DFT spectra for the low-energy isomers (1,1,9)-a (middle panel) and (1,1,9)-b (bottom panel) with their respective structures shown below (relative energies in eV). The insets in the calculated spectra are magnified by a factor of 10. The labels (1,1,9) correspond to the nomenclature (x,y,z) for $\text{Mg}_x\text{Si}_y\text{O}_z^+$. Mg, Si, and O atoms are depicted as blue, yellow, and red spheres, respectively.

Previous calculations of neutral pyroxene (MgSiO_3)_N clusters predicted the monomer ($N = 1$) to exhibit a rhombus-like MgSiO_2 structure with the third oxygen atom terminally bound to the Si atom.²⁶ The observation of the O–O stretch doublets in our spectra suggests that at least two oxygen atoms are bound as O_2 molecules, but more could be possible. Thus, it seems reasonable to consider for MgSiO_9^+ structures containing a pyroxene (MgSiO_3)-like core with three additional weakly bound oxygen molecules. Through using global optimization structural searches and density functional theory (DFT)-based calculations, such cluster cores were indeed found to be most energetically stable for MgSiO_3^+ (see Section S1.3 for computational methodology details), in which the unpaired spin is located on the terminal oxygen (cf. Figure S12). The relatively short Si–O bond length (1.57 Å) associated with this terminal silanone group indicates that it is a strong bond.^{27,28}

However, in the lowest energy isomer found for MgSiO_9^+ , the monomeric MgSiO_3 core does not have a terminal oxygen atom, but possesses an O_3 moiety forming a ring structure with the Si atom (isomer (1,1,9)-a in Figure 1). The remaining O atoms are in the form of two O_2 molecules interacting with the chain-like MgSiO_5 structure. Comparing DFT calculations of the bound O_3 moiety and the free singlet ozone molecule (cf. Figure S13), we see that the former is somewhat more bent ($+14^\circ$) and has a slightly longer O–O bond length ($+0.1$ Å). Like in ozone, the bound O_3 species is polar with the central O atom having a similar positive charge. The terminal O atoms in the O_3 species are less negatively charged than in free ozone because they bind to the Si atom of the pyroxene cluster core (see Figure S13). The two oxygen molecules are neutral and have triplet multiplicity. They are coordinated to the Mg atom

with a 2.16 Å Mg–O distance. Curiously, the O₂ inserted into the O₃ unit and the O₂ molecules interacting with the Mg atom all lead to a very similar energetic stabilization of the final system (~0.6 eV) with respect to the separate relaxed MgSiO₃⁺ cluster core. This energy is typical for a moderate nonbonding interaction, which is in line with the modest interaction between the O₂ molecules and the Mg center. However, the intimate incorporation of O₂ into the O₃ unit clearly arises via the formation of new chemical bonds. The strength of the Si–O₃ bonding is confirmed by considering the cluster core as an ozone molecule interacting with a MgSiO₂⁺ cluster, where the respective binding energy is 4.3 eV. Overall, however, the energetic bonding stabilization in the MgSiO₅⁺ core, with respect to the separated MgSiO₃⁺ cluster and O₂ molecule, is offset by the repulsive interaction between the positively polarized central oxygen of the O₃ unit and the Si cationic center. This repulsion acts to weaken the two Si–O bonds with the O₃ unit, which are ~0.2 Å elongated relative to typical Si–O bonds (see the Supporting Information). We also note that the doublet spin multiplicity of the MgSiO₃⁺ monomer is maintained in the MgSiO₅⁺ core, albeit with some spin delocalization over the O₃ unit.

The calculated vibrational spectrum of isomer (1,1,9)-a, displayed in the second panel of Figure 1, is in good agreement with the IR-MPD spectrum of MgSi¹⁶O₉⁺. Although in the first instance, one is tempted to disqualify the match for lack of an intense counterpart for band I, a closer inspection shows that each of the bands labeled has a predicted counterpart. Bands I and II are well reproduced by calculated bands associated with a symmetric (1149 cm⁻¹) and an asymmetric (987 cm⁻¹) stretch vibration of the O₃. These frequencies are relatively close to the observed values (1135 and 1089 cm⁻¹)²⁹ for free ozone, confirming the “ozonic” character of the O₃ unit. Bands III and IV then correspond to the symmetric (1053 cm⁻¹) and asymmetric (1098 cm⁻¹) stretch motion of the OSiO unit in the MgSiO₂ ring. A low-intensity band at 872 cm⁻¹ corresponding to the O₃ bending motion matches the observed frequency of band V, whereas the modes calculated at 651 cm⁻¹ (OSiO bending mode of the MgSiO₂ ring) and 585 cm⁻¹ (OMgO symmetric stretch) are in agreement with bands VI and VII. Finally, bands VIII and IX are well reproduced by the calculated modes at 489 cm⁻¹ (OMgO asymmetric stretch) and 380 cm⁻¹ (MgSiO₂ out of plane bending + MgSiO₃–SiO₃ stretch), respectively. Band VIII appears to have a low-frequency shoulder, which could reflect the calculated low-intensity mode at 441 cm⁻¹ (asymmetric stretch of the OSiO unit of the SiO₃ ring). This leaves only the small feature between bands V and VI, which cannot be explained by isomer (1,1,9)-a; we speculate that this may be a combination band. It should be mentioned that although all bands labeled I–IX are predicted in the calculated spectrum of isomer 1,1,9-a, their relative intensities are not always reflected well. In particular, bands I and V seem more intense than predicted, whereas the predicted intensity of band IV is higher than observed. This discrepancy is likely due to the multiple-photon absorption process in the experiment, for which intensities may deviate from those in the calculated linear absorption spectra.

Other isomers (1,1,9)-b to -d, each with three O₂ units weakly bound to the MgSiO₃⁺ cluster core, are found to be 0.16 eV, 0.20 eV, and 0.50 eV higher in energy, respectively (cf. Figures 1 and S6). These isomeric structures merely differ by the position of the three O₂ units, which leads to very similar vibrational spectra; therefore, only the spectrum of

isomer (1,1,9)-b is shown in Figure 1 (for others see Figure S6). The calculated spectra of all these isomers are in principle not in disagreement with the IR-MPD spectrum; however, none of them can explain all experimentally observed bands. In particular, none of them properly predicts the simultaneous observation of bands I and IV, which for isomer (1,1,9)-a are diagnostic for the O₃ unit—a group not found in the other isomers. The O₃ bending mode at 872 cm⁻¹ is replaced by a mode containing components from the terminal Si–O stretch motion. Thus, for all isomers, a mode around 870 cm⁻¹ is predicted, although of a different origin. The discrepancy between the observed strength for band I and its predicted intensity for isomer (1,1,9)-a may signal a minority population of isomer (1,1,9)-b.

To confirm the assignment of the experimental spectrum to isomer (1,1,9)-a, the IR-MPD spectrum of the isotopically labeled species MgSi¹⁸O₉⁺ can be considered (cf. Figure 1b). Again, all features of the experimental spectrum are well reproduced by the calculated spectrum of isomer (1,1,9)-a, whereas the other isomers cannot account for all experimentally observed bands. It should be mentioned that the low-intensity mode calculated at 1149 cm⁻¹ red-shifts upon isotopic labeling and overlaps with the neighboring band. Thus, instead of two separated bands, the first band is only slightly broadened on the blue side, which could explain the less resolved experimental features labeled I–III. Again, a (minor) contribution of isomer (1,1,9)-b cannot be ruled out.

Thus, it can be concluded the IR-MPD spectra of MgSi¹⁶O₉⁺ and MgSi¹⁸O₉⁺ are best described by isomer (1,1,9)-a, although small contributions of isomers (1,1,9)-b, (1,1,9)-c, and (1,1,9)-d cannot be completely excluded. Crucial is that the existence of a unique O₃ unit is mandatory to satisfactorily explain all features of the experimental spectrum. The spectra of MgSiO₇⁺ are very similar to those of MgSiO₅⁺, indicating a similar structure of the cluster core with only one of the weakly bound O₂ units removed (cf. Figure S8). The assignment of all calculated modes is summarized in Tables S1 and S2.

2.2. IR-MPD Spectroscopy and Structure of Mg₂SiO₉⁺

A second intense peak in the mass spectrum (*m* = 220 amu) corresponds to Mg₂Si¹⁶O₉⁺ (cf. Figures S1 and S4). The IR-MPD spectrum for this mass (Figure 2a) and its O-18 isotopologue (Figure 2b) shows six well-resolved bands. Bands I and II are again recorded at lower laser intensity (blue spectrum), demonstrating that only band I is significantly broadened under normal irradiation conditions. For Mg₂Si¹⁸O₉⁺, irradiation under full laser intensity results in the appearance of two more bands labeled (a) and (b) in Figure 2b. One could speculate that these bands are also visible in Figure 2a, but the signal-to-noise ratio does not permit a conclusion. Bands I and II for both isotopologues are likely saturated under high-intensity irradiation, resulting in a broadening and, in particular band I for Mg₂Si¹⁸O₉⁺, a flattened-off peak signaling a full depletion of the ion population. As for MgSiO₉⁺, two further bands (not shown here) are observed which can readily be assigned to the O–O stretch of an intact and quite unperturbed O₂ unit and to a combination band (cf. Figure S10). To gain more insight into these features, calculated vibrational spectra must be considered.

The odd number of oxygen atoms in the cluster suggests that this cluster does most likely not have an olivine (Mg₂SiO₄)-like cluster core but one which is one oxygen atom deficient. Structures for neutral olivine nanoclusters

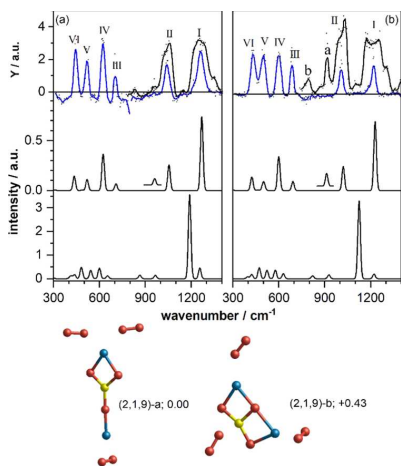


Figure 2. Top panels: IR-MPD spectra of (a) $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ and (b) $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$. The dots represent the average of typically four to five spectra, and the solid lines represent a five-point average. The spectra in blue have been obtained at reduced IR macropulse intensity. Lower panels: calculated harmonic DFT spectra for the low-energy isomers (2,1,9)-a (middle panel) and (2,1,9)-b (lower panel) with the respective structures shown below (relative energies in eV). The insets in the calculated spectra of isomer (2,1,9)-a are magnified by a factor of 1000 (left) and 100 (right), respectively. The labels (2,1,9) correspond to the nomenclature (x,y,z) for $\text{Mg}_x\text{Si}_y\text{O}_z^+$. Mg, Si, and O atoms are depicted as blue, yellow, and red spheres, respectively.

$(\text{Mg}_2\text{SiO}_4)_N$ (i.e., with an even number of oxygen atoms) were reported previously,²⁶ finding for $N = 1$ a Mg_2SiO_3 ring-like structure with the fourth oxygen atom terminally bound to the Si atom. This finding suggests that a similar ring-like structure could also exist for $\text{Mg}_2\text{SiO}_9^+$.

However, the lowest energy structure found for $\text{Mg}_2\text{SiO}_9^+$ consists of the same pyroxenic MgSiO_3 core described above with an additional Mg atom terminally bound to the nonbridging O atom (isomer (2,1,9)-a in Figure 2). The remaining oxygen atoms form three O_2 molecules, with two of them η^1 -bound to the Mg atom of the MgSiO_3 ring and one η^2 -bound to the terminal Mg atom. The former are relatively weakly bound to the $\text{Mg}_2\text{SiO}_3^+$ cluster core (0.47 eV) and can be regarded as distinct oxygen molecules. However, the latter O_2 is strongly bonded to the terminal Mg atom (1.47 eV) with correspondingly short O–Mg distances (1.91 Å; cf. Figure S14). It also has a significantly elongated O–O bond length (1.33 Å) and a small excess negative charge, indicating that it has superoxide character. This character is also reflected in a strongly red-shifted vibrational frequency.

The calculated vibrational spectrum of isomer (2,1,9)-a (cf. Figure 2, second panel) shows six bands, which reproduce all bands labeled I–VI in the IR-MPD spectra of $\text{Mg}_2\text{SiO}_9^+$. Band (a) for $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$ might be explained by a very low intensity mode that becomes visible under 100-fold magnification. In contrast, for $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$, this mode is predicted to be a factor of 10 weaker, which might explain the absence of this band in Figure 2a. Thus, merely band (b) in Figure 2b remains unexplained by isomer (2,1,9)-a. As for the unassigned band of $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ around 750 cm^{-1} (Figure 1a), we speculate that this is a combination band that becomes visible when irradiated at higher laser fluence.

A second structural motif found in the calculations is a T-shaped SiO_3 with the two Mg atoms forming a rectangle (structures (2,1,9)-b in Figure 2 and (2,1,9)-c in Figure S9), which results in significantly different spectra. Promisingly, these isomers show two low-intensity bands between 900 and 1100 cm^{-1} , which may account for bands (a) and (b). However, for isomer (2,1,9)-b, the strong O–O stretch of the η^2 -bound oxygen is red-shifted to 1189 cm^{-1} , and no clear sign for this isomer is found experimentally. The strongest mode of isomer (2,1,9)-c, again the O–O stretch, but now of the η^1 -bound O_2 molecule, is predicted at 1379 cm^{-1} for $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ and 1304 cm^{-1} for $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$, also making it difficult to assign bands (a) and (b) to this species.

In summary, the vibrational spectrum of isomer (2,1,9)-a is in favorable agreement with the IR-MPD spectrum of $\text{Mg}_2\text{SiO}_9^+$ and accounts for all experimentally observed bands except for the low-intensity band (b). The assignment of all calculated modes is summarized in Tables S3 and S4. The IR-MPD spectra for $\text{Mg}_2\text{SiO}_7^+$ (cf. Figure S14) are very similar to those of $\text{Mg}_2\text{SiO}_9^+$, suggesting that this is a very similar cluster structure with one spectator O_2 molecule less.

2.3. Implications for Interstellar Astrochemistry. As discussed above, ISM dust processing is consistent with the production of a high population of ultrasmall cationic pyroxenic species. Our experimental and theoretical infrared spectra could thus guide the possible observational identification of MgSiO_3 -based clusters in the diffuse ISM by the James Webb space telescope (JWST).³⁰ Previously, it has also suggested that pyroxene monomers could be detectable by high resolution microwave observations.^{12,31} If present, we further speculate that pyroxene monomer-based species could be relevant for astrochemical processes in the diffuse ISM.

From observations, it is found that the ISM is significantly depleted in oxygen relative to the expected abundance in typical dust grains (e.g., silicates, ices).³² For the denser regions of the ISM, where ice mantles start to grow on silicate grains, it has been suggested that highly hydroxylated nanosilicates could be one potential oxygen reservoir.¹⁰ For the diffuse ISM where only bare grains persist, our finding that cationic pyroxene monomers readily adsorb oxygen could point to a new reservoir for oxygen. The interaction strength of the oxygen molecules on the surface of amorphous silicates has been measured to be $\sim 0.08\text{ eV}$ and is likely to be too weak to provide a robust reservoir for oxygen in the harsh conditions of the diffuse ISM.³³ However, with our cationic silicate monomer-based clusters, O_2 molecules interact six to seven times more strongly (0.48–0.6 eV). For the (2,1,9)-a isomer of the $\text{Mg}_2\text{SiO}_9^+$ cluster, we show that oxygen can bind even more strongly as superoxide-like O_2 units. In addition to interactions with discrete O_2 units, our lowest energy $\text{Mg}_2\text{SiO}_9^+$ isomer (1,1,9)-a has an oxygen-rich core with a bound O_3 unit and an overall O-to-metal ratio of 4.5 (2.5 in the MgSiO_3 core). Compared with a maximum silicate dust O-to-metal ratio of 1.5 in stoichiometric pyroxene (MgSiO_3), the potentially high abundance of cationic pyroxene monomers could play a significant role in explaining the missing oxygen in the diffuse ISM.

In the $\text{Mg}_2\text{SiO}_9^+$ cluster, a Mg atom is bound to the MgSiO_3 monomer core. This species can be considered as the simplest initial step in silicate grain growth starting from a monomeric seed cluster. Indeed, nucleation of metal atoms/ions onto grain seeds is thought to be one of the most important processes in dust grain (re)formation in the cool ISM.²¹ Our results provide

tentative evidence that small ionized pyroxenic remnants of the dust destruction process could assist in the initial stages of silicate dust rebirth in the ISM.

3. CONCLUSIONS

We produced small silicate clusters from the ablation of a Mg_2Si target in the presence of oxygen and subsequent cooling. We used IR-MPD spectroscopy and DFT calculations to obtain the IR spectra and structures of the species formed. We focus on two abundant clusters (MgSiO_9^+ and $\text{Mg}_2\text{SiO}_9^+$), which are structurally found to be both based on the same MgSiO_3^+ pyroxene monomer core. In both cases, the cluster core is found to be interacting with six oxygen atoms. Four of the oxygen atoms in each case are associated with two oxygen molecules with a moderate nonbonding interaction with the respective cluster core. For MgSiO_9^+ , the further two oxygen atoms form an ozone-like O_3 unit, which is bonded to the cluster core. For the $\text{Mg}_2\text{SiO}_9^+$, the remaining oxygen atoms are bound to the cluster core as a superoxide-like species. The cluster production method used is akin to high-energy processing of silicate dust grains in the ISM. The potential presence of cationic pyroxenic monomers in the ISM, together with their strong interaction species with oxygen and ozone, could have significant implications for, for example, the missing oxygen in the diffuse ISM and the initial stages of the silicate dust rebirth in the ISM. Our IR spectra for these new monomeric pyroxene based species could also be used as a reference for future JWST observations of nanosilicate dust in the ISM.³⁰

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsearthspacechem.2c00186>.

Description of mass assignment, additional IR-MPD spectra, and assignment of experimentally observed bands; computational methodology and calculated structures, atom-partitioned charge, and spin populations of low energy clusters (PDF)

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Notes

The authors declare no competing financial interest.

In this work, no unexpected or unusually high safety hazards were encountered.

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■ REFERENCES

- (1) Gail, H.-P.; Sedlmayr, E. Inorganic dust formation in astrophysical environments. *Faraday Discuss.* **1998**, *109*, 303–319.
- (2) Goumans, T. P. M.; Bromley, S. T. Efficient Nucleation of Stardust Silicates via Heteromolecular Homogeneous Condensation. *Mon. Not. R. Astron. Soc.* **2012**, *420*, 3344–3349.
- (3) Potapov, A.; McCoustra, M. Physics and chemistry on the surface of cosmic dust grains: a laboratory view. *Int. Rev. Phys. Chem.* **2021**, *40*, 299.
- (4) Williams, D. A.; Cecchi-Pestellini, C. *The Chemistry of Cosmic Dust*; Royal Society of Chemistry: Cambridge, 2015.
- (5) Jones, A. P.; Tielens, A. G. G. M.; Hollenbach, D. J. Grain Shattering in Shocks: The Interstellar Grain Size Distribution. *Astrophys. J.* **1996**, *469*, 740.
- (6) Jones, A. P.; Nuth, J. A., III Dust destruction in the ISM: a re-evaluation of dust lifetimes. *Astron. Astrophys.* **2011**, *530*, A44.
- (7) Li, A.; Draine, B. T. On Ultrasmall Silicate Grains in the Diffuse Interstellar Medium. *Astrophys. J.* **2001**, *550*, L213–L217.
- (8) Oueslati, I.; Kerkeni, B.; Bromley, S. T. Trends in the adsorption and reactivity of hydrogen on magnesium silicate nanoclusters. *Phys. Chem. Chem. Phys.* **2015**, *17*, 8951–8963.
- (9) Kerkeni, B.; Bromley, S. T. Competing mechanisms of catalytic H_2 formation and dissociation on ultrasmall silicate nanocluster dust grains. *Mon. Not. R. Astron. Soc.* **2013**, *435*, 1486–1492.
- (10) Goumans, T. P. M.; Bromley, S. T. Hydrogen and oxygen adsorption on a nanosilicate – a quantum chemical study. *Mon. Not. R. Astron. Soc.* **2011**, *414*, 1285–1291.
- (11) Kerkeni, B.; Bacchus-Montabonel, M.-C.; Bromley, S. T. How hydroxylation affects hydrogen adsorption and formation on nanosilicates. *Mol. Astrophys.* **2017**, *7*, 1–8.
- (12) Escatlar, A. M.; Bromley, S. T. Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study. *Astron. Astrophys.* **2020**, *634*, A77.

- (13) Hensley, B. S.; Draine, B. T. Modeling the Anomalous Microwave Emission with Spinning Nanoparticles: No PAHs Required. *Astrophys. J.* **2017**, *836*, 179–192.
- (14) Hoang, T.; Vinh, N.-A.; Lan, N. Q. Spinning Dust Emission from Ultra-Small Silicates: Emissivity and Polarization Spectrum. *Astrophys. J.* **2016**, *824*, 18–28.
- (15) Henning, T. Cosmic Silicates. *Annu. Rev. Astron. Astrophys.* **2010**, *48*, 21.
- (16) Dorschner, J.; Begemann, B.; Henning, Th.; Jäger, C.; Mutschke, H. Steps toward interstellar silicate mineralogy. II. Study of Mg-Fe-silicate glasses of variable composition. *Astron. Astrophys.* **1995**, *300*, S03–S20.
- (17) Keller, L. P.; McKay, D. S. The nature and origin of rims on lunar soil grains. *Geochim. Cosmochim. Acta* **1997**, *61*, 2331.
- (18) Bradley, J. P. Chemically anomalous, preaccretionally irradiated grains in interplanetary dust from comets. *Science* **1994**, *265*, 925.
- (19) Kemper, F.; Vriend, W. J.; Tielens, A. G. G. M. The absence of crystalline silicates in the diffuse interstellar medium. *Astrophys. J.* **2004**, *609*, 826.
- (20) Weingartner, J. C.; Draine, B. T. Photoelectric Emission from Interstellar Dust: Grain Charging and Gas Heating. *Astrophys. J., Suppl. Ser.* **2001**, *134*, 263.
- (21) Zhukovska, S.; Dobbs, C.; Jenkins, E. B.; Klessen, R. S. Modeling Dust Evolution in Galaxies with a Multiphase, Inhomogeneous ISM. *Astrophys. J.* **2016**, *831*, 147.
- (22) Gail, H. P.; Sedlmayr, E. Dust Formation in Stellar Winds. In *Physical Processes in Interstellar Clouds (NATO ASI Series 210)*; Elmegreen, B. G.; Morfill, G. E.; Scholer, M., Eds.; Springer: Netherlands, 1987.
- (23) Bakker, J. M.; Lapoutre, V. J. F.; Redlich, B.; Oomens, J.; Sartakov, B. G.; Fielicke, A.; von Helden, G.; Meijer, G.; van der Meer, A. F. G. Intensity-Resolved Ir Multiple Photon Ionization and Fragmentation of C_{60} . *J. Chem. Phys.* **2010**, *132*, No. 074305.
- (24) Haertelt, M.; Lapoutre, V. J. F.; Bakker, J. M.; Redlich, B.; Harding, D. J.; Fielicke, A.; Meijer, G. Structure Determination of Anionic Metal Clusters Via Infrared Resonance Enhanced Multiple Photon Electron Detachment Spectroscopy. *J. Phys. Chem. Lett.* **2011**, *2*, 1720–1724.
- (25) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.
- (26) Escatlar, A. M.; Lazaukas, T.; Woodley, S. M.; Bromley, S. T. Structure and Properties of Nanosilicates with Olivine (Mg_2SiO_4)_N and Pyroxene ($MgSiO_3$)_N Compositions. *ACS Earth Sp. Chem.* **2019**, *3*, 2390–2403.
- (27) Avakyan, V. G.; Sidorkin, V. F.; Belogolova, E. F.; Guselnikov, S. L.; Guselnikov, L. E. AIM and ELF Electronic Structure/G2 and G3 π -Bond Energy Relationship for Doubly Bonded Silicon Species, H_2SiX ($X = E^{14}H_2, E^{15}H, E^{16}$)¹. *Organometallics* **2006**, *25*, 6007.
- (28) Zwijnenburg, M. A.; Sokol, A. A.; Sousa, C.; Bromley, S. T. The effect of local environment on photoluminescence: A time-dependent density functional theory study of silanone groups on the surface of silica nanostructures. *J. Chem. Phys.* **2009**, *131*, No. 034705.
- (29) Barbe, A.; Secroun, C.; Jouve, P. Infrared spectra of $^{16}O_3$ and $^{18}O_3$: Darling and Dennison resonance and anharmonic potential function of ozone. *J. Mol. Spectrosc.* **1974**, *49*, 171–182.
- (30) Zeegers, S. et al. Illuminating the Dust Properties in the Diffuse ISM with JWST, JWST Proposal. Cycle 1, ID #2183, 2021.
- (31) Valencia, E. M.; Worth, C. J.; Fortenberry, R. C. Enstatite ($MgSiO_3$) and forsterite (Mg_2SiO_4) monomers and dimers: highly detectable infrared and radioastronomical molecular building blocks. *Mon. Not. R. Astron. Soc.* **2020**, *492*, 276–282.
- (32) Whittet, D. C. B. Oxygen Depletion in the Interstellar Medium: Implications for Grain Models and the Distribution of Elemental Oxygen. *Astrophys. J.* **2010**, *710*, 1009–1016.
- (33) Jing, D.; He, J.; Brucato, J. R.; Vidali, G.; Tozzetti, L.; De Sio, A. Formation of Molecular Oxygen and Ozone on Amorphous Silicates. *Astrophys. J.* **2012**, *756*, 98–105.

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CHAPTER 9

Oxygen-rich Anionic Metal Silicate Clusters as Nucleation Seeds for Noctilucent Clouds

9.1 Introduction

The Earth's upper atmosphere is constantly bombarded by dust particles, with approximately 30 tons entering the atmosphere every day^{1,2}. These particles, typically silicate-rich with radii smaller than 250 microns, enter the atmosphere at extremely high velocities, resulting in the ablation of a significant portion of their mass at altitudes between 80 and 105 km¹. The ablated atoms, primarily Si, Mg and Fe, cool through collision with gas molecules and undergo chemical reactions with various atmospheric constituents such as ozone, oxygen and water³. The posterior aggregation of these species leads to the formation of what is known as Meteoric Smoke Particles (MSP). Two primary methods have been employed to observe and analyse MSPs: incoherent scatter radar⁴ and by sounding rocket payloads⁵.

The laboratory production of cationic nanosilicates discussed in Chapter 7 demonstrated the strong interaction of these positively charged particles with O₂ and O₃-like moieties. This suggests that if MSPs present in the upper atmosphere layers are positively charged, they could play a relevant role in atmospheric chemistry, particularly in ozone formation.

However, the abundance of free electrons in Earth's upper mesosphere, generated by ionizing solar radiation at altitudes ~ 90 km, makes the presence of cationic MSPs unlikely. Below 85 km, free electrons are significantly depleted due to their capture by electronegative species⁶, with MSPs acting as a potential electron sink. The detection of anionic MSPs using Faraday cups on sounding rocket payloads⁷ supports this hypothesis, indicating that cationic MSPs are not expected to be present in the ozone layer which lies between 15 and 40 km.

Negatively charged MSPs are of particular interest due to their significant role in atmospheric chemistry. They provide recombination sites for O and H₂ which explain the unexpected formation of water molecules in the mesosphere⁸. Additionally, they can serve as nucleation seeds, potentially participating in the condensation of Noctilucent clouds (NLCs)⁹. NLCs, first observed in 1885,¹⁰ are composed of water ice crystals formed in the upper mesosphere, making them the highest clouds in Earth's atmosphere. The increasing frequency and brightness of NLCs in recent decades have been linked to rising water vapor levels, driven by the anthropogenic-induced increase in methane, that oxidizes in the upper mesosphere, and radiative cooling induced by the increase of greenhouse gases¹¹.

In the present chapter, we present a collaborative work to characterize anionic nanosilicates synthesized in the lab and to explore the potential of these nanosilicates as NLCs nucleation seeds. The experimental synthesis of anionic nanosilicates has been carried out by laser ablation of a Si/Mg target. The resulting generated thermally excited atomic and ionic species are subsequently cooled through collisions, leading to the formation of negatively charged silicate species. The resulting nanoclusters are characterized by mass spectrometry, while their vibrational properties are investigated through the comparison of experimental IR-MPD spectra with those obtained from DFT calculations. Finally, the electron affinities of the generated nanoclusters were also computed to gain insight into their possible formation in the upper mesosphere.

The contributions of the author of the thesis to this collaborative work involved the computational modelling of the small nanosilicate clusters obtained experimentally. This was achieved through global optimisation searches combining MCBH and GOFEE methods. Additionally, the author also computed and analysed the harmonic vibrational modes of the lowest energy isomers, as well as the electronic affinities and binding energies.

9.2 Results

As discussed for cationic nanosilicates (see Chapter 7), the experimental cluster beam methodology is out of the scope of the present thesis and further details can be found in the accompanying research paper and in Appendix D. The simplest synthesized nanosilicate was MgSiO_6^- , but also a series of more complex clusters such as $\text{MgSi}_2\text{O}_8^-$, $\text{MgSi}_2\text{O}_7^-$, $\text{Mg}_2\text{SiO}_6^-$, and $\text{Mg}_2\text{SiO}_7^-$ were obtained. These isomers can be compositionally interpreted as versions of MgSiO_6^- with incorporated SiO_2 , SiO , Mg and MgO respectively. The experimental IR-MPD spectra of all these isomers is presented in Figure 1. The lack of bands above 1400 cm^{-1} , the region of free O_2 vibrations, is a direct indication of the absence of weakly bound O_2 , which is a clear contrast with cationic nanosilicates.

The modelled lowest energy isomer of MgSiO_6^- is formed by a MgSiO_2 silicate core with two superoxide-like O_2 molecules, with a total charge of $\sim -0.5\text{ e}$ in each one. Although the computed spectrum correctly reproduces most of the experimental signals, the presence of an intense band at $\sim 1100\text{ cm}^{-1}$, assigned to the Si-O_2 molecule stretching, rules out its formation in the experiment. Alternatively, an almost isoenergetic isomer (1,1,6)-b is found in which a MgSiO_3 core has an O_3 moiety bounded to Mg atom (see Figure 1). The computed spectrum correctly reproduces all seven experimental bands, albeit with an underestimation in the intensity of band III (SiO_3 symmetric stretch) and band IV (O_3 bending).

The intensity mismatch was found to arise from the inaccurate description of O_3 vibrations by DFT calculations using PBE0 functional. Computing the O_3 vibrational modes using PBE functional (red curves in Figure 1) resulted in a significant improvement of the band III and IV intensities, although with an expected worsening of the description of MgO and SiO modes.

For this reason, we restricted the use of PBE to the relevant O_3 vibrational modes. Using PBE, the O_3 symmetric stretching vibration increases with respect to PBE0 (almost null intensity) and shifts from 1192 to 966 cm^{-1} , matching the experimental band II. Most importantly, the O_3 asymmetric stretching vibration shifts to 956 cm^{-1} to 816 cm^{-1} matching very well with the measured band III. A minor problem with the use of PBE is the larger shift of the O_3 bending mode, from 714 to 653 cm^{-1} worsening the agreement with measured band IV.

The favoured formation of (1,1,6)-b with respect to (1,1,6)-a could potentially be explained by the preferential formation of a $MgSiO_3^-$ core rather than $MgSiO_2^-$, which is supported by the large binding energy of an O atom to the $MgSiO_2^-$ species (~ 8 eV).

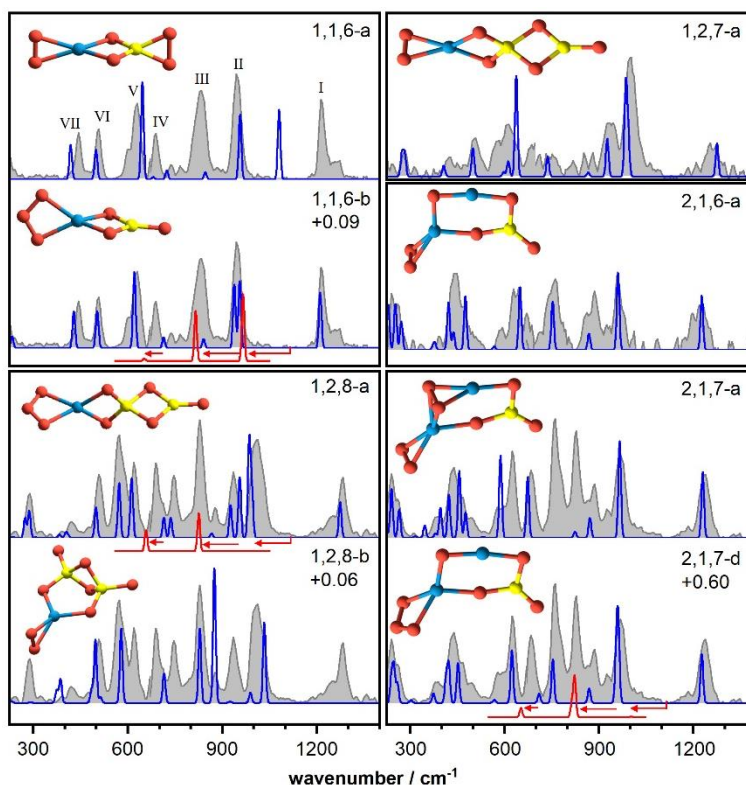


Figure 1: Experimental IR-MPD spectra (grey) of various $Mg_xSi_yO_z^-$ together with the DFT-calculated spectra (in blue; PBE0 functional, relative energies in eV) of the lowest energy isomers. Red curves represent the O_3 vibrational modes computed with the PBE functional. The cluster naming $x,y,z-n$ denotes the elemental composition of $Mg_xSi_yO_z^-$ and $n = a, b, c$ indicates the isomer sorted in order of increasing energy. Mg, Si, and O atoms are depicted as blue, yellow, and red spheres, respectively.

Binding a SiO_2 or a SiO unit to MgSiO_6^- leads to chain-like structures consisting of a MgSiO_2 and a Si_2O_2 ring, as their global minimum isomers (see Figure 1). In the case of $\text{MgSi}_2\text{O}_7^-$ the O_3 moiety is replaced by a superoxo-like O_2 unit while in $\text{MgSi}_2\text{O}_8^-$ this moiety is retained as well as the terminal Si-O bond.

The experimental spectra of these two isomers can be correctly reproduced by our modelled global minima, especially when using PBE to describe the O_3 vibrations in the $\text{MgSi}_2\text{O}_8^-$ isomer. Additionally, an almost isoenergetic $\text{MgSi}_2\text{O}_8^-$ isomer, without the O_3 group can be considered as possibly being formed in the experiment, as all the harmonic signals have their correspondence with experimental bands, although it cannot account for all of them.

On the other hand, if a Mg atom or an MgO unit is bound to the original MgSiO_6^- isomer, one obtains the $\text{Mg}_2\text{SiO}_6^-$ and $\text{Mg}_2\text{SiO}_7^-$ isomers. The lowest energy isomer of $\text{Mg}_2\text{SiO}_6^-$ consists of an $\text{Mg}_2\text{SiO}_3^-$ ring with a terminal oxygen atom on the Si and a superoxide-like O_2 bound to the Mg on the corner of the ring. The computed harmonic spectrum of this isomer is in very good agreement with all the bands observed in the IR-MPD spectrum. The addition of an extra oxygen, to form $\text{Mg}_2\text{SiO}_7^-$, leads to the distortion of the $\text{Mg}_2\text{SiO}_3^-$ ring because of the formation of a bridging O_2 molecule in the ring (see structure 2,1,7-a in Figure 1). The computed frequencies of this isomer agree with most of the experimental bands, but it is not capable of reproducing the band around 760 cm^{-1} , nor the intensity of the 825 cm^{-1} signal, which corresponds to the bridging O_2 stretching mode. The lowest energy isomer that we could find to reproduce this band is found at relatively high energy from the global minimum (+0.60 eV). In this new isomer (2,1,7-d in Figure 1) the superoxo-like O_2 is replaced by an O_3 moiety. The vibrational frequencies of this isomer are in excellent agreement with IR-MPD spectrum if the O_3 modes are computed with PBE functional.

The great agreement of 2,1,7-d isomer made us speculate that it is preferably formed in the experiment, even with its relatively large energy compared with 2,1,7-a isomer. In previous studies it was found that what determines the formation of anionic isomers is not the energetic stability,

but the vertical electron affinities (EAs) of the neutral clusters^{12,13}. The mechanism for this formation consists of the initial formation of neutral species followed by competitive electron attachment, which would favour clusters with high vertical EAs.

The high EAs of other isomers in the present work whose harmonic spectra agree with experiment (see Table 1), supports this type of anion selection mechanism.

Species	EA (vertical)	EA (adiabatic)
MgSiO ₆ (1,1,6-a)	3.53	4.55
MgSiO ₆ (1,1,6-b)	4.35	4.82
MgSi ₂ O ₇ (1,2,7-a)	3.51	5.23
MgSi ₂ O ₈ (1,2,8-a)	4.03	5.20
MgSi ₂ O ₈ (1,2,8-b)	3.66	4.88
Mg ₂ SiO ₆ (2,1,6-a)	3.96	4.48
Mg ₂ SiO ₇ (2,1,7-a)	2.27	4.22
Mg ₂ SiO ₇ (2,1,7-b)	3.78	5.21
Mg ₂ SiO ₇ (2,1,7-d)	3.75	4.44
Cl	4.58	4.58
NO ₃	3.66	3.86
HCO ₃	2.80	3.45

Table 1: Computed EAs (vertical and adiabatic) of a selection of Mg_xSi_yO_z clusters representing the neutral analogues to the anionic structures identified via IR-MPD spectroscopy and DFT calculations. For comparison EAs of highly electronegative species found in the mesosphere are also presented, as well as Fe-containing silicate.

As one can see from Table 1, the neutral analogues of the synthesized anions have very high adiabatic EAs. These are not only larger than the EAs of other species found in the mesosphere (Cl, NO₃ and HCO₃, but also than magnesium and silicon oxide clusters^{14,15} and stoichiometric olivine and pyroxene silicate nanoclusters¹⁶. We attributed these high EAs of the clusters to their high oxidation from superoxo- and O₃-like ligands.

Despite the difference in densities and reaction time scales between the experiments and the upper atmosphere, the formation mechanism of the studied anions is likely to be similar. Even when the thermodynamic minimum is not observed, the proposed mechanism of neutral isomer formation followed by electron attachments is a plausible scenario in the mesosphere.

Models of dust plasma predict that only approximately 6% of MSPs are negatively charged at 80–90 Km⁶. However, these models are sensitive to the charging efficiency of MSPs, which is poorly understood. The modelled clusters in this work, which represent analogues of MSPs, serve as an excellent opportunity to better predict the charging efficiency of MSPs, by modelling the kinetics of electron attachment to neutral clusters.

The details of the kinetic modelling are beyond the scope of present thesis and more details can be found in the accompanying research article draft. The main results extracted from this modelling is that a charged fraction between 0.03–0.18 is derived from our modelled isomers which agrees well with previous estimates of 0.06 highlighting the potential relevance of our clusters in atmospheric chemistry. In particular, these negatively charged silicate clusters are found to possess all the necessary attributes to be good candidate seeds for nucleating ice-based NLCs in the mesosphere.

9.3 Conclusions

These findings, combined with the additional data and analysis provided in the accompanying research article draft, support the following conclusions:

- 1- A series of small anionic nanosilicates have been successfully synthesized through cluster beam experiments and characterized by a combination of mass spectrometry, IR-MPD spectroscopy and DFT calculations.
- 2- Characterization revealed the preferential formation of oxygen-rich clusters ($\text{Mg}_x\text{Si}_y\text{O}_z^-$ with $z > 2(x+y)$). Structural analysis showed that oxygen can be incorporated as radicals, superoxo-like O_2 and O_3 units. Unlike cationic nanosilicates, O_3 units are bound to Mg atoms instead of Si atoms.
- 3- The formation of the nanosilicates in the experiment are selected by the vertical EAs of the neutral counterparts instead of the energetic stability of the resulting anions.
- 4- Generally, there is good agreement between experimental bands and harmonic IR spectra calculated by DFT (when using suitable functionals), confirming the suitability of this methodology to accurately describe the IR spectra of anionic nanosilicate
- 5- Kinetic modelling of electron attachment to neutral clusters reveals a charging efficiency between 3% and 18% depending on the exact cluster used. This is in good agreement with previous estimates required to simulate the MSP fraction in atmospheric measurements.
- 6- The highly oxidized anionic silicates studied in this work exhibit all the necessary chemical, electronic and optical properties to be suitable candidates for being nucleation seeds of NLCs in the upper mesosphere.

9.4 References

- ¹ Plane, J. M. C. Cosmic dust in the earth's atmosphere. *Chem. Soc. Rev.* **41**, 6507-6518 (2012).
- ² Carrillo-Sánchez, J. D.; Gómez-Martín, J. C. G.; Bones, D. L.; Nesvorný, D.; Pokorný, P.; Benna, M.; Flynn, G. J. and Plane, J. M. C. Cosmic dust fluxes in the atmospheres of Earth, Mars, and Venus. *Icarus*. **335**, 113395 (2020)
- ³ Plane, J. M. C.; Feng, W. and Dawkins, E. C. M. The Mesosphere and Metals: Chemistry and Changes. *Chemical Reviews*. **2015**, 115(10) , 4497–4541.
- ⁴ Strelnikova, I.; Rapp, M.; Raizada, S.; and Sulzer, M. Meteor smoke particle properties derived from Arecibo incoherent scatter radar observations. *Geophysical Research Letters*. **2007**, 34(15), L15815.
- ⁵ Hedin, J.; Gumbel, J. and Rapp, M. On the efficiency of rocket-borne particle detection in the mesosphere. *Atmospheric Chemistry and Physics*. **2007**, 7(14) 3701-3711.
- ⁶ Plane, J. M. C.; Saunders, R. W.; Hedin, J.; Stegman, J.; Khaplanov, M.; Gumbel, J.; Lynch, K. A.; Bracikowski, J. P.; Gelinas, L. J.; Friedrich, M.; Blindheim, S.; Gausa, M. and Williams, B. P. A combined rocket-borne and ground-based study of the sodium layer and charged dust in the upper mesosphere. *Journal of Atmospheric and Solar-Terrestrial Physics*. **2014**, **118** 151–160 (2014).
- ⁷ Gelinas, L. J.; Lynch, K. A.; Kelly, M. C.; Collins, R. L.; Widholm, M.; MacDonald, E.; Ulwick, J. and Mace, P. Mesospheric charged dust layer: Implications for neutral chemistry. *Journal of Geophysical Research: Space Physics*. **2005**, 110, A1.
- ⁸ Summers, M. E. and Siskind, D. E. Surface recombination of O and H₂ on meteoric dust as a source of mesospheric water vapor. *Geophysical research letters*. **1999**, 26(13) 1837-1840.
- ⁹ Saunders, R. W. and Plane, J. M. C. A photo-chemical method for the production of olivine nanoparticles as cosmic dust analogues. *Icarus*. **2011**, 212, 373-382.

- ¹⁰ Gadsden, M., Schröder, W. *Noctilucent Clouds* (Springer, New York, **1989**).
- ¹¹ Thomas, G. E.; Olivero, J. J. and Jensen, E. J. Relation between increasing methane and the presence of ice clouds at the mesopause. *Nature*. **1989**, 338(6215), p. 490-492.
- ¹² Kronik, L.; Fromherz, R.; Ko, E.; Ganteför, G. and Chelikowsky, J. R. Highest electron affinity as a predictor of cluster anion structures. *Nature materials* **2002**,1(1), 49-53.
- ¹³ Marom, N.; Kim, M. and Chelikowsky, J. R. Structure selection based on high vertical electron affinity for TiO₂ clusters. *Physical Review Letters*. **2012**,108(10), 106801.
- ¹⁴ Gutowski, M.; Skurski, P.; Li, X. and Wang, L. S. (MgO)_n-(n= 1–5) clusters: Multipole-bound anions and photodetachment spectroscopy. *Physical Review Letters*. **2000**,85(15), 3145.
- ¹⁵ Wang, L.-S.; Wu, H.; Desai, S. R.; Fan, J. and Colson, S. D. A photoelectron spectroscopic study of small silicon oxide clusters: SiO₂, Si₂O₃, and Si₂O₄. *The Journal of Physical Chemistry*. **1996**, 100(21), 8697-8700.
- ¹⁶ Escatllar, A. M. and Bromley, S. T. Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study. *Astronomy & Astrophysics*. **2020**, 634, p. A77.

Oxygen-rich Anionic Metal Silicate Clusters as Nucleation Seeds for Noctilucent Clouds

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Abstract

Meteoroid smoke particles (MSP) resulting from extraterrestrial dust impacting on the upper atmosphere are thought to play an important role in seeding the formation of mesoscopic ice-based noctilucent clouds (NLCs). Although likely to be small silicate-based species, the detailed physicochemical properties of these elusive MSP seeds are unknown. Knowing that ice formation is sensitive to MSP charging efficiency we focus on candidate species which can efficiently capture and retain charge. As in situ MSP characterisation is highly challenging, we mimic the atmospheric MSP formation process using laser ablation and collisional cooling to produce small anionic magnesium silicate clusters as MSP analogues. By detailed characterization using mass spectrometry, infrared multiple photon dissociation spectroscopy and density functional theory calculations, we find that these clusters have unusual oxygen-rich structures with incorporated superoxo-like or ozone-like units. We further show that the corresponding neutral clusters have extraordinarily high adiabatic electron affinities. Kinetic modelling further shows that these clusters have a significant charging efficiencies of 3 - 18%, which is fully in line with estimates required by models to simulate atmospheric measurements. Overall, our highly oxidised anionic silicate clusters exhibit all the necessary chemical, electronic and optical properties to be highly credible candidates for MSP-based NLC nucleation seeds in the upper mesosphere.

Introduction

Noctilucent clouds (NLCs) are a spectacular high-altitude ice-based phenomenon with an earliest recorded observation in 1885.¹ NLCs are the highest clouds in Earth's atmosphere, occurring in the upper mesosphere (~82-85 km). This near space region interacts significantly with incoming radiation and cosmic dust, while also being sensitive to changes in the lower atmosphere. The increased availability of atmospheric water vapour due to the anthropogenic-induced increase in methane (which is oxidized to H₂O in the middle atmosphere), together with radiative cooling induced by increasing greenhouse gases, has been linked to increasing frequency and brightness of NLCs in recent decades.^{2,3,4} The NLC ice mass is predicted to surge in the coming decades, which, due to the resulting increase in absorption of solar radiation, is likely to affect the photochemistry of the upper atmosphere.⁵ For water vapour to condense into ice crystals, suitable seed particles are required.⁶ The detailed nature of NLC condensation seeds is currently unknown, but they are widely thought to be nanosized meteoric smoke particles (MSPs),⁷ that are derived from ablated cosmic dust particles.^{8,9,10} As in situ characterisation of such species is extremely challenging,¹¹ here we employ dedicated cluster beam experiments to mimic the MSP formation process. A systematic evaluation of the structures and properties of the formed clusters reveals that they appear to fulfil the criteria required to be compelling candidate NLC seeds.

The Earth's upper atmosphere is under continual bombardment with around 30 tonnes of dust particles entering the atmosphere every day.^{12,13} These particles are typically silicate-rich with radii < 250 μm , and enter at hyperthermal velocities so that ~30% of the incoming mass ablates between 80 and 105 km altitude.¹² The ablated atoms (mainly Si, Mg and Fe) cool through collisions with gas molecules and then undergo chemical reactions with O₃, O₂, H₂O and CO₂.¹⁴ Subsequent aggregation of these species leads to the formation of MSPs. For MSPs to remain suspended above 80 km for more than a few hours against gravitational settling, they should be smaller than 2 nm in radius.¹⁵ MSPs have been measured as heavy ions by sounding rocket payloads^{16,17} and detected by incoherent scatter radar^{18,19}; they are found to have a typical size range between 0.5 and 2 nm radius, in accordance with models.^{20,21} The production of such MSPs is likely to be common to many planetary bodies which can hold an atmosphere (e.g. Venus, Mars, Titan, exoplanets).²¹

Incoming ionising solar radiation also leads to an abundance of free electrons in Earth's upper mesosphere (70–90 km). Below 85 km the electrons are typically depleted (by over 2 orders of magnitude) with respect to positive ions, due to their capture by strongly electronegative species.^{20,22} MSPs are a potential electron sink and, indeed, negatively-charged MSPs have been detected using Faraday cups on sounding rocket payloads.^{20,23,24,25}

The charging of MSPs would help these small species to overcome the Kelvin effect²⁶ (i.e., increased vapour pressure for particles with a small radius), making them more effective nucleation seeds. Such MSPs have been proposed as providing recombination sites for O and H₂ to explain the unexpected presence of water vapour in the mesosphere.²⁷ Based on detection data, models estimate that around 6% of all MSPs need to be charged at an altitude between 80 and 90 km, where the plasma and MSP densities are similar.²² This implies that some MSPs have very high electron attachment rates, while being resistant to various electron detachment processes.

To mimic the ablation and recondensation formation processes of negatively charged MSPs in a controlled laboratory setting, we use laser ablation of a Si/Mg surface to produce thermally excited atomic/ionic species which we react with a low concentration of gaseous oxygen, all the while collisionally cooling them with helium to form small negatively charged $\text{Mg}_x\text{Si}_y\text{O}_z^-$ clusters. We identify the structures of a range of size-selected $\text{Mg}_x\text{Si}_y\text{O}_z^-$ clusters by comparing experimental infrared multiple photon dissociation (IR-MPD) spectra with those from accurate quantum chemical calculations for candidate structures. Our formed $\text{Mg}_x\text{Si}_y\text{O}_z^-$ species are found to be unexpectedly oxygen-rich (i.e. $z > 2(x+y)$), where some oxygen is present as superoxo-like O₂ or ozone-like O₃ molecules as well as oxygen radicals. Our analysis reveals that the electron affinities (EAs) of the corresponding neutral “over-oxidised” $\text{Mg}_x\text{Si}_y\text{O}_z$ clusters are extremely high (typically > 4.2 eV) indicating an oxidation-induced increase in electronic stability. Based on kinetic considerations of electron attachment/detachment rates, we also show that these high-EA species have a charging efficiency of 3-18%, in good agreement with average values needed by models to simulate atmospheric measurements. Overall, these small, highly oxidized magnesium silicate clusters are thus highly credible candidate NLC nucleation seeds. Incorporation of the properties of such species in atmospheric/climate models should lead to an improved understanding of the chemistry of the upper atmosphere and help clarify the link between NLC formation and climate change.

Results and Discussion

IR-MPD Spectra of Negatively Charged $\text{Mg}_x\text{Si}_y\text{O}_z^-$ Clusters

Anionic magnesium silicate clusters were produced by pulsed laser ablation of a binary Mg_2Si target in the presence of a 1% O_2/He gas mixture and subsequently studied by IR-MPD spectroscopy, quantified in spectra as the depletion yield as a function of wavenumber (see section S1 of the Supporting Information (SI)). In the following we present in detail the spectrum of MgSiO_6^- as the simplest system by comparing it with calculated spectra of several isomeric structures, and subsequently evaluate structure growth by considering spectra of $\text{MgSi}_2\text{O}_8^-$ (SiO_2 added), $\text{MgSi}_2\text{O}_7^-$ (+ SiO), $\text{Mg}_2\text{SiO}_6^-$ (+ Mg), and $\text{Mg}_2\text{SiO}_7^-$ (+ MgO) (Figure 1). Spectra with isotopically labelled ^{18}O , vibrational mode assignment and further isomeric structures can be found in section S2 of the SI.

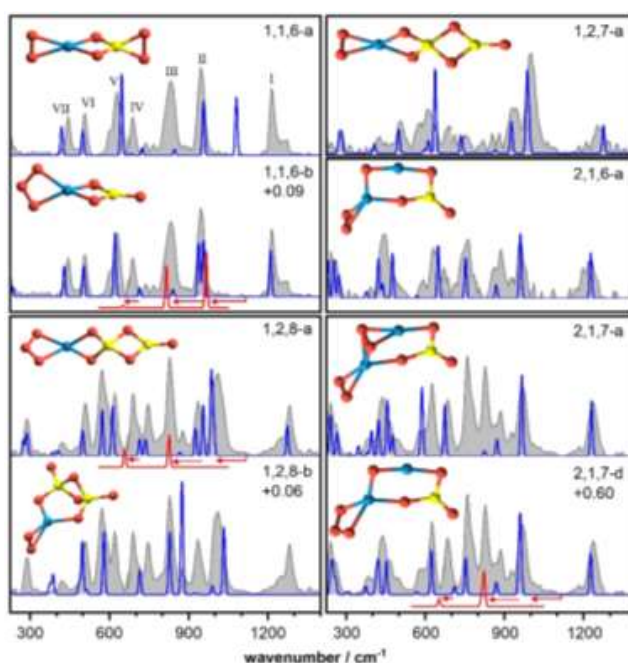


Figure 1: Experimental IR-MPD spectra (in grey) of various $\text{Mg}_x\text{Si}_y\text{O}_z^-$ together with the DFT-calculated spectra (in blue; PBE0 functional, relative energies in eV) of the lowest energy isomers. The red curves represent the O_3 modes of the shown structures obtained with the PBE functional. The IR-MPD spectra were measured in two independent runs and are the average of five ($650\text{--}1800\text{ cm}^{-1}$) and six ($225\text{--}700\text{ cm}^{-1}$) individual spectra, respectively, and a 3-point average of the individual data points. To achieve intensity match of the two spectra, the experimental spectrum in the high wavenumber range was multiplied with a factor of 3.9. The cluster naming $x,y,z\text{-n}$ denotes the elemental composition of $\text{Mg}_x\text{Si}_y\text{O}_z^-$ and $n = a, b, c$ indicates the isomer sorted in order of increasing energy (further isomers can be found in section S2 of the SI). Mg, Si, and O atoms are depicted as blue, yellow, and red spheres, respectively.

The IR-MPD spectrum of MgSiO_6^- shows seven bands (labelled I-VII) in 225 – 1400 cm^{-1} the spectral region. The lack of any bands above 1400 cm^{-1} (Figure S6 of the SI), the vibrational frequency of free oxygen molecules, already indicates a rather strong binding of all oxygen and the absence of any loosely bound O_2 units. This sharply contrasts with what was previously observed for cationic versions of highly oxidized magnesium silicates.²⁸ The calculated lowest energy isomer of MgSiO_6^- (isomer 1,1,6-a in Figure 1) consists of a MgSiO_2^- monomer with two superoxide-like O_2 units (total charge ~ -0.5 e). The computed spectrum does not fully agree with the experimental one; specifically, the strong predicted band at ~ 1100 cm^{-1} (Si-O_2 molecule stretching) is not observed in the experiment and the experimental band I is not reproduced by the calculations. However, a second almost isoenergetic isomer (1,1,6-b) was found, consisting of a MgSiO_3^- monomer with a terminally bound oxygen radical and an ozone-like O_3 unit. This structure is similar to the recently found structure of the cationic MgSiO_9^+ , but with the O_3 unit attached to the Mg rather than the Si atom.²⁸ The predicted vibrational spectrum of 1,1,6-b accounts for all seven experimentally observed bands, although the intensity of bands III (SiO_3 symmetric stretch) and IV (O_3 bending) are underestimated by the calculations and the frequency of the latter is predicted to be ~ 30 cm^{-1} too high. This intensity mismatch suggests a rather poor treatment of the O_3 unit by the PBE0 functional (similar to weakly bound O_2 units as recently observed for cationic clusters²⁸), while MgO and SiO modes are very accurately described. Indeed, a considerably improved match between the experimental and theoretical spectra can be achieved when calculating the O_3 modes with the PBE functional (red curve; since the PBE functional only improves the description of the O_3 bands but worsens the MgO and SiO modes, we restrict the red curve to the relevant O_3 modes): the intensity of the O_3 symmetric stretching vibration increases and the mode shifts from 1192 cm^{-1} (very low intensity with PBE0) to 966 cm^{-1} and, most importantly, the O_3 asymmetric stretching vibration shifts from 956 cm^{-1} to 816 cm^{-1} leading to a very good match with band III. A minor dissonant is that the O_3 bending vibration, a match for band IV, shifts maybe too much with PBE (714 cm^{-1} vs. 653 cm^{-1} with PBE0). The potential formation of isomer 1,1,6-b is further strengthened by the spectra obtained with isotopically enriched oxygen, $\text{MgSi}^{18}\text{O}_6^-$ (Figure S7 of the SI). A possible explanation for the favoured formation of isomer 1,1,6-b is the preferential formation of MgSiO_3^- monomer with respect to MgSiO_2^- . This scenario is supported by the large binding energy of an O atom to the MgSiO_2^- monomer (~ 8 eV). Therefore, this formation path would likely prevent the formation of isomer 1,1,6-a, leading to the observed predominance of isomer 1,1,6-b. We also note that the predicted very small energy difference between 1,1,6-a and 1,1,6-b is likely to be within the error of the theoretical calculations.

Adding a SiO_2 and SiO unit, respectively, to MgSiO_6^- leads to chain-like structures consisting of a MgSiO_2 and a Si_2O_2 ring. In the case of $\text{MgSi}_2\text{O}_8^-$ the terminal oxygen radical and the O_3 unit are retained (isomer 1,2,8-a), whereas in the case of $\text{MgSi}_2\text{O}_7^-$ the O_3 unit is replaced by a superoxo-like O_2 unit (isomer 1,2,7-a). The calculated vibrational spectrum of 1,2,8-a can explain all of the experimentally observed features, especially with the O_3 modes recalculated with the PBE functional (red curve). A second almost isoenergetic isomer 1,2,8-b with a more compact structure clearly fails to explain the IRMPD spectrum. The disappearance of O_3 in isomer 1,2,7-a is in agreement with the absence of the intense band around 830 cm^{-1} (band III for MgSiO_6^-). Instead, the superoxo-like O_2 (total charge $\sim -0.5\text{ eV}$, $d(\text{O}-\text{O}) = 1.33\text{ \AA}$) results in an O-O stretching mode at 1194 cm^{-1} which, however, has such a low intensity that it cannot be seen in the vibrational spectrum. All other predicted modes are in favourable agreement with the IR-MPD spectrum and can account for all experimentally observed bands, as well as in the isotopically labelled experiments (Figure S9 of the SI).

Next, we investigated the structural evaluation of the magnesium silicate clusters by addition of an Mg atom or an MgO unit. The lowest energy structure of $\text{Mg}_2\text{SiO}_6^-$ (isomer 2,1,6-a) consists of a six-membered Mg_2SiO_3 -ring with a terminal oxygen atom and a superoxide-like O_2 (total charge ~ -0.5) bound to one of the Mg atoms, similar to the previously predicted neutral olivine monomer Mg_2SiO_4 .⁴⁶ This structure predicts extremely well all features of the IR-MPD spectrum, with confirmation found in the spectra of the isotopically labelled $\text{Mg}_2\text{Si}^{18}\text{O}_6^-$ (Figure S10 of the SI). Addition of a further oxygen atom, yielding $\text{Mg}_2\text{SiO}_7^-$, leads to some distortion of the six-membered Mg_2SiO_3 ring due to the bridge-binding of this oxygen atom (isomer 2,1,7-a; $d(\text{O}-\text{O})=1.54\text{ \AA}$, O-O stretching at 824 cm^{-1}). This isomer can account for most of the experimentally observed features but clearly fails to explain the two intense bands around 760 cm^{-1} and 825 cm^{-1} . However, we found a higher energy (+0.60 eV) isomer 2,1,7-d (the somewhat lower energy isomers 2,1,7-b,c shown in Figure S11 of the SI do not match the spectrum) that is formed from 2,1,6-a by replacing the superoxo-like O_2 with an ozone-like O_3 ; this isomer is in excellent agreement with the experimental spectrum when the O_3 modes are calculated with the PBE functional. Although the co-existence of 2,1,7-a in the molecular beam cannot be excluded based on the vibrational spectrum, the high intensity of the 760 cm^{-1} band (which stems from the loss of >90% of all $\text{Mg}_2\text{SiO}_7^-$ clusters when irradiating at this frequency) indicates that 2,1,7-d is the only isomer present in the experiment. This leads us to speculate that 2,1,7-d is preferably formed and interconversion into the lower energy structure 2,1,7-a is hindered. This observation is in line with previous studies of anionic bare and deuterated silicon cluster and titanium oxide clusters,^{29,30} where high vertical EAs of neutral clusters determine the observed anions, rather than the energetic stability of the anions.

This was rationalized by a cluster formation mechanism starting with neutral species followed by electron attachment from the plasma created in a pulsed arc or laser vaporization source, respectively, and which favors isomers with high vertical EAs. If the interconversion into lower energy isomers is kinetically hindered, the clusters only relax to metastable structures on the time scale of the experiment. The isomers experimentally observed in the present study are the ones with the highest vertical EAs (1,1,6-b, 1,2,8-a, and 2,1,7-d) as will be discussed below (cf. Table 1), although other isomers are energetically more stable or (almost) isoenergetic.

In summary, comparison of the experimental IR-MPD spectrum with the calculated vibrational spectra of several isomers leads us to conclude that MgSiO_6^- consists of a pyroxene monomer and an ozone-like species, $(\text{MgSiO}_3)\text{O}_3^-$. Addition of a SiO_2 or SiO unit yields chain-like structures containing four-membered MgSiO_2 and Si_2O_2 rings, while addition of Mg or MgO yields six-membered Mg_2SiO_3 ring. All clusters contain terminally bound oxygen radicals and tend to form ozone-like O_3 units when sufficient oxygen is present. Only when the clusters lack one oxygen atom, the O_3 unit is replaced by a superoxo-like O_2 .

Atmospheric Relevance

Although the number densities and reaction time scales in the present experiment and in the atmosphere are different, the formation mechanism are likely not dissimilar with the helium adopting the role of coolant that air molecules have in the atmosphere, ensuring near-thermal equilibrium and dissipating excess energy in between the sequential adsorption steps in the growth process. Evidence for this ‘cold’ chemistry was found, for instance, in the structure determination of pure copper clusters, where each cluster of n atoms was shown to retain the structure of the cluster with one atom loss.³¹ Even in the case of 2-1-7, where we do not observe the thermodynamic minimum, the formation of the neutral thermodynamic minimum, followed by electron attachment appears a fully plausible growth scenario in the upper atmosphere.

Measurements with rocket-borne particle detectors have revealed the existence of negatively charged MSPs with typical radius ranging between 0.5 and 2 nm in the upper mesosphere.^{20,16,17} Of particular interest is the fraction of MSPs that are charged in this region where the plasma density and MSP density are similar. Models of dust plasmas predict that only around 6% of MSPs are charged between 80 and 90 km, so that the total MSP concentration – which is the important geophysical quantity – has to be estimated by multiplying the number measured by a significant factor (~ 16).²⁰ However, these models are sensitive to the MSP charging efficiency, which is poorly understood.

To address this problem, we use the above studied anionic magnesium silicate clusters, which represent appropriate analogues for MSPs with respect to both size and elemental composition, to study their charging efficiency under conditions of the upper mesosphere by kinetic modelling of electron attachment to neutral clusters as well as of potential competing processes leading to subsequent cluster destruction.

Table 1: Computed vertical and adiabatic electron affinities (EAs) of some $\text{Mg}_x\text{Si}_y\text{O}_z$ clusters representing the neutral analogues to the anionic structures identified via IR-MPD spectroscopy and DFT calculations as well as their energetically low-lying isomers. The structures of the neutral clusters (cf. Figure S12) are very similar to the anionic analogues, with the exception of 2,1,7-a that shows some structural rearrangements upon removing the extra electron. For comparison EAs are also given of some highly electronegative species in the mesosphere (Cl, NO_3 , HCO_3), the MgO -, SiO - and MgSiO -clusters reported in the literature, as well as the iron-containing FeSi_2O_7 . All values are in eV.

Species	EA (vertical)	EA (adiabatic)	Reference
MgSiO_6 (1,1,6-a)	3.53	4.55	This work
MgSiO_6 (1,1,6-b)	4.35	4.82	This work
MgSi_2O_7 (1,2,7-a)	3.51	5.23	This work
MgSi_2O_8 (1,2,8-a)	4.03	5.20	This work
MgSi_2O_8 (1,2,8-b)	3.66	4.88	This work
Mg_2SiO_6 (2,1,6-a)	3.96	4.48	This work
Mg_2SiO_7 (2,1,7-a)	2.27	4.22	This work
Mg_2SiO_7 (2,1,7-b)	3.78	5.21	This work
Mg_2SiO_7 (2,1,7-d)	3.75	4.44	This work
FeSi_2O_7	3.01	4.68	This work
Cl	4.58	4.58	This work
NO_3	3.66	3.86	This work
HCO_3	2.80	3.45	This work
$(\text{MgO})_n$		0.70-1.62	Ref. 32
Si_xO_y	0-3.75	0.46-2.6	Refs. 33, 34, 35, 36
olivine $(\text{Mg}_2\text{SiO}_4)_n$	0.6-1.1	1.98-2.65	Refs. 20, 36
pyroxene $(\text{MgSiO}_3)_n$	0.7-1.9	1.59-2.83	Refs. 20, 36

The neutral analogues to the anionic structures identified via IR-MPD spectroscopy and DFT calculations as well as their energetically low-lying isomers (< 0.3 eV of the respective minimum energy structures) all have very high adiabatic electron affinities (EAs) ranging between 4.22 and 5.21 eV. These EAs are not only considerably higher than the EAs of electronegative species in the mesosphere such as Cl, NO₃, HCO₃ (cf. Table 1), but also than the EAs of magnesium oxide clusters,³² stoichiometric and oxygen-rich silicon oxide clusters,^{33,34,35} and stoichiometric olivine- (Mg₂SiO₄) and pyroxene-like (MgSiO₃) silicate clusters.^{20,36} We attribute the extremely high EAs of the clusters found herein to the high oxidation leading to superoxo- and ozone-like ligands.

For calculating the charging efficiency, three clusters were chosen as model systems: MgSi₂O₇ (isomer 1,2,7-a) and Mg₂SiO₇ (isomer 2,1,7-b), the two clusters with the highest EAs, and Mg₂SiO₇ (isomer 2,1,7-a), the cluster with the lowest EA (Table 1). For comparison we have also calculated the charging efficiency for FeSi₂O₇ to evaluate the potential role of iron, which is likely present in MSPs. The necessary physical parameters for the anionic and neutral clusters were obtained by DFT calculations (Tables 1 and S6-S8). The rate constants for electron attachment k_{ea} calculated by RRKM theory are very large and close to the Langevin high-pressure-limits k_L at the pressure of the upper mesosphere (10^{-5} bar)²⁰ (see equation 1 in the Methods section and Table 2). These large rate coefficients can be attributed to the high densities of the rovibrational states, in turn caused by both the large EAs and the rather large number of low frequency vibrational modes (see Table S7), as well as their sizable polarizabilities and dipole moments (see Table S6). It is interesting to compare these rate coefficients with the expression from Natanson³⁷ (k_{ea}^{Nat} , equation 2). For k_{ea}^{Nat} to equal k_{ea} , the particle radius r_{MSP} would need to be 0.70, 0.57 and 0.45 nm for MgSi₂O₇ (isomer a), Mg₂SiO₇ (isomer a) and Mg₂SiO₇ (isomer b), respectively. These values are somewhat larger than the effective geometric radii of these molecules amounting to ~ 0.42 nm for MgSi₂O₇, and ~ 0.30 nm for both Mg₂SiO₇ isomers, which is consistent with the significant long-range forces caused by the large dipole moments and polarizabilities of the Mg-silicate molecules.

Once the anionic clusters have formed, they can potentially be destroyed by several processes: associative detachment with atomic oxygen, photodetachment, or via a neutralization reaction with a positive ion I⁺ (see Table 2). Among these, associative detachment with atomic O - which has a high concentration in the upper mesosphere¹⁴ - is calculated to be endothermic (see Table 2) for all of the studied clusters both at 0 and 220 K and thus not a likely process at low temperatures (< 220 K). We note that the reverse reactions are exothermic and correspond to dissociative electron attachment reactions, which can also produce Mg-silicate anions.

To estimate the rate constant k_{pd} for photodetachment – which could occur during daytime - the absorption cross sections were calculated as a function of wavelength as shown in Figure 2. Due to the large EAs, the thresholds for photodetachment lie at unusually low wavelengths in the near UV. Convoluting these cross sections up to their respective thresholds with the solar actinic flux (averaged over a solar cycle) from the semi-empirical SOLAR2000 model³⁸ gives very low photodetachment rates, k_{pd} , on the order of 10^{-4} - 10^{-3} s⁻¹ (Table 2; for comparison a value of 0.3 s⁻¹ was obtained for O₂⁻³⁹).

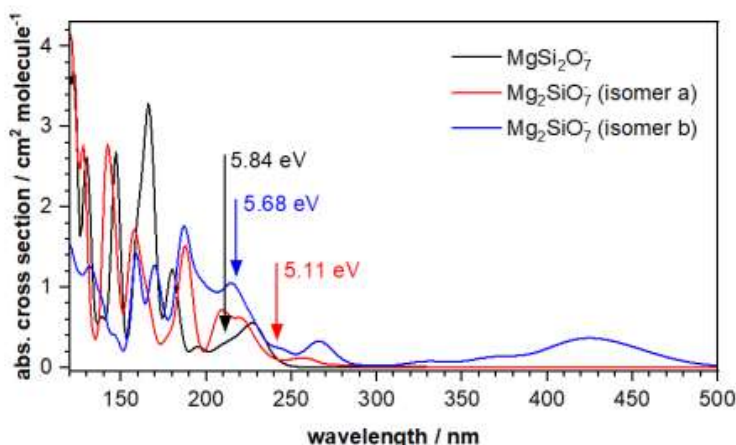


Figure 2. Calculated absorption cross sections for anionic MgSi₂O₇⁻ (isomer 1,1,7-a; black curve), Mg₂SiO₇⁻ (isomer 2,1,7-a; red curve) and Mg₂SiO₇⁻ (isomer 2,1,7-b; blue curve) as a function of the wavelength. The arrows indicate the electron photodetachment thresholds calculated as the energy difference between the anionic and neutral clusters, both in their relaxed geometries.

Finally, rate constants for the reaction with positive ions were calculated using the expression derived by Natanson³⁷ under assumption of a mean positive ion mass of 100 amu and the above estimated r_{MSP} . At a temperature of 200 K the rate constants k_{nr} are on the order of $(2.4 - 3.8) \cdot 10^{-8}$ cm³ molecule⁻¹ s⁻¹ (see Table 2). Finally, considering all of these processes the fraction of charged particles can be calculated. Under assumption of an electron density of 50 cm⁻³ at 80 km height (a typical plasma density at this height is 1000 cm⁻³, with an electron density that is ~5% of this^{20,24,40}) the fraction is 0.18 for MgSi₂O₇⁻, 0.05 for Mg₂SiO₇⁻ isomer a as well as 0.03 for isomer b. It should be noted that replacing Mg by Fe does not notably change the electron affinity, rate constants, and charging efficiency, validating our model of magnesium silicate particles. Considering the uncertainties and assumptions in the dust plasma models used to estimate the 0.06 charged fraction, our values 0.03-0.18 based on accurate calculation of the properties of well-characterised experimental anionic MSP analogues are consistent with current estimates, which validates the view that the negative heavy ions measured by rocket-borne payloads and radar are a small fraction of the total MSP population.^{24,41,42}

Overall, this systematic analysis shows that the properties of our oxygen-rich MSP analogues comply with all the necessary criteria for being viable nucleation seeds for NLCs.

Table 2: Rate coefficients for various processes and fraction of anionic clusters (Mt = Mg or Fe).

Reaction		MgSi ₂ O ₇ (isomer a)	Mg ₂ SiO ₇ (isomer a)	Mg ₂ SiO ₇ (isomer b)	FeSi ₂ O ₇
$\text{Mt}_x\text{Si}_y\text{O}_z + \text{e}^- \rightarrow \text{Mt}_x\text{Si}_y\text{O}_z^-$	$k_{ea}^{(a)}$	$2.18 \cdot 10^{-6}$ $(T/200)^{-0.610}$	$1.49 \cdot 10^{-6}$ $(T/200)^{-0.577}$	$1.02 \cdot 10^{-6}$ $(T/200)^{-0.524}$	$1.58 \cdot 10^{-6}$ $(T/200)^{0.578}$
$\text{Mt}_x\text{Si}_y\text{O}_z^- + \text{O} \rightarrow \text{Mt}_x\text{Si}_y\text{O}_{z+1} + \text{e}^-$	$\Delta H^0^{(b)}$	2.56	0.69	0.51	1.60
$\text{Mt}_x\text{Si}_y\text{O}_z^- + \text{O} \rightarrow \text{Mt}_x\text{Si}_y\text{O}_{z+1} + \text{e}^-$	$\Delta H^0^{(c)}$	3.01	1.13	0.96	2.07
$\text{Mt}_x\text{Si}_y\text{O}_z^- + h\nu \rightarrow \text{Mt}_x\text{Si}_y\text{O}_z + \text{e}^-$	$k_{pd}^{(d)}$	$6.6 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$
$\text{Mt}_x\text{Si}_y\text{O}_z^- + \text{I}^+ \rightarrow \text{Mt}_x\text{Si}_y\text{O}_z + \text{I}$	$k_{nr}^{(a)}$	$3.8 \cdot 10^{-8}$	$3.1 \cdot 10^{-8}$	$2.4 \cdot 10^{-8}$	$3.3 \cdot 10^{-8}$
$\frac{[\text{Mt}_x\text{Si}_y\text{O}_z^-]}{[\text{Mt}_x\text{Si}_y\text{O}_z]} = \frac{k_{ea}[\text{e}^-]}{k_{pd} + k_{nr}[\text{I}^+]}$	(e)	0.16	0.05	0.03	0.02

(a) bimolecular reactions in units $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; (b) enthalpy in eV at 0 K; (c) enthalpy in eV at 220 K and the typical pressure in the mesosphere of 10^{-5} bar; (d) unimolecular reaction in units s^{-1} , obtained by using adiabatic electron affinities; (e) $[\text{I}^+]$ is the total plasma density

Conclusions

We produced anionic magnesium silicate clusters by laser ablation of a solid Si/Mg precursor material in the presence of a He gas with low O₂ concentration, mimicking the ablation and recondensation process of negatively charged silicate MSPs in the upper mesosphere. Subsequent characterization of the formed species via a combination of mass spectrometry, IR-MPD spectroscopy, and quantum-chemical calculations revealed the preferred formation of oxygen rich clusters ($\text{Mg}_x\text{Si}_y\text{O}_z^-$ with $z > 2(x+y)$) in which some oxygen is bound as oxygen radicals, superoxo-like O₂ and/or ozone-like O₃ units to four- and six-membered MgSiO rings. Furthermore, we show that the corresponding neutral counterparts have extraordinarily high adiabatic electron affinities (> 4.2 eV), a necessary pre-requisite for their formation and survival in the upper mesosphere. Indeed, kinetic modelling of electron attachment to the highly oxidized neutral clusters in competition with various anion destruction processes reveals a significant charging efficiency of 3-18%, depending on the exact cluster size and composition. To match mesoscopic observations, simulations require that the average charging efficiency should be around 6%. The good agreement between these independently obtained values, underlines the potential atmospheric relevance of our clusters

In summary, our highly oxidised anionic silicate clusters exhibit all the necessary chemical, electronic and optical properties to be highly credible candidates for MSP-based NLC nucleation seeds in the upper mesosphere. Our study provides fundamental new insights into the potential nature and properties of MSPs and could help towards providing a molecular-level understanding of MSP charging efficiency. In addition to these physicochemical results, incorporation of our results into atmospheric/climate models should also lead to an improved understanding of NLC formation and the wider chemistry of MSPs in the upper mesosphere.

Methods

Experimental Methods

Anionic magnesium silicate clusters were produced by pulsed laser ablation of a rotating MgSi rod target (Mg:Si = 2:1 molar ratio) using the second harmonic of a Nd:YAG laser (532 nm). The ablation took place in a 3 mm diameter and 60 mm long growth channel in the presence of a short pulse of helium carrier gas seeded with 1% oxygen. The gas mixture was then expanded into vacuum forming a molecular beam, which was shaped by a 2 mm diameter skimmer and a 0.45 mm slit aperture, before entering the intracavity region where it interacted with the IR laser beam of the Free Electron Laser for Intra Cavity Experiments (FELICE, 225–1800 cm⁻¹; a 10 μs macropulse with picosecond duration micropulses at 1 GHz repetition rate; spectral width set to ~0.5% FWHM of the central wavenumber) crossing it at an angle of 35°. A few microseconds after interaction with FELICE, all ions were extracted by a set of pulsed high-voltage plates into a reflectron time-of-flight mass spectrometer and detected with a micro-channel plate detector.^{43,44} To correct for long-term source fluctuations, the experiment was operated at twice the FELICE repetition rate, allowing for the recording of reference mass spectra in between successive FELICE pulses.

Whenever the IR frequency was in resonance with an IR-active vibrational mode of a given complex, multiple IR photons were absorbed sequentially, leading to a heating of the complex and finally to its fragmentation, and consequently to a depletion of the detected signal in the mass channel of the complex. The IR-MPD spectra shown in this contribution represent the depletion yield $Y(\tilde{\nu})$ at wavenumber $\tilde{\nu}$, obtained via the equation $Y(\tilde{\nu}) = \ln [I(\tilde{\nu})/I_0]/P(\tilde{\nu})$ where $I(\tilde{\nu})$ and I_0 are the mass peak intensities with and without laser light, respectively, and $P(\tilde{\nu})$ is the macropulse energy. In the linear absorption approximation, the absorption probability is the product of IR absorption cross section and photon flux.

In reconstructing the photon flux from the macropulse energy, the wavelength dependence of the beam geometry and of the photon energy cancel out, but the dependence of spectral bandwidth on wavelength must be corrected for. Therefore, to obtain a more faithful comparison between experimental and calculated band intensities the latter are divided by the wave-number.

Theoretical Methods

In our initial searches for stable anionic magnesium silicate clusters, we assumed that the experimentally obtained clusters consisted of an anionic silicate core interacting in a non-bonded fashion with oxygen molecules. Following this idea, we obtained low energy candidates for the anionic cores using the Monte Carlo basin hopping algorithm⁴⁵ (MCBH) in combination with a polarizable classical interatomic potential (IP). This approach has previously been shown to be effective in finding low energy silicate cluster isomers.⁴⁶ Once the low energy cluster core structures were obtained, we systematically sampled different positions for the surrounding oxygen molecules. The General Utility Lattice Program (GULP)⁴⁷ was used to perform the IP-based local optimisations needed during the MCBH searches.

In addition to our IP-based searches, we also used Global Optimization with First-principles Energy Expression (GOFEE)⁴⁸ searches to obtain low energy cluster candidates. GOFEE uses single-point calculations to widely sample the potential energy landscape of cluster configurations while dynamically training a surrogate machine learning energy model. We performed this sampling using Density Functional Theory (DFT) based calculations. Using the surrogate model, GOFEE can efficiently evaluate forces and perform energy minimizations with an accuracy approaching the level of the single-point DFT sampling. The DFT calculations employed the PBE0 hybrid exchange correlation functional⁴⁹ and a light-tier 1 numerical atom-centered orbital basis set.⁵⁰ Although computationally more expensive than our IP-based searches, the GOFEE approach does not depend on a specific IP parameterisation.

The structures of all obtained cluster candidates from both sets of searches were reoptimized using DFT-based calculations using the PBE0 functional and a tight-tier 2 numerical atom-centered orbital basis set.⁵³ We note that PBE0-based DFT calculations have been shown to be accurate for computing the energetics of small oxide clusters interacting with oxygen molecules, with respect to renormalized second-order perturbation theory calculations.⁵¹ Non-bonded dispersive interactions were also considered using the Tkatchenko-Scheffler method⁵². All DFT-based calculations were carried out using the Fritz Haber Institute Ab Initio Molecular Simulations package (FHI-AIMS).⁵³

For the 5-10 lowest energy cluster isomers found for each composition, we also used the PBE0/tight-tier 2 level of DFT theory to calculate their harmonic IR spectra. Previous studies have shown that DFT calculations using PBE0 provide accurate IR spectra but tend to systematically slightly overestimate the computed frequency values when compared with accurate theoretical data for pyroxenic and olivinic neutral monomers⁵⁴, and experimental values for cationic nanosilicates²⁸, and bulk crystalline olivinic⁵⁵ and pyroxenic⁵⁶ materials. To compensate for this effect, we apply a constant 3% redshift (i.e. a 0.97 scaling factor) to all our calculated frequencies. Additionally, for a better visual comparison with the experimentally obtained spectra, we broadened each computationally obtained signal by convolving it with a gaussian lineshape function with a full width at half maximum of 20 cm⁻¹. For specific vibrations involving bound O₃ moieties, DFT calculations using the PBE functional⁵⁷ were employed to correct the known deficiencies of using the PBE0 functional for such cases (e.g. ozone⁵⁸).

Adiabatic EAs were calculated as the energy difference between the optimized structures of the neutrals and anions. The structures of the neutral clusters were obtained by DFT-based (PBE0/tight-tier 2) relaxation of the anionic structures with one electron less. Vertical electron affinities (EA) were calculated from the energy difference between the optimized neutral cluster structure and the anion at the same geometry.

Determination of Rate Constants

The rate coefficients for electron attachment to these molecules were calculated using Rice-Ramsperger-Kassel-Markus (RRKM) theory with an inverse Laplace transform solution of the Master Equation.⁵⁹ Electron attachment occurs through formation of an excited adduct anion; this can either dissociate again to the neutral and an electron, be stabilized by collision with a third body (which is N₂ or O₂ in the mesosphere/lower thermosphere), or dissociate to anion and neutral products i.e. dissociative attachment (which we do not include in the RRKM calculation). For these reactions, the internal energy of the adduct was divided into a contiguous set of grains (width 60 cm⁻¹), each containing a bundle of rovibrational states. Each grain was then assigned a microcanonical rate coefficient for dissociation, using inverse Laplace transformation²⁰ to link directly to the high pressure-limiting of the electron-molecule recombination rate coefficient k_L given by modified Langevin theory according to:

$$k_L = 2\pi e\chi \sqrt{\frac{\alpha}{4\pi\epsilon_0\mu}} \quad (1)$$

where α is the volume polarizability of the Mg-silicate, e is the electronic charge, ϵ_0 is the vacuum permittivity, μ is the reduced mass of the e^- - silicate collision pair and χ is a correction for s -wave scattering.⁶⁰

Due to the large dipole moments (particularly for MgSi_2O_7), the calculated Langevin rate is increased compared to equation (1) using the parameterization from Su and Chesnavich for polar molecules.⁶¹

The density of states of the adduct was calculated using the Beyer-Swinehart algorithm for the vibrational modes (without correcting for anharmonicity), and a classical densities of states treatment for the rotational modes. The vibrational frequencies and rotational constants for the three Mg-silicate molecules and their respective anions are given in Tables S7 and S8 of the SI. For comparison, rate constants were also calculated using the expression from Natanson³⁷:

$$k_{ea}^{Nat} = \pi r_{MSP}^2 \sqrt{\frac{8k_B T}{\pi m_e}} \cdot \left(1 + \sqrt{\frac{e^2}{8\epsilon_0 r_{MSP} k_B T}} \right) \quad (2)$$

where k_B is the Boltzmann constant, m_e is the mass of an electron, and r_{MSP} the radius of the particle.

Supporting Information

Assignment of mass peaks; IR-MPD spectra of $\text{Mg}_x\text{Si}_y^{16}\text{O}_z^-$ and $\text{Mg}_x\text{Si}_y^{18}\text{O}_z^-$ as well as calculated spectra for further isomers; Calculated properties of selected neutral and anionic clusters

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References

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- ¹ Gadsden, M., Schröder, W. *Noctilucent Clouds* (Springer, New York, 1989).
- ² G. E. Thomas, J. J. Olivero, E. J. Jensen, W. Schroeder, O. B. Toon, Relation between increasing methane and the presence of ice clouds at the mesopause *Nature* **338**, 490–492 (1989).
- ³ Thomas, G. E. & Olivero, J. Noctilucent clouds as possible indicators of global change in the mesosphere. *Adv. Space Res.* **28**, 937–946 (2001).
- ⁴ Lübken, F.-J., Berger, U., Baumgarten, G. On the anthropogenic impact on long-term evolution of noctilucent clouds. *Geophys. Res. Lett.* **45**, 6681–6689 (2018).
- ⁵ Lübken, F.-J., Baumgarten, G., Grygalashvyly, M., Vellalassery, A., Absorption of Solar Radiation by Noctilucent Clouds in a Changing Climate. *Geophys. Res. Lett.*, **51**, e2023GL107334 (2024).
- ⁶ Duft, D., Nachbar, M., Leisner, T., Unravelling the microphysics of polar mesospheric cloud formation. *Atmos. Chem. Phys.* **19**, 2871e2879 (2019).
- ⁷ Saunders, R. W. & Plane, J. M. C. A photo-chemical method for the production of olivine nanoparticles as cosmic dust analogues. *Icarus*. **212**, 373–382 (2011).
- ⁸ Gumbel, J. & Megner, L. Charged meteoric smoke as ice nuclei in the mesosphere: Part 1: A review of basic concepts. *J. Atmos. Sol.-Terr. Phys.* **71**, 1225–1235 (2009).
- ⁹ Gumbel, J. & Megner, L. Charged meteoric smoke as ice nuclei in the mesosphere: Part 2: A feasibility study. *J. Atmos. Sol.-Terr. Phys.* **71**, 1236–1244 (2009).
- ¹⁰ Hervig, M. E. et al. The content and composition of meteoric smoke in mesospheric ice particles from SOFIE observations. *J. Atmos. Sol.-Terr. Phys.* **84–85**, 1–6 (2012).
- ¹¹ J. Hedin, F. Giovane, T. Waldemarsson, J. Gumbel, J. Blum, R. M. Stroud, L. Marlin, J. Moser, D. E. Siskind, K. Jansson, R. W. Saunders, M. E. Summers, P. Reissaus, J. Stegman, J. M. C. Plane, M. Horányi, The MAGIC meteoric smoke particle sampler, *J. Atmos. Sol.-Terr. Phys.* **118**, 127–144. (2014).
- ¹² Plane, J. M. C. Cosmic dust in the earth's atmosphere. *Chem. Soc. Rev.* **41**, 6507–6518 (2012).
- ¹³ Carrillo-Sánchez, J. et al. Cosmic dust fluxes in the atmospheres of Earth, Mars, and Venus. *Icarus*. **335**, 113395 (2020)
- ¹⁴ Plane, J. M. C., Feng, W. & Dawkins, E. C. M. The Mesosphere and Metals: Chemistry and Changes. *Chem. Rev.* **115**, 4497–4541 (2015).
- ¹⁵ Kalashnikova, O., Horanyi, M., Thomas, G. E. & Toon, O. B. Meteoric smoke production in the atmosphere. *Geophys. Res. Lett.* **27**, 3293–3296 (2000).
- ¹⁶ Hedin, J., Gumbel, J. & Rapp, M. On the efficiency of rocket-borne particle detection in the mesosphere. *Atm. Chem. Phys.* **7**, 3701–3711 (2007).
- ¹⁷ Arnyx, K. et al. In-situ measurement of smoke particles in the wintertime polar mesosphere between 80 and 85 km altitude. *J. Atmos. Sol.-Terr. Phys.* **70**, 61–70 (2008).
- ¹⁸ Strelnikova, I., Rapp, M., Raizada, S., & Sulzer, M. Meteor smoke particle properties derived from Arecibo incoherent scatter radar observations. *Geophys. Res. Lett.* **34**, L15815 (2007).
- ¹⁹ Fentzke, J. T. et al. D region meteoric smoke and neutral temperature retrieval using the poker flat incoherent scatter radar. *Geophys. Res. Lett.* **39**, L21102 (2012).
- ²⁰ Plane, J. M.C. et al. A combined rocket-borne and ground-based study of the sodium layer and charged dust in the upper mesosphere. *J. Atmos. Terr. Phys.* **118** 151–160 (2014).

-
- ²¹ Molina-Cuberos, J. G., Lopez-Moreno, J. J. & Arnold, F. Meteoric layers in planetary atmospheres. *Space Sci. Rev.* **137**, 175-191 (2008).
- ²² Verronen, P. T., Andersson, M. E., Marsh, D. R., Kovács, T., & Plane, J. M. C. WACCM-D whole atmosphere community climate model with D-region ion chemistry. *J. Adv. Model. Earth Sy.* **8**, 954-975 (2016).
- ²³ Gelinas, L. J. et al. Mesospheric charged dust layer: Implications for neutral chemistry. *J. Geophys. Res.* **110**, A01310 (2005).
- ²⁴ Friedrich, M., Rapp, M., Plane, J. M. C. & Torkar, K. M. Bite-outs and other depletions of mesospheric electrons. *J. Atmos. Sol.-Terr. Phys.* **73**, 2201-2211 (2011).
- ²⁵ Friedrich, M. et al. Multi-instrument comparisons of D-region plasma measurements. *Ann. Geophys.* **31**, 135-144 (2013).
- ²⁶ Skinner, L. M. & Sambles, J. R. The Kelvin equation--A review. *J. Aerosol Sci.* **3**, 199-210 (1972).
- ²⁷ Summers, M. E. & Siskind, D. E. Surface recombination of O and H₂ on meteoric dust as a source of mesospheric water vapor. *Geophys. Res. Lett.* **26**, 1837-1840 (1999).
- ²⁸ Guiu, J. M. et al. Cluster beam study of (MgSiO₃)⁺-based monomeric silicate species and their interaction with oxygen: implications for interstellar astrochemistry. *ACS Earth Sp. Chem.* **6**, 2465-2470 (2022).
- ²⁹ L. Kronik, R. Fromherz, E. Ko, G. Ganteför, J. R. Chelikowsky Highest electron affinity as a predictor of cluster anion structures, *Nat. Mater.* **1**, 49-53 (2002).
- ³⁰ N. Marom, M. Kim, J. R. Chelikowsky, Structure Selection Based on High Vertical Electron Affinity for TiO₂ Clusters, *Phys. Rev. Lett.* **108**, 106801 (2012).
- ³¹ O. V. Lushchikova, D. M. M. Huitema, P. López-Tarifa, L. Visscher, Z. Jamshidi, J. M. Bakker, Structures of Cu_n⁺ (n = 3-10) Clusters Obtained by Infrared Action Spectroscopy, *J. Phys. Chem. Lett.* **10**, 2151-2155 (2019).
- ³² Gutowski, M., Skurski, P., Li, X. & Wang, L-S. (MgO)_n⁻ (n = 1-5) clusters: multipole-bound anions and photodetachment spectroscopy. *Phys. Rev. Lett.* **85**, 3145-3148 (2000).
- ³³ Wang, L-S., Wu, H., Desai, S. R., Fan, J. & Colson, S. D. A photoelectron spectroscopic study of small silicon oxide clusters: SiO₂, Si₂O₃, and Si₂O₄. *J. Phys. Chem.* **100**, 8697-8700 (1996).
- ³⁴ Wang, L-S., Nicholas, J. B., Dupuis, M., Wu, H. & Colson, S. D. Si₃O_γ (γ = 1 - 6) clusters: models for oxidation of silicon surfaces and defect sites in bulk oxide materials. *Phys. Rev. Lett.* **78**, 4450-4453 (1997).
- ³⁵ Flikkema, E. & Bromley, S. T. Dedicated global optimization search for ground state silica nanoclusters: (SiO₂)_N (N = 6-12) *J. Phys. Chem. B.* **108**, 9638-9645 (2004).
- ³⁶ Escatllar, A. M. & Bromley, S. T. Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study. *Astronom. Astrophys.* **634**, A77 (2020).
- ³⁷ Natanson, G. L. On the theory of the charging of microscopic aerosol particles as a result of capture of gas ions. *Soviet Phy. Tech. Phys.* **5**, 538-551 (1960).
- ³⁸ Tobiska, W. K. et al. The SOLAR2000 empirical solar irradiance model and forecast tool. *J. Atmos. Sol.-Terr. Phys.* **62**, 1233-1250 (2000).
- ³⁹ Woo, S. B., Branscomb, L. M. & Beaty, E. C. Sunlight photodetachment rate of ground state O₂⁻. *J. Geophys. Res.* **74**, 2933-2940 (1969).
- ⁴⁰ Rapp, M. Rocket-borne in situ measurements of meteor smoke: charging properties and implications for seasonal variation. *J. Geophys. Res.* **115**, D00116 (2010).

-
- ⁴¹ Fentzke, J. T., Janches, D., Strelnikova I. & Rapp, M. Meteoric smoke particle properties derived using dual-beam Arecibo UHF observations of D-region spectra during different seasons. *J. Atmos. Sol.-Terr. Phys.* **71**, 1982–1991 (2009).
- ⁴² Friedrich, M. et al. Electron loss and meteoric dust in the mesosphere. *Ann. Geophys.* **30**, 1495–1501 (2012).
- ⁴³ Bakker, J. M. et al. Intensity-resolved IR multiple photon ionization and fragmentation of C₆₀. *J. Chem. Phys.* **132**, 074305 (2010).
- ⁴⁴ Haertelt, M. et al. Structure determination of anionic metal clusters via infrared resonance enhanced multiple photon electron detachment spectroscopy. *J. Phys. Chem. Lett.* **2**, 1720–1724 (2011).
- ⁴⁵ Wales, D. J. & Doye, J. P. K. Global optimization by basin-hopping and the lowest energy structures of Lennard-Jones clusters containing up to 110 Atoms. *J. Phys. Chem. A.* **101**, 5111–5116 (1997).
- ⁴⁶ Escatllar, A. M., Lazaukas, T., Woodley, S. M. & Bromley, S. T. Structure and properties of nanosilicates with olivine (Mg₂SiO₄)_N and Pyroxene (MgSiO₃)_N compositions. *ACS Earth Sp. Chem.* **3**, 2390–2403 (2019).
- ⁴⁷ Gale, J. D. GULP: A computer program for the symmetry-adapted simulation of solids. *J. Chem. Soc., Faraday Transactions.* **93**, 629–637 (1997).
- ⁴⁸ Bisbo, M. K. & Hammer, B. Efficient global structure optimization with a machine-learned surrogate model. *Phys. Rev. Lett.* **124**, 086102 (2020).
- ⁴⁹ Adamo, C. & Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **110**, 6158–6170 (1999).
- ⁵⁰ Blum, V. et al. Ab initio molecular simulations with numeric atom-centered orbitals. *Comput. Phys. Commun.* **180**, 2175–2196 (2009).
- ⁵¹ Bhattacharya, S., Levchenko, S. V., Ghiringhelli, L. M. & Scheffler, M. Stability and metastability of clusters in a reactive atmosphere: theoretical evidence for unexpected stoichiometries of Mg_mO_x. *Phys. Rev. Lett.* **111**, 135501 (2013).
- ⁵² Tkatchenko, A. & Scheffler, M. Accurate molecular Van Der Waals interactions from ground-state electron density and free-atom reference data. *Phys. Rev. Lett.* **102**, 073005 (2009).
- ⁵³ Jensen, S. R. et al. The Elephant in the Room of Density Functional Theory Calculations. *J. Phys. Chem. Lett.* **8**, 1449–1457 (2017).
- ⁵⁴ Guiu, J. M., Escatllar, A. M. & Bromley, S. T. How Does Temperature Affect the Infrared Vibrational Spectra of Nanosized Silicate Dust? *ACS Earth Sp. Chem.* **5**, 812–823 (2021).
- ⁵⁵ de la Pierre, M. et al. Performance of six functionals (LDA, PBE, PBESOL, B3LYP, PBE0, and WC1LYP) in the simulation of vibrational and dielectric properties of crystalline compounds. the case of forsterite Mg₂SiO₄. *J. Comput. Chem.* **32**, 1775–1784 (2011).
- ⁵⁶ Demichelis, R. The infrared spectrum of ortho-enstatite from reflectance experiments and first principle simulations. *Mon. Not. R. Astron. Soc.* **420**, 147–154 (2012).
- ⁵⁷ Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys Rev Lett.* **77** 3865–3868 (1996).
- ⁵⁸ A comparison of DFT-calculated ozone frequencies using different functionals can be found at: <https://cccbdb.nist.gov/>
- ⁵⁹ De Avillez Pereira, R., Baulch, D. L., Pilling, M. J., Robertson, S. H. & Zeng, G. Temperature and pressure dependence of the multichannel rate coefficients for the CH₃ + OH System. *J. Phys. Chem.* **101**, 9681–9693 (1997).

⁶⁰ Troe, J., Miller, T. M. & Viggiano, A. A. Low-energy electron attachment to SF₆. I. Kinetic modeling of nondissociative attachment. *J. Chem. Phys.* **127**, 244303(2007).

⁶¹ Su, T. & Chesnavich, W. J. Parametrization of the ion–polar molecule collision rate constant by trajectory calculations. *J. Chem. Phys.* **76**, 5183-5185 (1982).

CHAPTER 10

Understanding the Size-dependent Structural Properties and Infrared Spectra of Silicate Dust Grains via Atomistic Nucleated Growth Simulations

10.1 Introduction

Silicate dust grains are thought to be freshly formed mainly in the circumstellar envelopes of oxygen-rich AGB stars through high-temperature nucleation processes¹. At typical distances of 3 to 10 stellar radii from an AGB star's surface, the temperature is sufficiently low (*e.g.* 900 - 1100K), and the density is sufficiently large to allow the formation of significant quantities of dust². Early theoretical studies, performed by Gail, Ferrarotti and Sedlmayr, predicted the preferential condensation of forsterite from the available Mg, SiO and H₂O monomers in these regions, even when the abundance of Si is higher than Mg³⁻⁵. Although silicates are highly refractory materials, in such extreme environments their initial homogeneous nucleation is strongly thermodynamically hindered. It has thus been suggested that the silicates nucleate on small seeds of more refractory materials (*e.g.* TiO₂, Al₂O₃)⁶. Once a suitable seed has been formed computational modelling studies have shown how nanosilicates could subsequently grow following a series of oxidation and metal atom incorporation steps⁷.

Despite the significant advances made to understand silicate dust grain formation, most previous works have focused on thermodynamic equilibrium models based on the condensation of bulk grains. Such approaches do not consider the atomistic level dynamical details of the growth process. Since silicate dust plays a key role in many astronomical processes, from planetary formation to catalyzing molecule formation, understanding how their structural and spectral properties evolve during the growth process could provide crucial insights into these phenomena. Additionally, given the challenges in directly detecting nanosilicates in astronomical observations, simulating their growth and deriving their characteristic properties could allow for an indirect study of these particles by linking them with some more observationally amenable processes (*e.g.* formation or destruction of observable chemical species).

In this work, in collaboration with Dr. Antoni Macià, we developed the NAGGS (Nucleated Atomistic Grain Growth Simulator) code that we used to simulate the atomistically detailed growth of nucleated silicate dust grains. The growth simulation is achieved by sending atoms or molecules, one by one, towards an initial seed, which is assumed to be already formed. From the NAGGS simulations, we have analysed how different properties of nanosilicate grains evolve with size. Additionally, we consider different nucleation conditions by controlling the temperature during the growth process and/or the chemical composition of the growing grains. In this way we can examine the resultant differences or similarities of their properties depending on these conditions. One important feature of the NAGGS code is the ability to track IR spectra, which are well known to have notable size-dependent differences between nanosilicate and bulk grains⁸. By computing the harmonic IR spectra of the growing grains, we can derive the characteristic spectra of different nanosilicate populations with a given average grain size. In this way it is possible to analyse the evolution of the IR spectra with grain size and thus to determine at what size is sufficient to exhibit bulk-like IR spectra. This information is observationally valuable for astronomers in order to better understand how the observed 10 and 18 micron silicate IR features relate to silicate dust size and composition.

10.2 Results

The NAGGS code

The primary objective of the NAGGS code is to model the growth of dust grains from an initial nucleated seed, by sending atoms or molecules towards the seed one by one using MD simulations. A summary of the steps that NAGGS carries out is illustrated in Figure 1.

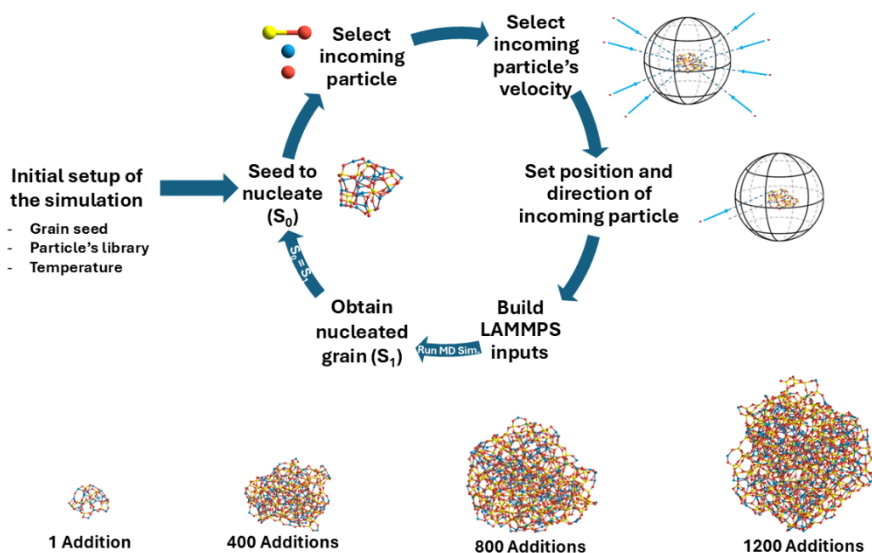


Figure 1: Upper: Summary of the steps carried out by the NAGGS code. Mg, Si and O atoms are represented as blue, yellow and red spheres respectively. Lower: Nucleated growth of a nanosilicate grain with respect to the number of monomeric additions.

Before executing the simulations, the user defines some parameters: 1) the structure of the initial seed particle, 2) a library of incoming monomers *i.e.* the atoms/molecules that will be sent to the seed, 3) the desired chemical composition of the grains (*e.g.* for silicates this could bias the stoichiometry to pyroxenic (Mg:Si ratio = 1) or olivinic (Mg:Si ratio = 2) grains), and 4) the temperature of the simulation.

In this work, we modelled the growth of nanosilicate grains as a sequential addition of Mg, SiO and O following the nucleation/growth mechanism suggested in previous work⁷.

Note that O monomers are used instead of OH or H₂O molecules following the simplifying and reasonable assumption that these latter species mainly act to add O to the growing particle and liberate gaseous H₂ in the process. At each step, NAGGS randomly selects a particle from the library of suitable monomers (*e.g.* SiO, Mg and O for silicates) applying probability weights to ensure that the evolving silicate composition aligns with the target stoichiometry. Specifically, if a cation-based monomer (Mg or SiO in our simulations) is introduced in one step, in the subsequent addition an anion is selected (O in our simulations) and *vice versa*. To select between the positively charged species the following probabilities were used:

$$P_{SiO} = \frac{Mg:Si_{ratio}}{Mg:Si_{ratio} + 1} \quad 1$$

$$P_{SiO} = \frac{1}{Mg:Si_{ratio} + 1} \quad 2$$

To demonstrate the ability of NAGGS to grow grains with a desired chemical composition, Figure 2 presents the evolution of the deviation in the Mg:Si ratio from the corresponding target stoichiometry. Initially, pyroxenic grains exhibit large deviation, as they originate from a seed grain with olivinic composition. However, as the simulation progresses, the chemical composition is progressively adjusted, and the deviation decreases, reaching relatively low values by the end of the simulation. On the other hand, olivinic grains start with a perfect ratio, which fluctuates throughout the simulation. Nevertheless, similar to pyroxenic grains, the ratio stabilizes to the target composition by the end of the simulation.

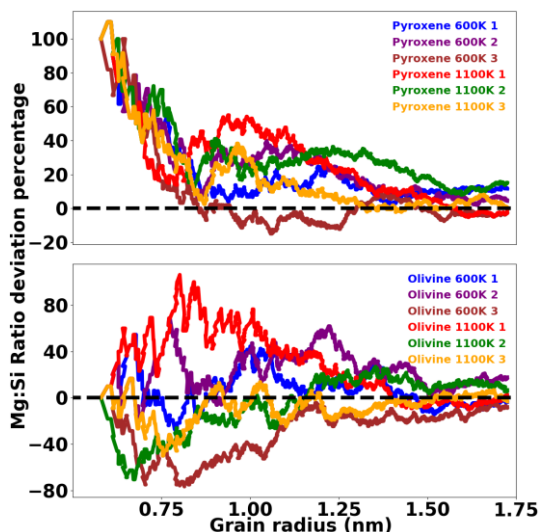


Figure 2: Size-dependent convergence of the Mg:Si ratio for pyroxenic (top) and olivinic (bottom) grain compositions, grown at 600 K and 1100 K. For each chemical composition and temperature, three different simulations are shown.

Once an incoming monomer is chosen, its velocity is determined from a Maxwell-Boltzmann distribution, consistent with the user's specified temperature. The monomer is then placed randomly around the seed grain to a distance computed as:

$$distance = r + 1 + v * 0.3 \quad 3$$

where r is the radius of the seed, and v is the incoming monomer velocity. The additive constant 1, and the velocity-dependent term act as a security threshold, ensuring that the incoming monomer starts sufficiently far from the seed. This prevents immediate, unphysical collisions or force spikes that could destabilize the simulation, particularly at higher velocities. It also ensures a smooth and physically meaningful approach towards the seed grain.

To determine the direction of the incoming monomer movement, a vector is drawn from the seed's center of mass. To introduce variability in the impact position, a random offset is applied to this vector. Using this information, the code generates the necessary inputs for LAMMPS⁹, which then performs the classical MD simulations. After each MD run, the resulting structure serves as the seed for the next iteration.

Each MD simulation carried out in LAMMPS is divided into two phases. First, the incoming monomer is temporarily removed, and the internal temperature of the grain is equilibrated to the target value during 2.5 ps using a Berendsen thermostat under the canonical ensemble (NVT: constant number of atoms, volume and temperature).

After this phase, the production phase is carried out. In this stage, the incoming monomer is reintroduced at the precomputed position and velocity, and the simulation is run for 1.5 ps under the microcanonical ensemble (NVE: constant number of atoms, volume and energy). This duration was found to be long enough for the particles to fully dissipate the energy of the impacting monomer in the growing grain upon and after collision.

Details regarding the FF parameters used in the MD simulations, along with an evaluation of their suitability for accurately describing silicate structures and their energetic stability, can be found in Appendix E.

To analyse how the physical properties of different nanosilicates evolve with size under varying conditions, we carried out four different types of nucleated growth simulations in which we controlled the composition and the temperature:

- Pyroxenic composition at 600K
- Pyroxenic composition at 1100K
- Olivinic composition at 600K
- Olivinic composition at 1100K

Each simulation consisted of 1200 nucleation events, with the initial seed being a low energy minimum structure of a 70 atom olivine cluster (Mg_2SiO_4)₁₀, obtained in previous studies⁸. The same seed structure was employed in all simulations to avoid any potential dependence of the growth process on initial conditions. Each simulation type was also performed ten times. All reported results for each analyzed property are computed as a statistical average over all ten runs for the corresponding simulation type. In this section only a subset of the results is presented. The remaining data are included in Appendix E.

Grain Radius

To estimate the average radius of the growing silicate grains, we assume that they have a spherical shape. The moment of inertia (I) of a solid sphere can be obtained from its mass (M) and radius (R) using equation 4:

$$I = \frac{2}{5} M \cdot R^2 \quad (4)$$

Therefore, the radius of the modelled grains can be computed using the following equation:

$$R = \sqrt{\frac{5I}{2M}} \quad (5)$$

Since the growing grains are not perfectly spherical, we used the average of the grain's moments of inertia to compute the radius. The evolution of grain radius, presented in Figure 3, shows a wide range of sizes covered by the NAGSS simulations, ranging from particles containing only a few tens of atoms to larger particles with radii > 1.5 nm. These results show that olivinic grains tend to be slightly smaller than pyroxenic grains for the same number of atoms, indicating a more compact atomical structure. We note that Li and Draine¹⁰ defined ultrasmall silicate grains as those with radii ≤ 1.5 nm. Therefore, our simulations can be said to provide insights into silicates through molecular, ultrasmall and nanoscale size regimes.

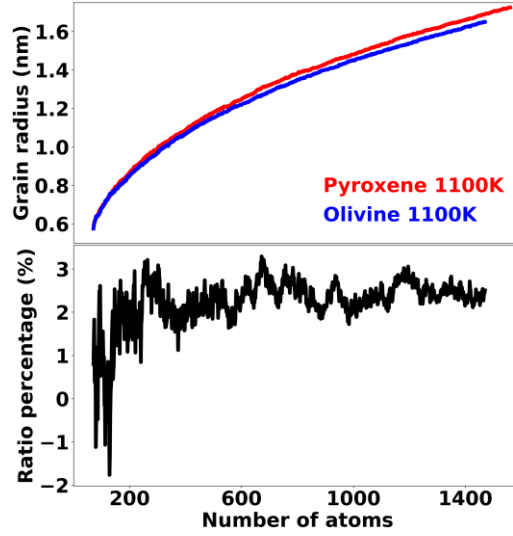


Figure 3: Evolution of silicate grain radius (top) of pyroxene (red) and olivine (blue) grains at 1100K with respect to the number of atoms in the grain. Bottom panel shows the corresponding ratio (as a percentage) of the radii of pyroxene to olivine grains. The results for each grain composition are obtained from averages over ten nucleated growth simulations.

Grain Sphericity

Sphericity (Ψ) is a measure of how closely the shape of a particle approximates a perfect sphere. This metric is defined as the ratio between the surface area of a sphere with the same volume as the object under study and the actual object's surface area¹¹:

$$\Psi = \frac{\pi^{1/3}(6V_{obj})^{2/3}}{A_{obj}} \quad (6)$$

where V_{obj} is the volume of the object and A_{obj} its surface area. Sphericity values close to 1 indicate shapes close to spherical, while lower values indicate deviations from sphericity. These lower values can arise from two main factors. First, the grain may have a less compact shape than a sphere. On the other hand, large surface roughness can reduce sphericity by increasing the surface area without modifying the volume. In Figure 4 we show how the sphericity of grains depends on their roundness and surface roughness. Notice that highly spherical particles with a large surface roughness (top right) have relatively low sphericity values.

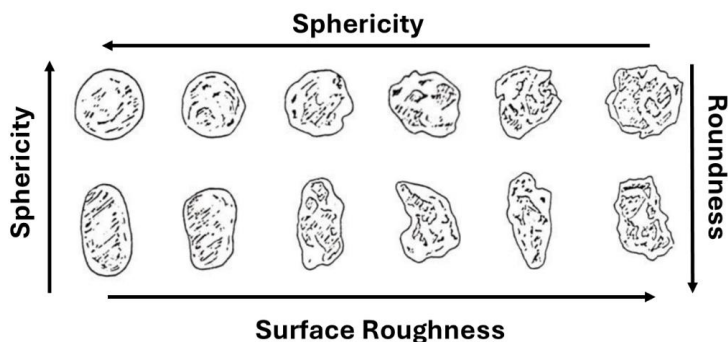


Figure 4: Evolution of sphericity depending on surface roughness and grain roundness. Figure adapted from reference 12.

To obtain the volume and surface area of the grains we employed the MoloVol code¹³, which computes the van der Waals volume and van der Waals surface of atomic structures.

The results presented in Figure 5 clearly show that the sphericity of grains tends to decrease as they grow. This tendency is especially apparent for pyroxenic grains. Since NAGGS adds incoming atoms in a stochastic and statistically isotropic way, highly spherical particles are expected to form. However, collisions of monomers with the grain during the growth process can also cause structural roughness to emerge on the grain surface, leading to a reduction in sphericity (see Figure 4).

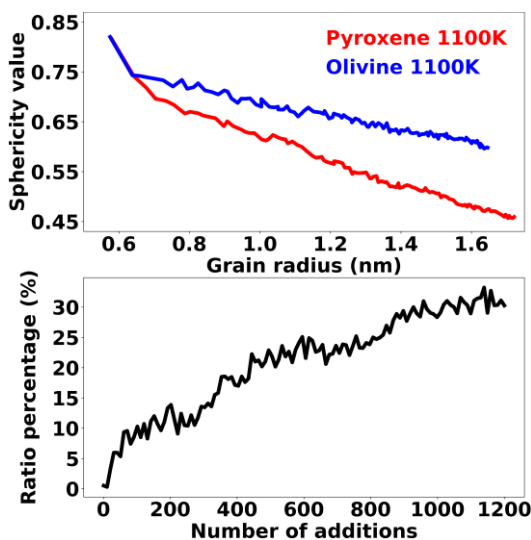


Figure 5: Top: Silicate grain sphericity evolution with respect to increasing grain radius for pyroxene (red) and olivine (blue) grains at 1100 K. Bottom: the ratio (as a percentage) of pyroxene sphericity to olivine sphericity. The results are obtained from averages over ten nucleated growth simulations.

Grain Shape

To better understand the origin of the decrease in sphericity of growing grains, we analysed the shape of the grains independently of the surface roughness. To achieve this, we used the inertial moments (I_x , I_y , I_z) of the grains, which can be derived from their atomistic structures and masses.

By examining the inertial moments, we can classify the grain shape as prolate ($I_z = I_y > I_x$), oblate ($I_z > I_y = I_x$) or spherical ($I_z = I_y = I_x$). In cases where all three inertia moments differ, the grain shape lies between a prolate and an oblate spheroid.

The evolution of these ratios with respect to grain size is shown in Figure 6. From these results, we observe that silicate grains tend to become more spherical when growing, as expected. However, during the growth process grains tend to be slightly prolate.

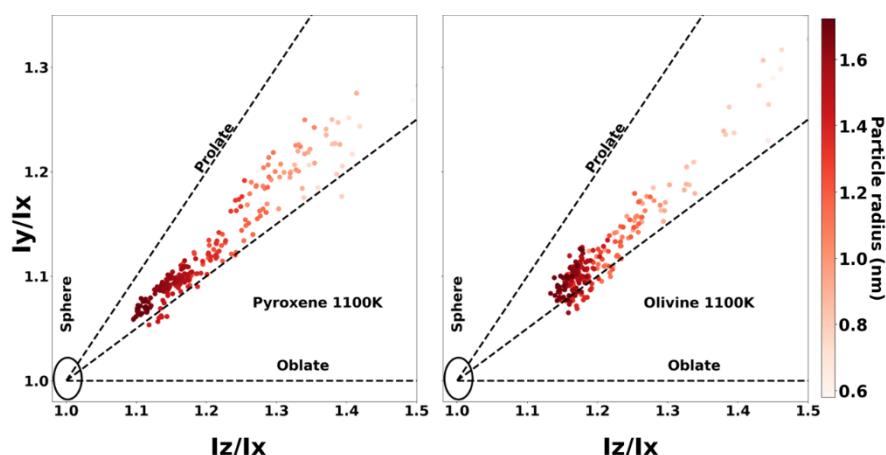


Figure 6: Silicate grain shape evolution for simulations of pyroxenic (left) and olivinic (right) grains at 1100K. The results are obtained from averages over ten nucleated growth simulations.

Grain surface area

If the particles become more spherical as they grow, the decrease in sphericity observed in Figure 5 should be attributed to an increase in surface roughness. To confirm this, we compared the surface area of the growing grains with that of a perfect sphere.

The results presented in Figure 7 clearly show a significant excess in surface area with olivine grains having around 80% excess surface area and pyroxene grains having over 120% excess surface area by the end of the simulations.

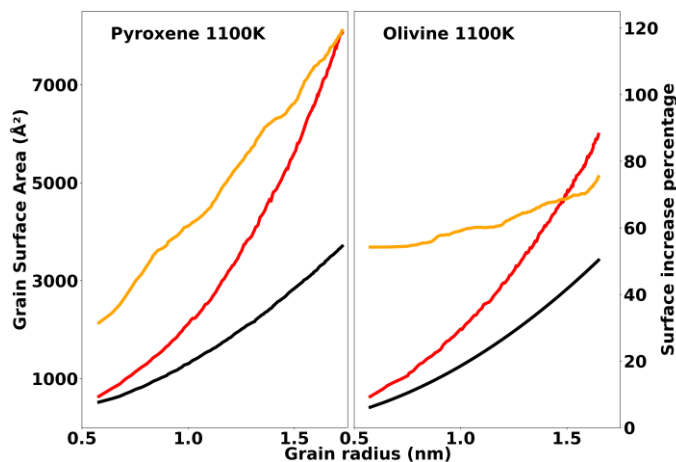


Figure 7: Surface area of growing grains (red line) and of a sphere with same radius as the grain (black line) referred to left y-axis. The orange line shows the percentage of excess surface area of the grains with respect to the corresponding sphere. Results are shown for pyroxenic (left) and olivinic (right) grains at 1100K. The results are obtained from averages over ten nucleated growth simulations.

Additionally, by directly visualizing the surface of typical olivinic and pyroxenic grains (see Figure 8) it is evident that, while the grain shape remains close to being spherical, the pyroxenic grains exhibit considerably more surface roughness.

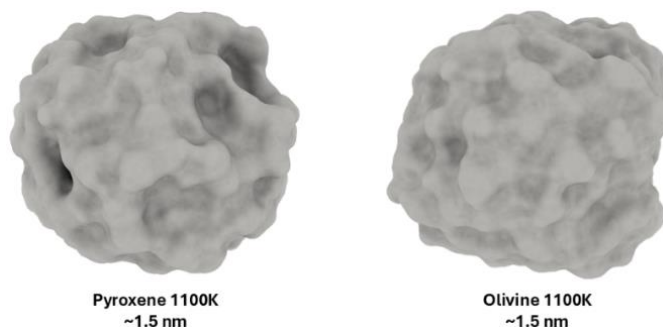


Figure 8: Visual representation of the surfaces of two typical grains with pyroxene (left) and olivine (right) composition. Both grains were obtained by nucleated growth simulations at 1100K and have ~1.5 nm radii.

Silica segregation

Mg-rich silicates can be thought of as solid mixtures of MgO (i.e. magnesia) and SiO₂ (i.e. silica). In pyroxenic crystals, the 1:1 (SiO₂)(MgO) mixture forms oxygen-sharing linear chains of SiO₄ tetrahedra, with Mg²⁺ occupying the space between the chains. In contrast, in the relatively silica-poor (SiO₂)(MgO)₂ mixture in olivine crystals, the SiO₄ tetrahedra are isolated, with Mg²⁺ ions filling the space between them. In amorphous pyroxenic grains these tendencies promote silica-segregated regions to form more easily than in amorphous olivinic grains.

To analyse the presence of silica segregated regions in our grains we employ the Q^{*n*} notation, where *n* denotes the number of Si-O units bonded to an individual silicon atom. This classification leads to an assignment of each silicon atom in a grain to one of five groups with *n* ranging from 0 to 4 (see Figure 9).

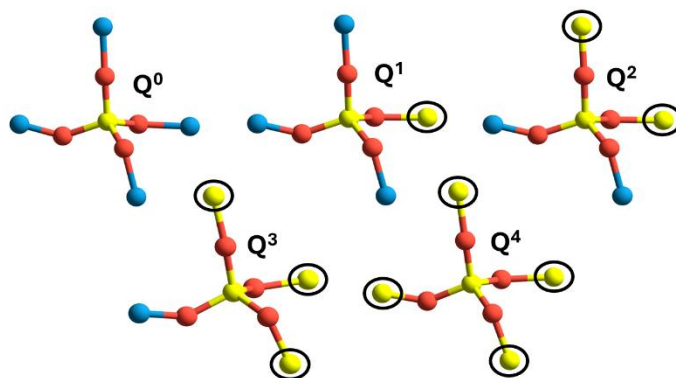


Figure 9: Examples of Si atoms belonging to different Q^{*n*} groups. Mg, Si and O atoms are represented as blue, yellow and red spheres respectively. The reference Si atom in each case is the Si atom in the center of each tetrahedron.

According to this scheme, a high proportion of Q² Si atoms would indicate the presence of silica chains while a dominance of Q⁰ and Q¹ would suggest an atomistic structure more in line with that of olivine crystals. Conversely, a larger presence of Q³ and Q⁴ Si atoms would imply the formation of dendritic silica chains.

Figure 10, shows the distribution of Q^n centers at three different stages of the growth simulations. The results confirm that pyroxenic grains exhibit prominent silica segregated regions, characterized by significant amounts of Q^2 Si centers. In contrast, olivinic grains show more limited segregation with most Si atoms falling into the Q^0 group.

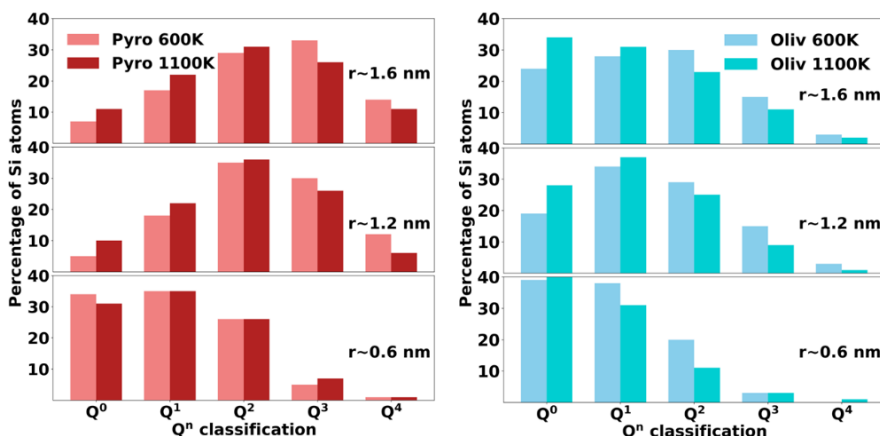


Figure 10: Evolution of Q^n populations at different stages of growth for pyroxenic grains (left) and olivine (right) at 600 K and 1100 K. The results are obtained from averages over ten nucleated growth simulations.

Additionally, simulations carried out at higher temperatures result in lower silica segregation *i.e.* most Si atoms are found in groups with smaller n compared to their lower-temperature counterparts. This effect is attributed to the increased atomic mobility at higher temperatures, that allows atoms to move and occupy lower energy positions. Specifically, in olivinic grains, the temperature increase enhances Q^0 group while reducing groups with $n > 1$. In contrast, for pyroxenic grains, higher temperatures reduce groups with $n > 2$, while Q^2 remains the most populated group.

To further analyse the relationship between temperature and silica segregation, we carried out simulated annealing of various grains. This procedure involved heating the grains to 1600K over 500 ps, starting from its growth temperature. Afterwards the temperature was held constant for 1000 ps before being decreased stepwise by 100 K every 100 ps, with each decrease followed by a 200 ps equilibration period. This stepwise procedure was repeated until the original temperature was reached.

The comparison shown in Figure 11, demonstrates that annealing clearly reduces the degree of silica segregation in the grains. In all cases, simulated annealing leads to an increase of the fraction Q^0 and Q^1 centers. This effect is more pronounced in olivine than in pyroxene grains, where the largest group is Q^2 , suggesting that they possess several 1D Si-O-Si chain-like structures.

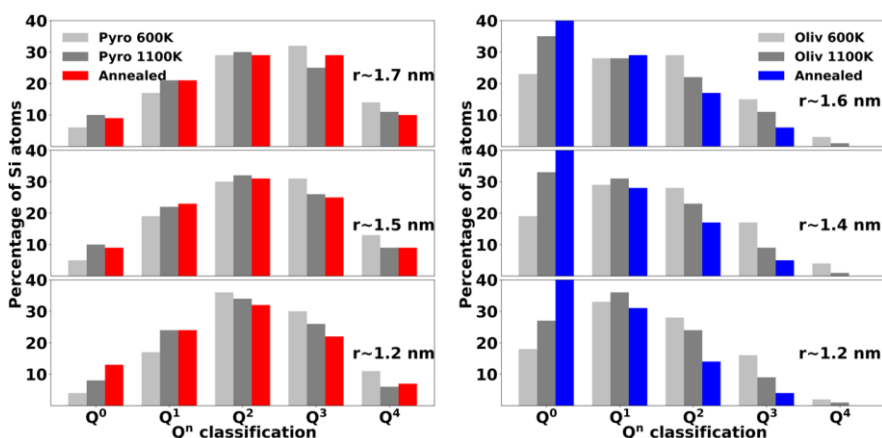


Figure 11: Comparison of the Q^n populations between annealed pyroxene (red) olivine (blue) and non-annealed (grey) grains at different stages of the simulation of pyroxenic (left) and olivine (right) compositions. The results are obtained from an average over ten nucleated growth simulations.

To more directly illustrate the relatively higher degree of silica segregation in pyroxenic grains, Figure 12 shows a cross-sectional view of the atomistic structure of a typical pyroxenic and olivinic grain. In the pyroxenic grain more extended (Si-O-Si)-linked regions (i.e. regions dominated by red and yellow colors) are clearly observed. On the other hand, in olivinic grains the distribution is more uniform with Mg atoms occupying more space between distributed small, localized regions of Si-O bonding.

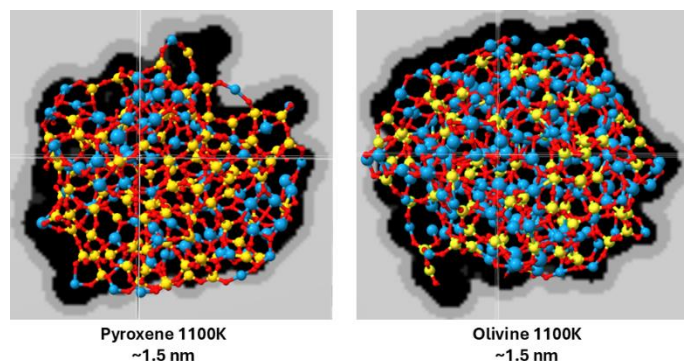


Figure 12: Visual representation of cross sections of the atomistic structure of two grains with pyroxenic composition (left) and olivinic composition (right). Both grains were obtained by nucleated growth simulations at 1100K and have a ~1.5 nm radii. Mg, Si and O atoms are represented as blue, yellow and red spheres respectively.

Dipole moments

The evolution of the dipole moments of the silicate grains is a crucial parameter for assessing their potential to emit in the microwave region of the electromagnetic spectrum. This is particularly important in astronomical environments, as small nanosilicates are proposed as potential carriers of the Anomalous Microwave Emission (AME). The AME is a foreground feature, observed in the 10-60 GHz range, and is observed in various astrophysical environments¹⁴. The ability of nanosilicates to emit microwave radiation and to reproduce AME models has been confirmed by computational modelling based on DFT calculations¹⁵.

As has been discussed in Chapter 5, the parameter used to evaluate the potential of a grain to emit microwaves is:

$$\beta = \frac{\mu}{\sqrt{N}} \quad (7)$$

where μ is the total dipole moment of the grain in units of Debye and N is the number of atoms in the grain. If this value is larger than 0.3, previous studies have found that ultrasmall silicate grains can be viable carriers of the AME¹⁶.

To analyze the evolution of the β parameter during the nucleated growth simulations, we calculated the dipole moments of the grains by considering the atoms as point charges according to the FF described in Appendix E.

The results displayed in Figure 13, indicate that throughout the nucleation process, the β values for the grains remain well above the 0.3 threshold, demonstrating that these grains retain the ability to emit microwave radiation that is compatible with the AME. Additionally, temperature appears to influence the β value evolution with size. At lower temperature, β tends to increase with grain size, while at higher temperature it decreases. This behavior can be attributed to the increased mobility of the atoms at higher temperature, allowing them to find more stable positions, which tends to reduce the total dipole moment of the grain.

It is also important to note, however, that the value of β alone cannot be considered a definitive indicator of a grain's ability to emit microwaves. One additional requirement is that the grains must spin fast enough. Therefore, although the β values presented exceed the minimum intensity threshold, it is possible, especially for the largest grains, that they may not spin fast enough to emit microwave radiation that is consistent with the AME frequency range.

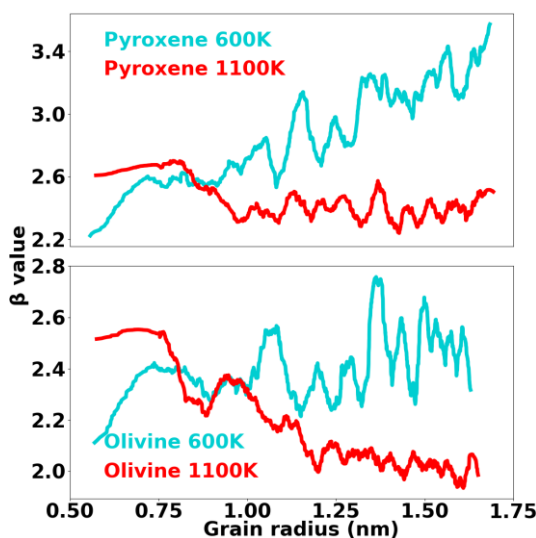


Figure 13: β value evolution during the simulation of pyroxenic (top) and olivine (bottom) grains, at 600 K (blue) and 1100 K (red). The results are obtained from averages over ten nucleated growth simulations.

Infrared spectra

As extensively discussed in previous chapters of this thesis, IR spectroscopy is the primary tool to study silicate dust present in different astronomical environments. It has also been noted that the IR spectra of small nanosilicates differs from those of amorphous bulk grains, and that these differences could make nanosilicates detectable using JWST observations (see Chapter 6).

The growth of nanosilicate grains must, therefore, influence their IR spectra, as with increasing size the IR spectra of the grains must converge to that of the bulk. However, it is not possible to predict beforehand which size grains become spectrally bulk-like. To address this question, we computed the IR spectra of all the grains in our simulations. Once the spectra were obtained, we built the characteristic IR spectra of different nanosilicate populations by weighting their spectra according to the size of the grain using Gaussian distribution with standard deviation of 0.1 nm.

Figure 14 presents the IR spectra of different grain size populations. To compute the spectra a different FF, previously shown to be accurate to compute silicates IR, was employed¹⁷.

In Appendix E, a discussion of the accuracy of the employed FF to obtain harmonic IR spectra, with respect to harmonic DFT-PBE0 can be found.

The spectra in Figure 14 show that populations with grain radii < 1 nm maintain differences with respect to typical IR spectra of bulk amorphous silicates. However, as the grains grow, these differences diminish, and in the population of larger grain sizes the IR spectra become almost indistinguishable from those of bulk silicates. The clearest indicator of this spectral evolution is the shift observed in the signal around 11 microns. This signal, which is expected to be observable with JWST (see chapter 6), moves to shorter wavelengths as the grains grow, eventually merging with the ~ 9 microns signal to produce the characteristic 10-micron signal observed in bulk silicates. Another less easily detectable indicator is the signal that initially emerges around 16 microns.

As the grains grow, this signal gradually shifts to longer wavelengths, eventually appearing in the 18 micron region, where bulk amorphous silicate signals are expected. As shown in Chapter 6, this signal is more intense for olivinic grains.

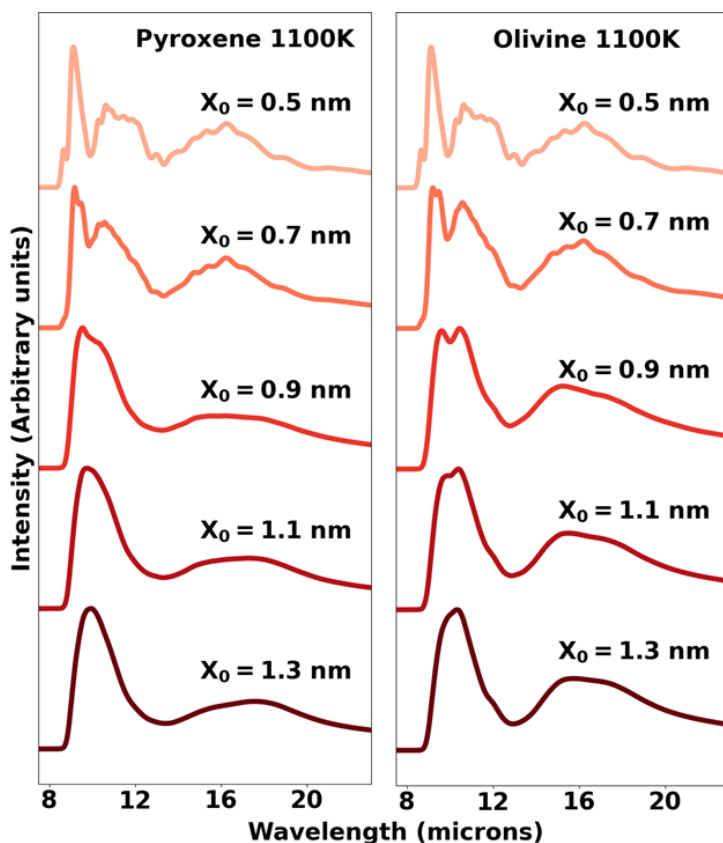


Figure 14: Evolution of IR spectra of different grain size populations containing pyroxene (left) and olivine (right) grains at 1100 K. X_0 values indicate the average radius of the grain in the population.

To study the effect of thermal annealing on the IR spectra, we carried out simulated annealing of the grains obtained three different sizes, following the analysis of silica segregation above (see Figure 11). The comparison between the IR spectra from the non-annealed and annealed grains is shown in Figure 15. This comparison reveals that the primary effect of annealing on the IR spectra is a reduction in the intensity of the region between the two main signals at 10 and 18 microns. This reduction could be linked to the relaxation of some Si-O bonds during annealing, which leads to bond shortening and a corresponding shift in vibrational frequencies to shorter wavelengths.

Additionally, the 15–16-micron signal shifts to longer wavelengths. Since this signal corresponds to O-Si-O bending modes, its shifting would be attributed to the relaxation of these angles, resulting in reduced strain and therefore lower vibrational energy.

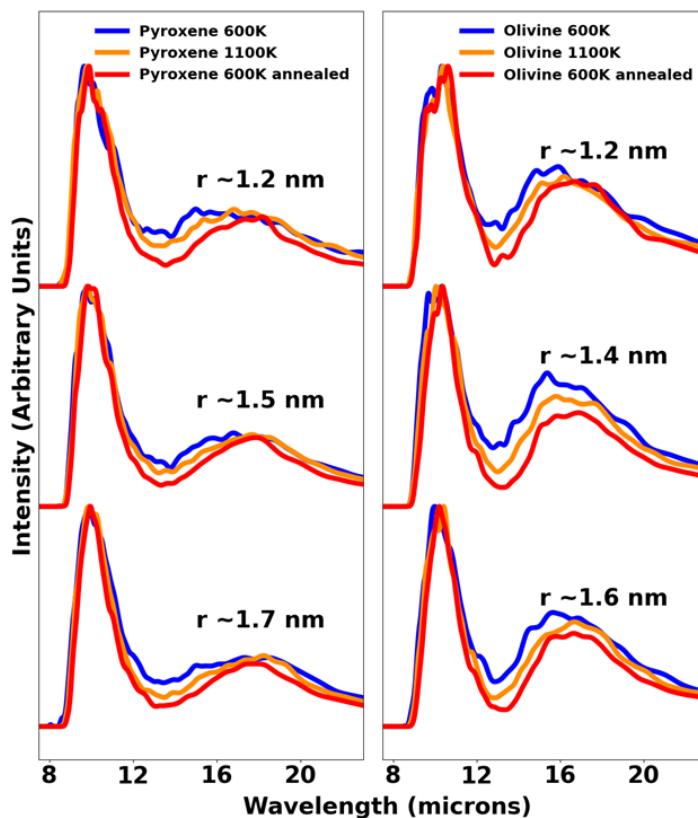


Figure 15: Comparison of IR spectra for annealed (red lines) and non-annealed grain at 600 K (blue lines) and 1100 K (orange lines) for three different grain size populations with pyroxenic (left) and olivine (right) compositions. The spectra are obtained from averages of ten nucleated growth simulations.

10-micron signal fitting

One of the procedures employed by astronomers to study the spectroscopic features in their IR observations consists of fitting the signals using different types of analytical functions. For the 10-micron signal, the most used functions are Gaussian or skewed Gaussian functions. These functions have been shown to yield good results to fit this feature, even accounting for the deviations observed at 11 microns, which are typically attributed to the presence of crystalline silicates¹⁸.

Here, we aimed to mimic the process of fitting astronomical observations by using a Gaussian function combined with a skewed Gaussian function to fit the region between 7.5 and 13 microns of the spectra of the populations presented in Figure 14.

As shown in Figure 16, the fittings provide qualitatively good results based on visual inspection, although the region between 11.6 and 13 microns is not well reproduced for populations containing nanosilicates with radii > 0.9 nm. Nevertheless, the key outcome from these fittings is that two (skewed) Gaussian functions are required to accurately fit this region of the spectra.

The Si-O stretching wavelength depends on bond length as observed in silicate glass networks^{19,20}. The presence of two distinct signals in this region of the spectra could be explained by the existence of two Si-O bond length populations. The two IR signals in small grains could arise from the limited possibilities in which Si and O atoms can bond, possibly leading to two dominant Si-O bond lengths.

As grains grow, we expect the number bonding configurations to increase, resulting in a broader range of bond lengths that cause the two signals to merge as observed in Figure 14. To confirm this hypothesis, we analyzed the Si-O bond lengths in all the grains obtained from our simulations. We then classified these distances into two groups based on the degree of perturbation caused by surrounding atoms. We take the least perturbed case to be an isolated terminal Si-O. We note that we did not obtain a significant portion of such bonds. Cases with Si-O-Mg bonds were found to induce a relatively low perturbation to the Si-O bond.

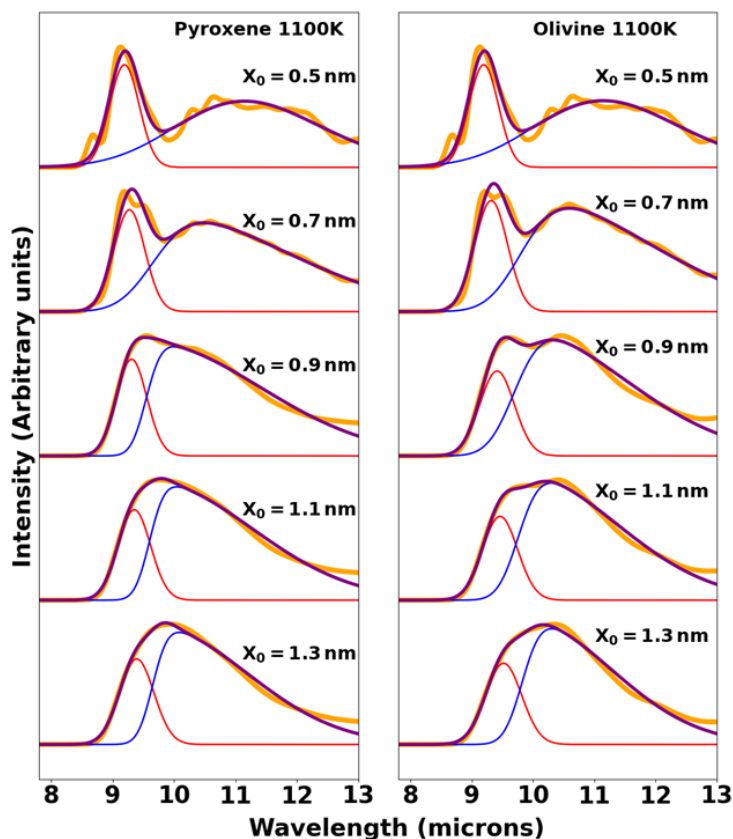


Figure 16: Fitting (purple) of the IR spectra of grain populations in Figure 14 (Orange) using a Gaussian function (red) and a skewed Gaussian function (blue).

In contrast, Si-O-Si and Si-O-Mg₂ groups, where the presence of a neighboring Si or Mg atoms induced a greater distortion of Si-O bond and were classified as more perturbing to the corresponding Si-O bond.

Figure 17 presents the histogram of Si-O bond lengths, weighted according to the average radii of the grains in the population, using the same procedure applied to construct the IR spectra in Figure 14). The histograms are divided in two according to the aforementioned grouping into low and high Si-O perturbations. As seen in these histograms, the populations containing the smallest grains exhibit two relatively narrow distributions of the Si-O bond lengths, with most values clustering around ~ 1.62 or ~ 1.66 Å.

These narrow well-separated distributions would then cause the presence of two distinct IR signals, as observed in the corresponding IR spectra in Figure 14.

As the grains grow, the bond length distribution broadens allowing a greater range of possible Si-O perturbation scenarios. This causes a broadening of the distributions and therefore the broadening of the IR signals, as well as their combination to form a single band. Additionally, it is important to note that the population of the group containing Si-O-Si bonds is larger in pyroxene than in olivine. This can be easily attributed to the larger degree of silica segregation already observed in Figure 10

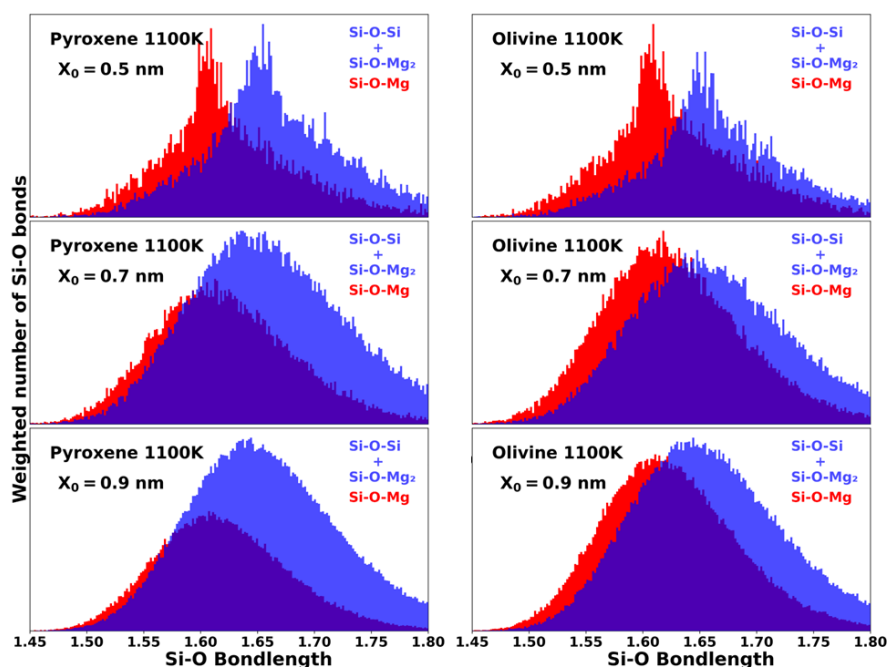


Figure 17: Histograms showing the weighted number of Si-O bonds with a given bond length, for different Si-O environments, for a population of grains with average radii of 0.5 (top), 0.7 (middle) and 0.9 nm (bottom). The grain populations are the same as in the spectra of Figure 14

10.3 Conclusions

These findings, combined with the additional data and analysis provided in Appendix E support the following conclusions:

- 1- The NAGGS code to simulate the nucleated growth of dust grains has been developed. NAGGS allows the simulation of grain growth at different astronomically relevant chemical compositions at any desired temperature.
- 2- The simulations carried out using NAGGS have been used to provide insights into a range of silicate grain sizes, from the molecular level and ultrasmall silicate to larger nanograins containing thousands of atoms
- 3- The sphericity of the silicate grains decreases as they grow. An analysis into the origin of the sphericity reduction allows us to conclude that it is caused by an increase in the surface roughness of the grains, while their shape is highly spherical.
- 4- The simulated silicate grains are susceptible of having silica segregation regions in their structure, especially the grains with pyroxenic composition. Thermal annealing of the grains largely reduces the silica segregation in olivinic grains.
- 5- Silicate grains have large enough dipole moments to emit microwave emission compatible with the observed AME, although for larger grains their rotation rate should be studied to confirm this.
- 6- The IR spectra of small silicate grains (radii < 0.9 nm) exhibit large differences with respect to amorphous bulk silicate IR spectra. This difference is mostly observed as a signal at ~ 11 microns that disappears in larger grains to produce IR spectra more in line with those observed for amorphous bulk silicates.

- 7- The annealing of silicate grains produces a reduction of the IR intensity close to ~13 microns and a reduction of the intensity close to ~16 microns but does not significantly change the overall shape of the spectra.
- 8- The IR spectra of the grains between 8 and 13 microns can be well fitted by a combination of a Gaussian function and a skewed Gaussian function.
- 9- The analysis of the Si-O bond length distribution shows the presence of two types of Si-O bonds, depending on the degree of perturbation caused by surrounding atoms. Small nanosilicates exhibit narrower Si-O bond length distributions that are in line with the 9 and 11 micron signals observed in the IR spectra. Larger grains have broader Si-O bond length distributions, in agreement with the merging of the two associated bands in the IR spectra.

10.4 References

- ¹ Gail, H.-P.; Sedlmayr, E. Inorganic dust formation in astrophysical environments. *Faraday Discuss.* 1998, 109, 303–319
- ² Gail, H.-P. and Sedlmayr, E. Dust formation in stellar winds. II-Carbon condensation in stationary, spherically expanding winds. *Astronomy and Astrophysics*. **1985**, 148(1) 183-190.
- ³ Gail, H.-P. and Sedlmayr, E. Mineral formation in stellar winds. I. Condensation sequence of silicate and iron grains in stationary oxygen rich outflows. *Astronomy and Astrophysics*, v. 347, p. 594-616 (1999), 1999, vol. 347, p. 594-616.
- ⁴ Ferrarotti, A. S. and Gail, H.-P. Composition and quantities of dust produced by AGB-stars and returned to the interstellar medium. *Astronomy & Astrophysics*, 2006, vol. 447, no 2, p. 553-576.
- ⁵ Ferrarotti, A. S. and Gail, H.-P. Mineral formation in stellar winds-III. Dust formation in S stars. *Astronomy and Astrophysics*. **2002**, 382(1), 256-281.
- ⁶ Gobrecht, D.; Plane, J. M. C.; Bromley, S. T.; Decin, L.; Cristallo, S. and Sekaran, S. Bottom-up dust nucleation theory in oxygen-rich evolved stars. Aluminium oxide clusters. *Astronomy and Astrophysics*. **2022**, 658, A167.
- ⁷ Goumans, T. P. M. and Bromley, S. T. Efficient nucleation of stardust silicates via heteromolecular homogeneous condensation. *Monthly Notices of the Royal Astronomical Society*. **2012**, 420(4), 3344-3349.
- ⁸ Escatllar, A. M.; Lazaukas, T.; Woodley, S. M. and Bromley, S. T. Structure and properties of nanosilicates with olivine (Mg₂SiO₄)_N and pyroxene (MgSiO₃)_N compositions. *ACS Earth and Space Chemistry*. **2019**, 3(11), 2390-2403.
- ⁹ Thompson, A. P.; Aktulga, H. M.; Berger, R.; Bolintineanu, D. S.; Brown, W. M.; Crozier, P. S.; Veld, P. J.; Kohlmeyer, A.; Moore, S. G.; Nguyen, T. D.; Shan, R.; Stevens, M. J.; Tranchida, J.; Trott, C. and Plimpton, S. J. LAMMPS-a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Computer physics communications*. **2022**, 271, 108171.

- ¹⁰ LI, A. and Draine, B. T. On ultrasmall silicate grains in the diffuse interstellar medium. *The Astrophysical Journal*. **2001**, 550(2), L213.
- ¹¹ WADELL, Hakon. Volume, shape, and roundness of quartz particles. *The Journal of geology*. **1935**, 43(3), 250-280.
- ¹² Eager, D.; Chapman, C.; Qi, Y.; Ishac, K. and Hossain, Md I. Additional criteria for playground impact attenuating sand. *Applied Sciences*. **2021**, 11(19), 8805.
- ¹³ Maglic, J. B. and Lavendomme, R. MoloVol: an easy-to-use program for analyzing cavities, volumes and surface areas of chemical structures. *Applied Crystallography*. **2022**, 55(4), 1033-1044.
- ¹⁴ Cepeda-Arroita, R.; Harper, S. E.; Dickinson, C.; Rubiño-Martín, J. A.; Génova-Santos, R.T.; Taylor, A. C.; Pearson, T. J.; Ashdown, M.; Barr, A.; Barreiro, R. B.; Casaponsa, B.; Casa, F. J.; Chiang, H. C.; Fernandez-Cobos, R.; Grumitt, R. D. P.; Guidi, F.; Heilgendorff, H. M.; Herranz, D.; Jew, L. R. P.; Jonas, J. L.; Jones, M. E.; Lasenby, A.; Leech, J.; Leahy, J. P.; Martínez-González, E.; Peel M. W.; Piccirillo, L.; Poidevin, F.; Readhead, A. C. S.; Rebolo, R.; Ruiz-Granados, B.; Sievers, J.; Vansyngel, F.; Vielva, P. and Watson, R. A. Detection of spectral variations of Anomalous Microwave Emission with QUIJOTE and C-BASS. *Monthly Notices of the Royal Astronomical Society*. **2021**, 503(2), 2927-2943.
- ¹⁵ Escatllar, A. M. and Bromley, S. T. Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study. *Astronomy and Astrophysics*. **2020**, vol. 634, p. A77.
- ¹⁶ Hensley, B. S. and Draine, B. T. Modeling the anomalous microwave emission with spinning nanoparticles: no PAHs required. *The Astrophysical Journal*. **2017**, 836(2), 179.
- ¹⁷ Walker, A. M.; Wright, K. and Slater, B. A computational study of oxygen diffusion in olivine. *Physics and Chemistry of Minerals*. **2003**, 30, 536-545.
- ¹⁸ Do-Duy, T.; Wright, C. M.; Fujiyoshi, T.; Glasse, A.; Siebenmorgen, R.; Smith, R.; Stecklum, B. and Sterzik, M. Crystalline silicate absorption at 11.1 μ m: ubiquitous and abundant in embedded YSOs and the interstellar medium. *Monthly Notices of the Royal Astronomical Society*. **2020**, 493(3), 4463-4517.

¹⁹ Liu, H.; Hahn, S. H.; Ren, M.; Thiruvillamalai, M.; Gross, T. M.; Du, J.; van Duin, A. C. T. and Kim, S. H. Searching for correlations between vibrational spectral features and structural parameters of silicate glass network. *Journal of the American Ceramic Society*. **2020**, 103(6), 3575-3589.

²⁰ Liu, H.; Kaya, H.; Lin, Y. T.; Ogrinc, A. and Kim, S. H. Vibrational spectroscopy analysis of silica and silicate glass networks. *Journal of the American Ceramic Society*. **2022**, 105(4), 2355-2384.

CHAPTER 11

General Conclusions

In the present thesis various aspects and properties of nanosilicates have been investigated through computational modeling, with the aim of improving our understanding of these crucial dust species in a range of astronomical environments and processes. The research has primarily focused on the accurate determination of the vibrational modes of different nanosilicate grains. This work provides deeper and more detailed insights into these spectra and the associated underlying atomistic structure. This work thus significantly refines empirical bulk-derived models of small silicate grains commonly used by the astronomical community. Additionally, this work has also studied the potential detectability of nanosilicates through IR observations, providing predictions that could help the interpretation of future astronomical observations by JWST.

Although the results and conclusions of the research have been previously covered at the end of each chapter, the overall conclusions of the thesis are presented here.

- Harmonic vibrational frequencies obtained using DFT with PBE0 and B3LYP functionals show strong agreement with those derived from high level *ab initio* electronic structure methods, thus confirming their reliability for studying nanosilicates.

- The IR spectra of small nanosilicates are significantly influenced by temperature, which can induce conformational pre-melting transitions between energetically similar isomers.
- Vibrational mode distributions obtained from DFT calculations deviate substantially from models based on the extrapolation of mode distributions of bulk materials, highlighting the difference behavior of nanoscale silicates
- Previous empirical estimates of the instantaneous temperature rise of nanosilicates upon UV radiation absorption were likely underestimated by 35–80K, indicating a potentially higher IR emission for these species than previously predicted.
- Water molecule adsorption on the surface of nanosilicates does not affect their capacity to be the source of the AME. This holds for both molecular and dissociative addition of water. While successive addition of dissociated water molecules tends to slightly reduces the dipole moments of the grains, it does not enough to affect its potential contribution to AME.
- The IR spectra of nanosilicate populations containing around 100 different isomers, with a range of chemical composition and sizes, differ significantly from those of amorphous bulk silicates. These distinct spectral signals may be detectable with future JWST observations of both the diffuse and dense ISM.
- Harmonic vibrational frequencies obtained using DFT with PBE0 are in good agreement with the experimental spectra of cationic nanosilicates. This agreement allowed the definite structural assignment of the first ever nanosilicates produced in cluster beams. The experimentally produced clusters matched the lowest energy clusters found by global optimization searches. The strong interaction between these positively charged nanosilicates and oxygen may contribute to the observed oxygen depletion in the ISM.

- PBE0-based DFT harmonic vibrational frequencies of anionic nanosilicates are in good agreement with the measured IR spectra of nanosilicates produced in cluster beam experiments. This collaborative effort showed that the formation of nanosilicate anions is determined by the vertical EAs of the neutral species rather than their energetic stability. The computationally determined structures and properties of these species possess all the necessary requirements to be excellent candidate seeds for the nucleation of NLCs.
- The development of a code to model the nucleated growth of nanosilicate grains possessing up to 1000's of atoms has enabled the investigation of the size-dependency of various physical properties of this complex process with different temperatures and grain composition.
- Using the nucleated nanosilicate grain growth code, the IR spectra of nanosilicate populations with average radii below 0.9 nm are found to display clear differences from those of amorphous bulk silicates. The main size-dependent difference is an IR feature around 11 microns, which gradually blueshifts as the grains grow, eventually merging with the 9-micron feature to form a bulk-like signal near 10 microns.
- Throughout the entire grain growth process, the 10-micron region of the nanosilicates IR spectra can be well fitted using a combination of a Gaussian function and a skewed Gaussian function. These two functions are correlated with the presence of two distinct Si-O bond length populations in the grains, that depend on the degree of bond strength perturbation caused by surrounding atoms.

APPENDIX A

Supporting Information for:
How Does Temperature Affect the
Infrared Vibrational Spectra of
Nanosized Silicate Dust?

Supporting Information for:

How does Temperature Affect the Infrared Vibrational Spectra of Nanosized Silicate Dust?

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S1. Obtaining IR spectra from AIMD simulations

The equation for the transition probability between two different vibrational states, as function of the incidental radiation, can be expressed by means of Fermi's Golden Rule

$$P(\omega) = \frac{\pi F^2}{2\hbar^2} |\langle \phi_f | \hat{\mu} | \phi_i \rangle|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega)], \quad \text{Eq. 1}$$

where ω is the frequency of the incidental radiation, F is the electric field, $\hat{\mu}$ is the total dipole moment operator, ϕ_f and ϕ_i are the final and initial wavefunctions of the system respectively, and ω_{fi} the energy difference between the initial and final state defined as:

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} \quad \text{Eq. 2}$$

From this transition probability, one can derive the expression for the IR absorption cross section, $\alpha(\omega)$, in the Schrödinger representation:

$$\alpha(\omega) = \frac{4\pi^2}{3\hbar c n} \omega (1 - e^{-\beta\hbar\omega}) \sum_f \sum_i p_i |\langle \phi_f | \hat{\mu} | \phi_i \rangle|^2 (\omega_{fi} - \omega), \quad \text{Eq. 3}$$

where p_i is the probability to find the system in the initial vibrational state, c is the speed of light, n is the refraction index of the medium that (assumed to be 1 in all our studied cases), $\beta = \frac{k_B}{T}$, with k_B being the Boltzmann's constant and T the temperature of the system. The factor of $1/3$ is used to average over all the polarization directions of the radiation field.

From this absorption cross section, it is possible to define an absorption lineshape $I(\omega)$ to express $\alpha(\omega)$ in the Heisenberg representation:

$$I(\omega) = \frac{3\hbar c \alpha(\omega)}{4\pi^2 \omega (1 - e^{-\beta\hbar\omega})} = \sum_f \sum_i p_i |\langle \phi_f | \hat{d} | \phi_i \rangle|^2 (\omega_{fi} - \omega) \quad \text{Eq. 4}$$

$$\alpha(\omega) = \frac{4\pi^2}{3\hbar c n} \omega (1 - e^{-\beta\hbar\omega}) I(\omega) \quad \text{Eq. 5}$$

Therefore, to obtain $\alpha(\omega)$ the only term that one needs to compute is $I(\omega)$. It can be proved^{1,2} that the absorption lineshape can be computed from the Fourier transform of the dipole autocorrelation function, $C_\mu(t)$:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} C_\mu(t) dt \quad \text{Eq. 6}$$

$$C_\mu(t) = \langle \mu(0) \cdot \mu(t) \rangle, \quad \text{Eq. 7}$$

where $\mu(t)$ is time dependent total dipole moment of the system. To obtain the lineshape, and therefore the IR absorption cross section (see equation 5), this autocorrelation function can be obtained from tracking the total dipole moment of the system at each step of an AIMD simulation.

S2. Full list of calculated wavelengths and intensities for the P-2 nanocluster from a harmonic IR calculation using the PBE0 functional. Zero intensity indicates that the vibrational frequency is not IR active.

Wavelength	Intensity (Debye² a.m.u./Å²)
8.85	18.638
9.09	0.000
10.71	0.000
11.70	6.271
12.73	8.461
13.03	11.674
13.14	0.000
15.88	0.000
16.47	1.215
17.41	2.508
17.48	0.000
19.14	0.000
19.24	0.000
21.42	5.907
23.49	0.000
25.39	0.000
26.40	0.000
26.53	1.720
29.52	0.015
31.63	0.000
33.76	0.656
38.79	0.103
49.45	0.000
87.62	1.391

S3. Full list of calculated wavelengths and intensities for the P-2 nanocluster from a harmonic IR calculation using the B3LYP functional. Zero intensity indicates that the vibrational frequency is not IR active.

Wavelength	Intensity (Debye² a.m.u./Å²)
9.01	18.568
9.27	0.000
10.92	0.000
11.95	5.365
13.05	8.580
13.32	12.225
13.37	0.000
16.22	0.000
16.52	1.164
17.68	0.000
17.85	2.415
19.27	0.000
19.88	0.000
21.74	5.832
23.99	0.000
25.76	0.000
26.68	0.000
26.87	1.565
29.88	0.020
31.94	0.000
34.46	0.559
38.98	0.101
48.41	0.000
84.93	1.333

S4. Full list of calculated wavelengths and intensities for the O-2 nanocluster from a harmonic IR calculation using the PBE0 functional.

Wavelength (μm)	Intensity (Debye ² a.m.u./Å ²)
9.27	19.202
9.45	1.319
10.84	8.744
11.09	0.173
11.31	11.328
12.00	6.118
13.13	3.174
14.08	12.180
14.87	0.295
14.99	0.460
15.32	2.349
15.57	3.754
17.06	0.183
17.11	0.155
18.90	1.144
19.52	2.186
20.67	0.003
20.88	0.851
21.84	0.202
23.47	1.891
23.71	2.959
25.00	0.016
28.91	0.160
30.65	0.466
30.98	4.025
32.56	0.008
33.70	0.186
34.59	1.301
37.79	0.030
41.24	0.424
43.55	0.222
52.26	0.114
56.66	0.336
71.51	1.117
111.15	0.428
235.39	0.207

S5. Full list of calculated wavelengths and intensities for the O-2 nanocluster from a harmonic IR calculation using the B3LYP functional.

Wavelength (μm)	Intensity (Debye ² a.m.u./Å ²)
9.47	19.548
9.68	1.395
11.14	7.555
11.30	3.109
11.59	9.282
12.14	7.160
13.22	1.615
14.39	11.677
15.17	0.449
15.36	0.602
15.39	1.253
15.60	4.889
17.20	0.347
17.34	0.155
19.07	1.386
19.54	1.498
20.81	0.588
20.87	0.012
22.01	0.572
23.98	1.716
24.03	2.688
25.36	0.003
28.65	0.209
30.82	2.216
31.55	2.537
33.06	0.016
33.75	0.135
34.88	1.020
38.67	0.041
41.27	0.448
43.16	0.080
50.41	0.137
57.71	0.289
73.42	1.056
102.12	0.137
106.16	0.425

S6. Full list of calculated wavelengths and intensities for the O-2 (C2 conformation) nanocluster from a harmonic IR calculation using the PBE0 functional.

Wavelength (μm)	Intensity (Debye ² a.m.u./Å ²)
9.28	18.453
9.51	1.653
9.74	8.794
11.03	4.692
11.55	0.874
12.33	3.256
13.80	1.003
13.96	15.263
14.92	6.302
15.51	0.179
15.81	1.911
16.09	1.428
16.79	0.347
17.58	0.289
18.57	2.795
19.92	2.484
20.51	1.598
21.81	0.186
21.88	0.267
22.53	1.721
23.80	1.612
24.64	0.301
26.68	0.964
28.89	0.957
31.20	1.577
33.16	1.468
34.56	0.780
36.62	0.114
38.00	0.820
42.95	0.147
48.41	0.703
54.88	0.698
69.41	0.368
74.66	0.860
78.65	0.106
90.22	0.269

S7. Full list of calculated wavelengths and intensities for the O-2 (C2 conformation) nanocluster from a harmonic IR calculation using the B3LYP functional.

Wavelength (μm)	Intensity (Debye ² a.m.u./Å ²)
9.44	19.067
9.68	1.138
9.90	8.751
11.27	4.471
11.74	0.760
12.59	3.695
14.00	2.483
14.21	12.081
15.13	6.822
15.69	0.129
15.98	2.054
16.31	1.263
17.06	0.355
17.76	0.301
18.82	2.681
20.11	2.152
20.81	1.716
21.97	0.157
22.16	0.142
23.04	2.004
24.25	1.744
25.05	0.354
27.24	0.729
29.43	0.999
31.47	1.803
33.54	1.191
34.98	1.103
37.00	0.150
38.29	0.650
43.43	0.134
50.27	0.636
54.93	1.029
68.36	0.339
75.31	0.097
79.21	0.689
86.85	0.262

S8. List of experimentally determined wavelengths and oscillator strengths for crystalline Mg_2SiO_4 Forsterite¹ compared with selected wavelengths, intensities and oscillator strengths for the olivinic (Mg_2SiO_4) O-2 nanocluster from a harmonic IR calculation using the PBE0 functional.

Forsterite crystal (ref. Error! Bookmark not defined.)		O-2 nanocluster (present work)		
Experimental oscillator strength (adimensional)	Experimental wavelength (μm)	DFT-calculated (PBE0) wavelength (μm)	DFT-calculated (PBE0) intensity (Debye ² a.m.u./ $\text{\AA}^2$)	DFT-calculated (PBE0) oscillator strength (adimensional)
0.32	10.22	10.84	8.744	1.596e-4
0.17	10.42			
0.62	11.44	11.31	11.328	2.068e-4
0.4	11.45			
0.43	19.78	19.52	2.186	3.990e-5
0.35	19.81			
0.24	23.82	23.47 23.71	1.891 2.959	3.452e-5 5.402e-5
0.81	23.88			
0.63	24.30			
1.49	24.68			
0.52	25.18	25.00 28.91	0.016 0.160	2.921e-7 2.921e-6
0.96	26.10			
1.22	28.41			
0.32	33.78	33.70 34.59	0.186 1.301	3.395e-6 2.375e-5
1.21	34.16			
1.61	34.38			

S9. List of experimentally determined wavelengths and oscillator strengths for crystalline MgSiO_3 Enstatite² compared with selected wavelengths, intensities and oscillator strengths for the pyroxenic $(\text{MgSiO}_3)_2$ P-2 nanocluster from a harmonic IR calculation using the PBE0 functional.

Enstatite crystal (ref. Error! Bookmark not defined.)		P-2 nanocluster (present work)		
Experimental oscillator strength (adimensional)	Experimental wavelength (μm)	DFT-calculated (PBE0) wavelength (μm)	DFT-calculated (PBE0) intensity ($\text{Debye}^2 \text{ a.m.u./\AA}^2$)	DFT-calculated (PBE0) oscillator strength (adimensional)
0.002	8.68	8.85	18.638	3.402e-4
0.145	9.48			
0.524	10.64	11.70	6.271	1.144e-4
0.102	17.99	17.41	2.508	4.578e-5
0.074	22.28	21.42	5.907	1.078e-4
0.096	22.94			
0.922	26.99	26.53	1.720	3.140e-5
1.330	30.64	29.52	0.015	2.738e-7
0.125	34.09	33.76	0.656	1.198e-5

References

¹ de la Pierre, M.; Orlando, R.; Maschio, L.; Doll, K.; Ugliengo, P.; Dovesi, R. Performance of Six Functionals (LDA, PBE, PBESOL, B3LYP, PBE0, and WC1LYP) in the Simulation of Vibrational and Dielectric Properties of Crystalline Compounds. The Case of Forsterite Mg_2SiO_4 . *J. Comput. Chem.* 2011, 32, 1775–1784.

² Demichelis, R.; Suto, H.; Nöel, Y.; Sogawa, H.; Naoi, T.; Koike, C.; Chihara, H.; Shimobayashi, N.; Ferrabone, M.; Dovesi, R. The infrared spectrum of ortho-enstatite from reflectance experiments and first-principle simulations, *Mon. Not. R. Astron. Soc.* 2012, 420, 147–154.

APPENDIX B

Supporting Information for:
Efficiency of interstellar nanodust
Heating: Accurate Bottom-up
Calculations of Nanocilicates
Specific Heat Capacities

Supporting Information for:

Efficiency of Interstellar Nanodust Heating: Accurate Bottom-up Calculations of Nanosilicate Specific Heat Capacities

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S1 Effect of anharmonicity

To estimate the maximal effect of anharmonic frequency shifts, we took the largest temperature-induced downshift observed for some frequencies in small nanosilicates in our previous work (~5% at 800K)¹ and applied it to all frequencies for the 35-atom pyroxene (i.e. $(\text{MgSiO}_3)_7$) and olivine (i.e. $(\text{Mg}_2\text{SiO}_4)_5$) species. In Fig. S1a we plot the resulting “maximally anharmonic” vibrational mode spectra and the corresponding BFM mode spectrum for 35 atoms. Overall, the shifted spectral distributions do not change significantly with respect to the harmonic case. With respect to the bare harmonic spectra, the anharmonic pyroxene spectrum now coincides with the BFM spectrum between 700 cm^{-1} and 1000 cm^{-1} , but the olivine spectrum shows a greater overall mismatch with the BFM spectrum (see also Fig. 4 in the main text).

The resultant effect of this frequency downshift on the specific heat capacity with respect to that obtained from is very small. Specifically, in Fig. S2 we show the difference in the specific heat capacity resulting from downshifted mode spectra for the 35-atom pyroxene and olivine species with respect to those derived from the corresponding harmonic mode spectra. The resultant difference in the temperature of these nanosilicates (with respect to energy) compared to that calculated using the harmonic vibrational spectra is shown in Fig. S3. Here, the temperatures are maximally affected by 3.5-4.0% for very low energies, but with increasing energy the difference in temperature between the maximally anharmonic and harmonic approaches decreases significantly.

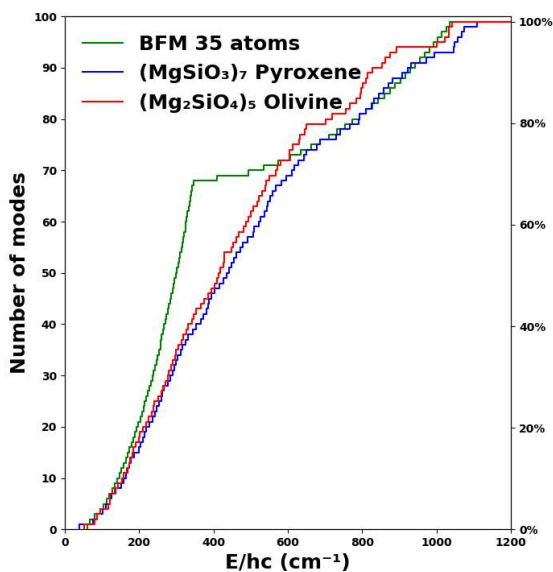


Figure S1 Vibrational mode spectra for 35-atom pyroxene (i.e. $(\text{MgSiO}_3)_7$) and olivine (i.e. $(\text{Mg}_2\text{SiO}_4)_5$) nanosilicates after application of a 5% downshift in all frequencies (i.e. maximally anharmonic) with respect to the corresponding BFM spectrum.

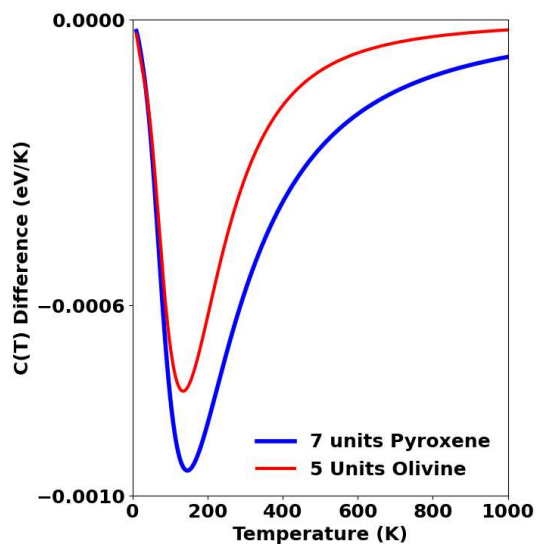


Figure S2. Difference in $C(T)$ calculated using the maximally anharmonic vibrational spectra with respect to $C(T)$ based on the harmonic vibrational spectra for 35-atom pyroxene (i.e. $(\text{MgSiO}_3)_7$) and olivine (i.e. $(\text{Mg}_2\text{SiO}_4)_5$) nanosilicates.

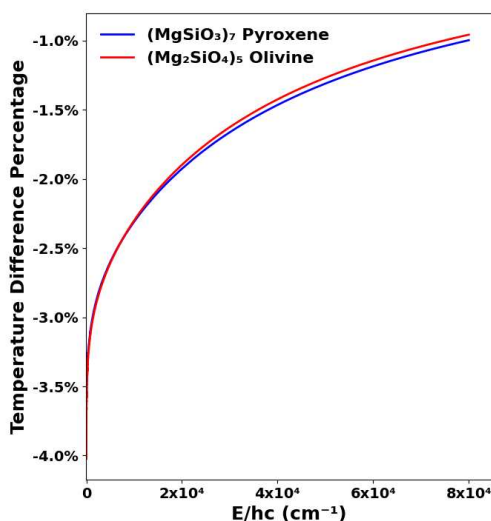


Figure S3. Percentage change in temperature of 35-atom pyroxene (i.e. $(\text{MgSiO}_3)_7$) and olivine (i.e. $(\text{Mg}_2\text{SiO}_4)_5$) nanosilicates with respect to energy as calculated using the maximally anharmonic vibrational spectra with respect to the temperature calculated using the harmonic vibrational spectra.

S2 Cartesian coordinates of metastable silicate dimers

Pyroxene isomers

Isomer 2:

10

$(\text{MgSiO}_3)_2$ 2nd isomer

Mg	-2.80820614	2.68486963	0.91914789
Mg	-0.67664681	-0.24206989	-1.10450779
Si	-2.6424027	1.32478257	-1.18982681
Si	-1.93422345	0.32795385	0.99748922
O	-0.87627754	-0.84707909	0.74418243
O	-3.42967538	2.69561035	-0.93486856
O	-2.41357017	1.26502003	2.2042514
O	-1.8921193	0.5836224	-2.39475733
O	-3.20918911	0.16043695	-0.10163372
O	-1.26969941	1.56337721	-0.08992473

Isomer 3:

10

$(\text{MgSiO}_3)_2$ 3rd isomer

Mg	0.65423788	-0.37484312	-0.81969484
Mg	-1.83203011	1.74348272	0.06482119
Si	-2.3451357	-0.78611903	-1.79554438

Si	0.39366047	1.23918846	1.05527673
O	0.12726478	1.57761033	-0.50453472
O	1.33384967	-0.0155445	1.08081398
O	-0.79487457	-1.18390255	-1.60252602
O	-3.30700587	-1.52584862	-2.72505024
O	-0.82579967	1.82514109	1.84852549
O	-2.75968588	0.49022221	-0.90243018

Olivine isomers:

Isomer 2:

14

(Mg₂SiO₄)₂ 2nd isomer

O	0.96548026	-2.63651933	1.59906559
Si	-0.3235138	-2.10788641	0.79229676
O	0.41979945	-0.76024505	-0.00021708
O	-1.14878965	-2.89032507	-0.34891871
O	-0.07724183	1.72735189	0.55083267
Mg	-1.42201277	0.53925945	1.17513145
Si	1.10216667	0.81686245	-0.20787842
O	-1.55780831	-1.31002345	1.58920909
O	2.51789689	0.54885824	0.51021163
Mg	-1.00545578	1.45834564	-1.35079005
O	-2.40804361	0.42673481	-0.56022127
O	0.84846113	1.20808136	-1.75002985
Mg	2.13675839	-1.24457064	1.03049939
Mg	-2.43383004	-1.47360089	-0.3493842

Isomer 3:

14

(Mg₂SiO₄)₂ 3rd isomer

O	-0.93595215	-0.52041685	2.11523282
Si	0.38778406	-0.95563131	1.32993186
O	3.30436814	-0.07787728	-0.04750157
O	-1.36066389	2.12882746	0.09014434
O	0.45673887	0.11736719	-0.05180572
Mg	2.69664036	-1.68133417	0.86241713
Si	0.19593226	1.86882173	-0.14424553
O	0.84969027	2.20034048	1.36125614
O	0.88944655	-2.34939793	0.68005857
Mg	-1.10883503	1.34806242	1.84124148
O	1.77186775	-0.55672583	2.21876054
O	1.15772429	2.12873678	-1.40287505
Mg	1.98915125	0.40544978	-1.33508867
Mg	2.39620028	1.03648552	1.37511267

¹ Mariñoso Guiu, J.; Macia Escatllar, A.; Bromley, S. T. How Does Temperature Affect the Infrared Vibrational Spectra of Nanosized Silicate Dust? *ACS Earth Space Chem.* **2021**, 5, 4, 812–823. DOI: 10.1021/acsearthspacechem.0c00341

APPENDIX C

Supporting Information for:
Cluster Beam Study of $(\text{MgSiO}_3)^+$
Based Monomeric Silicate Species
and Their Interactions with Oxygen:
Implications for Interstellar
Astrochemistry

Cluster Beam Study of (MgSiO₃)⁺-based Monomeric Silicate Species and their Interaction with Oxygen: Potential Astronomical Relevance

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S1 Methods

S1.1 Experimental method

Cationic magnesium silicate clusters were produced by pulsed laser ablation of a rotating MgSi rod target (Mg:Si = 2:1 molar ratio) using the second harmonic of a Nd:YAG laser. The ablation took place in a 3 mm diameter and 60 mm long growth channel in the presence of a short pulse of helium carrier gas seeded with 1% oxygen. The gas mixture was then expanded into vacuum forming a molecular beam, which was shaped by a 2 mm diameter skimmer and a 0.45 mm slit aperture, before entering the intracavity region where it interacted with the IR laser beam of the Free Electron Laser for Intra Cavity Experiments (FELICE, 310–2000 cm⁻¹; a 10 μs macropulse with picosecond duration micropulses at 1 GHz repetition rate; spectral width set to ~0.5% FWHM of the central frequency) crossing it at an angle of 35°. A few microseconds after interaction with FELICE, all ions were extracted by a set of pulsed high-voltage plates into a reflectron time-of-flight mass spectrometer and detected with a microchannel plate detector.^{1,2}

To correct for long-term source fluctuations, the experiment was operated at twice the FELICE repetition rate, allowing for the recording of reference mass spectra in between successive FELICE pulses. Whenever the IR frequency was in resonance with an IR-active vibrational mode of a given complex,

multiple IR photons were absorbed sequentially, leading to a heating of the complex and finally to its fragmentation, and consequently to a depletion of the detected signal in the mass channel of the complex. The IR-MPD spectra shown in this contribution represent the depletion yield $Y(\tilde{\nu})$ at wavenumber $\tilde{\nu}$, obtained via the equation

$$Y(\tilde{\nu}) = -\frac{1}{P(\tilde{\nu})} \ln \left[\frac{I(\tilde{\nu})}{I_0} \right]$$

where $I(\tilde{\nu})$ and I_0 are the mass peak intensities with and without laser light, respectively, and $P(\tilde{\nu})$ is the macropulse energy. To reduce the IR fluence with which the complexes are irradiated, the whole instrument can be translated up to 300 mm from the focus position leading to a 30-fold reduction in fluence but increased overlap between the laser and molecular beam and thus an increased signal to noise ratio. All spectra presented in this work were recorded 300 mm from the focus. To reduce the IR intensity further, the overlap between laser and molecular beams can be purposely misaligned such that the molecular beam only observes the lower intensity part of the laser beam. Such a reduced IR intensity typically leads to an increased spectral resolution of strong vibrational transitions at the cost of no longer detecting weaker bands. To get the best possible spectral information, IR-MPD spectra were obtained under two different conditions with the molecular beam observing the high and the lower intensity part of the laser beam.

S1.2 Assignment of mass peaks

Laser ablation of a binary MgSi target in the presence of a 1% $^{16}\text{O}_2/\text{He}$ pulse results in a typical distribution of magnesium silicate clusters as shown in Figure S1a. This mass spectrum is unusually rich due to the natural isotope distributions of magnesium and silicon, which leads to multiple mass peaks for each cluster size formed. Furthermore, 1% O_2 in the He carrier gas results in the preferred production of oxygen-rich clusters ($\text{Mg}_x\text{Si}_y\text{O}_z^+$ with $z > x+y$). Reduction of the oxygen percentage only reduces the overall cluster production but does not change the cluster size and composition distribution, showing the necessity of oxygen for the cluster formation process. Due to (1) the natural isotope distribution of Mg and Si which results in partially overlapping isotope distributions of different clusters and (2) the similar masses of Si_2 and MgO_2 units ($m(^{28}\text{Si}_2)=55.95$ u and $m(^{24}\text{Mg}^{16}\text{O}_2)=55.97$ u)³ as well as O_3 and Mg_2 units ($m(^{16}\text{O}_3) = 47.98$ u and $m(^{24}\text{Mg}_2)=47.97$ u, a mass difference that cannot be resolved in the TOF mass spectrometer)⁴ an unambiguous assignment of the individual mass peaks is not straightforward and must be done with particular care. Therefore, the experiments have been repeated with isotopically labeled oxygen ($^{18}\text{O}_2$) mixed into the He carrier gas as well with bare Si and Mg targets, respectively. The shift of individual mass signals upon isotopic labeling together with the calculated mass distribution arising (some examples are shown below) from the natural abundance of the Mg and Si isotope allows for a reliable assignment of the mass peaks. Furthermore, clusters of the same stoichiometry but produced with $^{16}\text{O}_2$ and $^{18}\text{O}_2$, respectively, are expected to exhibit similar patterns in the IR-MPD spectra with some spectral shifts due to the different masses of the oxygen isotopes. Comparison

with IR-MPD spectra obtained for clusters produced with bare Si and Mg targets, respectively, support or exclude the assignment to Si_yO_z^+ and Mg_xO_z^+ clusters. Based on all these considerations, we were able to unambiguously assign four series of clusters shown in Figure S1: the magnesium oxides $\text{MgO}_{6,8,10}^+$ and $\text{Mg}_2\text{O}_{5,7,9}^+$ as well as the magnesium silicates $\text{MgSiO}_{5,7,9,11}^+$ and $\text{Mg}_2\text{SiO}_{7,9,11}^+$. All other mass peaks cannot be assigned unambiguously and will not be further considered.

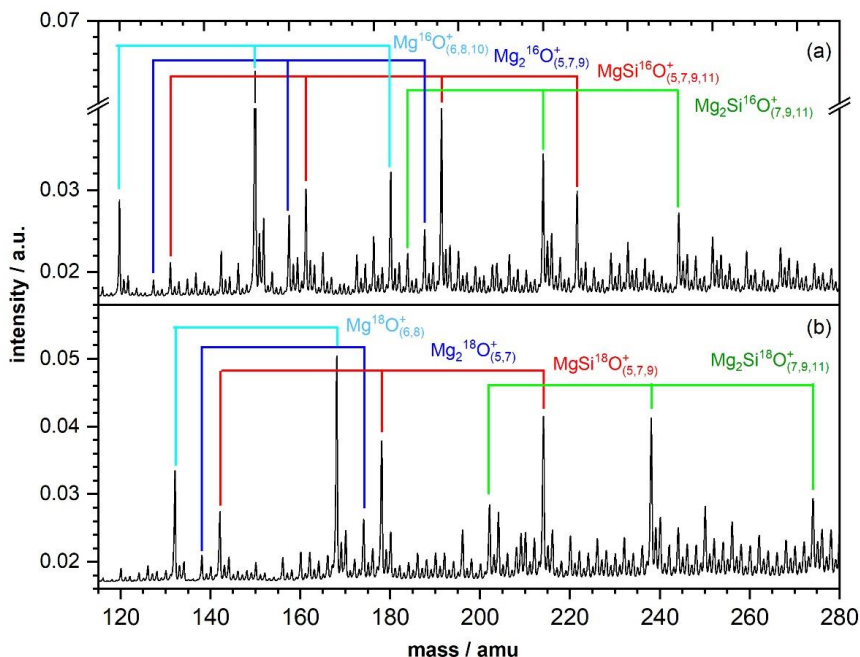


Figure S1. Ion mass distributions obtained by laser ablation of a Mg:Si = 2:1 target in the presence of a short pulse of helium carrier gas seeded with (a) 1% $^{16}\text{O}_2$ and (b) 1% $^{18}\text{O}_2$. The labeled mass signals were unambiguously assigned to the given stoichiometries based on isotope distribution patterns and the IR-MPD spectra.

S1.3 Computational methodology

To obtain different cluster isomers compatible with the experimental stoichiometries (see above) we initially assumed that clusters consist of a cationic bonded silicate core interacting with three oxygen molecules. We obtained candidate low energy isomers for each of the cores (MgSiO_3 and Mg_2SiO_3) using global optimization searches employing the Monte Carlo basin hopping algorithm⁵ and a polarizable classical interatomic potential (IP) as detailed in previous studies.⁶ For each silicate cationic core structure, we systematically sampled different positions around the core of the three interacting oxygen molecules. The structures of all candidates were optimized using Density Functional Theory (DFT) based calculations with the PBE0⁷ hybrid exchange correlation functional, and an accurate tight-tier 2 numerical atom-centered orbital basis set.⁸ Non-bonded dispersive interactions were described using the Tkatchenko-Scheffler method.⁹ For all structures, harmonic IR spectra were calculated to confirm that

our structures correspond to true energy minima and for comparison with the experimental IR spectra. All DFT calculations were carried out with the Fritz Haber Institute Ab Initio Molecular Simulations package (FHI-AIMS).¹⁰

In addition to species with a core surrounded by separate O₂ molecules, we also tested configurations in which one or more oxygen molecules were more intimately interacting with the core and/or with other oxygen molecules. In all cases several spin states were evaluated. We note that in one of the low energy isomers reported we find that the monomeric pyroxene core is so intimately bound to an O₂ molecule that it forms a O₃ ozone-like moiety (unlike all other reported isomers in which the three O₂ molecules remain separate). We further note that DFT calculations using the PBE0 functional have been shown to be suitable for calculating the relative energetics of small oxide clusters interacting with oxygen in various ways with respect to benchmark renormalized second-order perturbation theory calculations.¹¹ The PBE0 functional was also shown to be suitable for calculating the energetics of O₃ interacting/reacting with a small molecule relative to multiconfigurational quantum chemical calculations.¹²

In our calculations we assume that the experimentally prepared clusters are cooled enough so that finite temperature anharmonic effects are minimal. Accurate high-level quantum chemical calculations of the neutral bare pyroxenic MgSiO₃ monomer have confirmed that anharmonicity hardly affects the pure harmonic IR spectrum.¹³ Harmonic DFT calculations using the PBE0 functional have also been shown to accurately reproduce the infrared spectra of bulk crystalline olivine¹⁴ and pyroxene¹⁵, as well as the spectra of neutral olivinic and pyroxenic monomers.¹⁶ We note that DFT calculations using the PBE0 functional overestimate the frequency of the stretching vibration for the free O₂ molecule by ~200 cm⁻¹. As the O-O stretch vibrations (1400 - 1600 cm⁻¹) associated with weakly bound O₂ molecules are spectrally well separated from the main signature silicate vibrations (300 - 1200 cm⁻¹), we mainly use the frequencies for the latter calculated using the PBE0 functional to identify experimentally produced isomers. As a separate theoretical check on the high frequency part of the experimental spectra we also performed vibrational calculations on all isomers using the PBE¹⁷ functional which recovers the stretching vibrational frequency of the free O₂ molecule relatively well (although being poor for silicate vibrations).

S2 Assignment of mass peaks

S2.1 Assignment of mass m = 196 amu

One of the most intense signals in the mass spectrum obtained with a mixed MgSi target in the presence of helium seeded with ¹⁶O₂ is at mass m = 196 (cf. Figure S1). This mass can in principle be assigned to several different cluster stoichiometries, namely Si₃¹⁶O₇⁺, MgSi¹⁶O₉⁺, Mg₃Si¹⁶O₆⁺ or Mg₅Si¹⁶O₃⁺ (and some further oxygen-poor stoichiometries which we consider very unlikely to be produced). To determine the most likely stoichiometry, the experimentally detected isotope distribution (black curves in the

top panel of Figures S2) is compared with the isotope distribution of these clusters calculated on the basis of the natural abundance of Mg and Si (red curves in the top panel Figure S2). The best agreement between the experimental and the calculated isotope distribution is clearly given for $\text{MgSi}^{16}\text{O}_9^+$. To confirm this assignment, the experiments have been repeated with isotopically labeled oxygen, $^{18}\text{O}_2$ (Figure S2, bottom panel). The mass signal at $m = 214$ corresponding to $\text{MgSi}^{18}\text{O}_9^+$ is the only one that is comparable in intensity to the $m = 196$ amu signal in the $^{16}\text{O}_2$ experiment, whereas all other mass signals shown in the relevant mass spectral regions are considerably lower. The bottom panel of Figure S2 displays the theoretically obtained isotope distributions of $\text{Si}_3^{18}\text{O}_7^+$, $\text{MgSi}^{18}\text{O}_9^+$, $\text{Mg}_3\text{Si}^{18}\text{O}_6^+$ and $\text{Mg}_5\text{Si}^{18}\text{O}_3^+$ (green curves) together with the experimental mass spectra (black curves) in the corresponding mass regions. Again, the best agreement is obtained for $\text{MgSi}^{18}\text{O}_9^+$. Assignment of $m = 196$ amu in the $^{16}\text{O}_2$ experiments to the pure silicate cluster $\text{Si}_3^{16}\text{O}_7^+$ can be excluded upon comparison with the IR-MPD spectrum recorded on the mass of 196 amu produced with a pure Si target (in this case $m = 196$ amu can be unambiguously assigned to $\text{Si}_3^{16}\text{O}_7^+$) as shown in Figure S3. Finally, the assignment of $m = 196$ amu to $\text{MgSi}^{16}\text{O}_2^+$ is further substantiated by the similarity of the IR-MPD spectra (Figure 1 of the main text) recorded at $m = 196$ amu (with $^{16}\text{O}_2$) and $m = 214$ amu (with $^{18}\text{O}_2$), which show very similar patterns and spectral shifts consistent with the different masses of the oxygen isotopes.

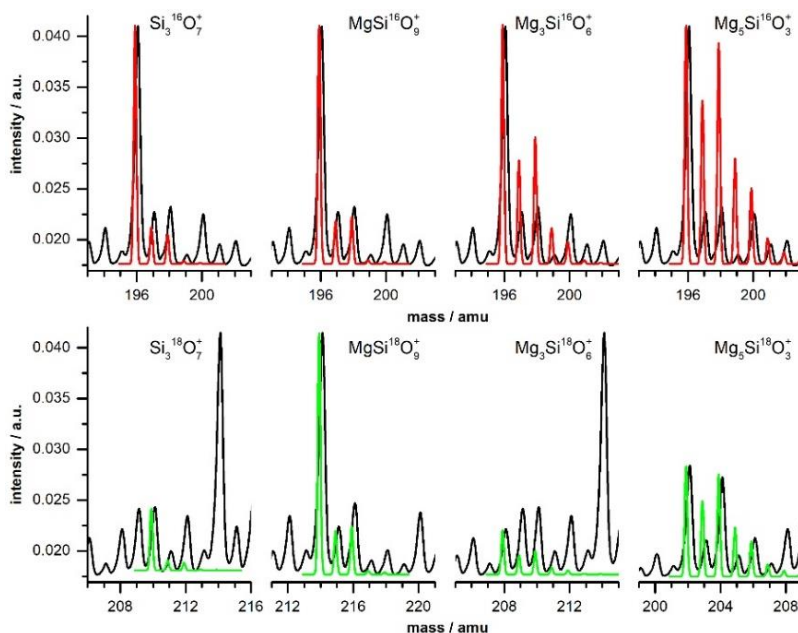


Figure S2: (top row) Experimentally obtained mass spectrum (black curves) around 196 amu obtained by laser ablation of a MgSi target in the presence of $^{16}\text{O}_2$. Also shown are theoretical isotope distributions (red curves) obtained on basis of the natural abundance of Mg and Si for several stoichiometries corresponding to a mass of 196 amu. (bottom row) Theoretical isotope distributions for the same clusters but with isotopically labeled $^{18}\text{O}_2$ (green curves) together with the experimental mass spectra in the corresponding mass regions.

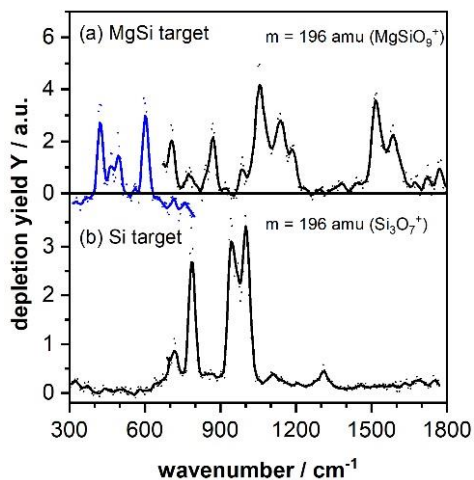


Figure S3: IR-MPD spectra obtained on the mass channel of 196 amu of the cluster distribution generated with a (a) mixed MgSi target and (b) a pure Si target, respectively. The mass $m = 196$ amu in the cluster distribution generated with a pure Si target (b) corresponds to the cluster stoichiometry $\text{Si}_3^{16}\text{O}_7^+$. In contrast, $m = 196$ amu in the cluster distribution obtained with a MgSi target (a) can in principle be assigned to different cluster stoichiometries as shown in Figure S2. Due to the significantly different IR-MPD spectra (a) and (b) an assignment to $\text{Si}_3^{16}\text{O}_7^+$ can be clearly excluded. The blue spectrum has been obtained at reduced IR macropulse intensity. The dots of the experimental spectra represent the sum of typically four to five spectra and the solid lines are obtained by a five-point average.

S2.2 Assignment of mass $m = 220$ amu

A second intense mass signal in the mass spectrum obtained with a mixed MgSi target in the presence of helium seeded with $^{16}\text{O}_2$ is at mass $m = 220$ amu (cf. Figure S1). This mass can in principle be assigned to $\text{Si}_5^{16}\text{O}_5^+$, $\text{MgSi}_3^{16}\text{O}_7^+$, $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$, $\text{Mg}_4\text{Si}^{16}\text{O}_6^+$ or $\text{Mg}_6\text{Si}^{16}\text{O}_3^+$ (and again some further oxygen-poor stoichiometries which we deem very unlikely to be produced). To determine the most likely stoichiometry, the experimentally detected isotope distribution (black curves in the top panel of Figures S4) is compared with the isotope distribution of these clusters calculated on the basis of the natural abundance of Mg and Si (red curves in the top panel Figure S4). The best agreement between the experimental and the calculated isotope distribution is given for $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$, but $\text{MgSi}_3\text{O}_7^+$ cannot be completely excluded based on these mass spectra alone. However, the mass spectrum obtained using $^{18}\text{O}_2$ shows only a very small signal at the mass of $\text{MgSi}_3^{18}\text{O}_7^+$, whereas the signal corresponding to the mass of $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$ appears in comparable intensity as $m = 220$ amu. The calculated isotope distribution of $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$ is also in favorable agreement with the experimentally observed isotope distribution.

Assignment of $m = 220$ amu to the pure silicate cluster $\text{Si}_5^{16}\text{O}_5^+$ can be excluded upon comparison of the IR-MPD spectra recorded for $m = 220$ amu produced with a pure Si target (in this case $m = 220$ amu can be unambiguously assigned to $\text{Si}_5^{16}\text{O}_5^+$) as shown in Figure S5. The assignment of $m = 220$ amu to $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ is confirmed beyond doubt by the similarity of its IR-MPD spectrum in comparison to the one recorded at $m = 238$ amu with $^{18}\text{O}_2$. Both spectra (cf. Figure 2 of the main text) show very similar patterns with some spectral shifts as expected to occur due to the different masses of the oxygen isotopes.

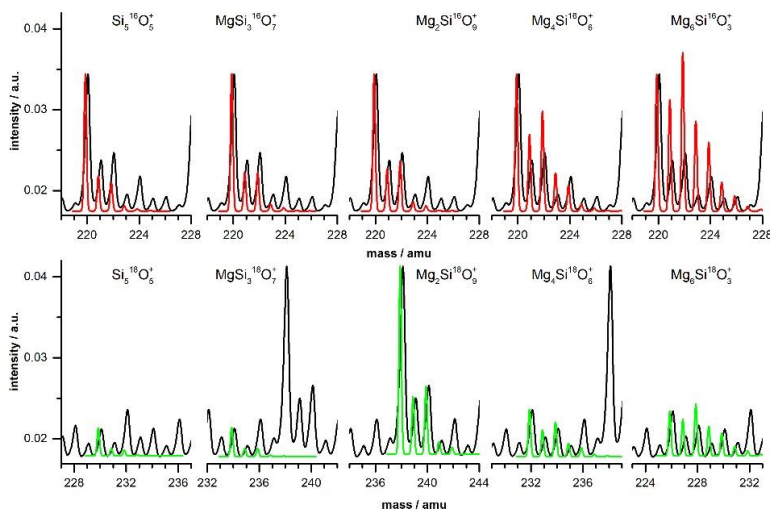


Figure S4: (top row) Experimentally obtained mass spectrum (black curves) around 220 amu obtained by laser ablation of a MgSi target in the presence of $^{16}\text{O}_2$. Also shown are theoretical isotope distributions (red curves) obtained on basis of the natural abundance of Mg and Si for several stoichiometries corresponding to a mass of 220 amu. (bottom row) Theoretical isotope distributions for the same clusters but with isotopically labeled $^{18}\text{O}_2$ (green curves) together with the experimental mass spectra in the corresponding mass regions.

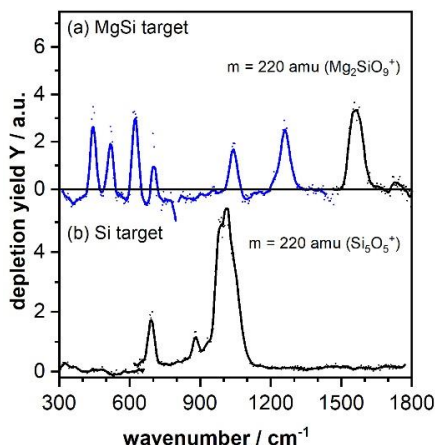


Figure S5: IR-MPD spectra obtained on the mass channel of 220 amu of the cluster distribution generated with a (a) mixed MgSi target and (b) a pure Si target, respectively. The mass $m = 220$ amu in the cluster distribution generated with a pure Si target (b) corresponds to the cluster stoichiometry $\text{Si}_5^{16}\text{O}_5^+$. In contrast, $m = 220$ amu in the cluster distribution obtained with a MgSi target (a) can in principle be assigned to different cluster stoichiometries as shown in Figure S4. Due to the significantly different IR-MPD spectra (a) and (b) an assignment to $\text{Si}_5^{16}\text{O}_5^+$ can be clearly excluded. The blue spectrum has been obtained at reduced IR macropulse intensity. The dots of the experimental spectra represent the sum of typically four to five spectra and the solid lines are obtained by a five-point average.

S3 Additional vibrational spectra and mode assignment

S3.1 IR-MPD spectra of MgSiO_9^+

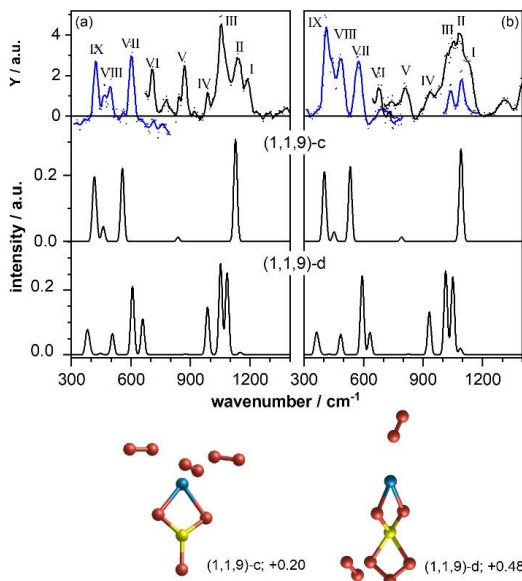


Figure S6: IR-MPD spectra of (a) $\text{MgSi}^{16}\text{O}_9^+$ and (b) $\text{MgSi}^{18}\text{O}_9^+$ shown in the 2000-1300 cm^{-1} spectral region together with the PBE0-calculated vibrational spectra of isomers (1,1,9)-c and (1,1,9)-d. The spectra of other iso-

meric structures are shown in the main text. The labels (x,y,z) correspond to $\text{Mg}_x\text{Si}_y\text{O}_z^+$. The dots of the experimental spectra represent the sum of typically four to five spectra and the solid lines are obtained by a five-point average. Mg, Si, and O atoms are depicted as cyan, yellow, and red spheres, respectively.

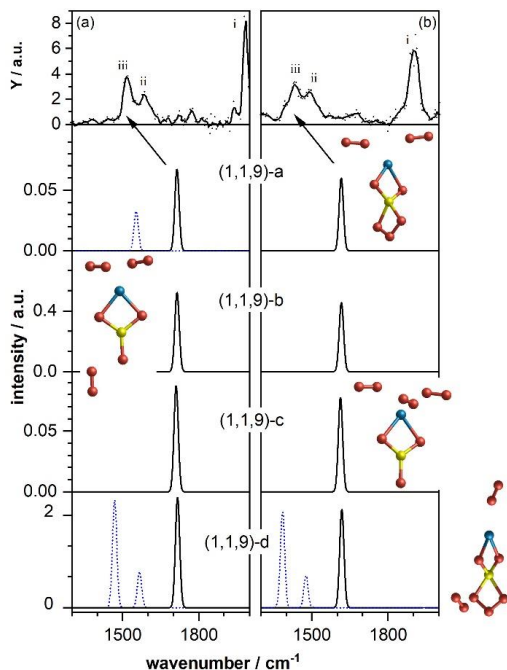


Figure S7: IR-MPD spectra of (a) $\text{MgSi}^{16}\text{O}_9^+$ and (b) $\text{MgSi}^{18}\text{O}_9^+$ shown in the 2000-1300 cm^{-1} spectral region together with the calculated vibrational spectra of several isomeric structures. The black and dotted blue spectra were calculated using the PBE0 and PBE functionals, respectively. The black spectra for isomer (1,1,9-d) are magnified by a factor of 50. The spectra in the 1400-300 cm^{-1} region are discussed in the main text. The labels (x,y,z) correspond to $\text{Mg}_x\text{Si}_y\text{O}_z^+$. The dots of the experimental spectra represent the sum of typically four to five spectra and the solid lines are obtained by a five-point average. Mg, Si, and O atoms are depicted as cyan, yellow, and red spheres, respectively.

The IR-MPD spectra of $\text{MgSi}^{16}\text{O}_9^+$ and $\text{MgSi}^{18}\text{O}_9^+$ in the 2000-1300 cm^{-1} spectral region (Figure S7) both show a double peak (labeled ii and iii) at 1585/1515 cm^{-1} ($\text{MgSi}^{16}\text{O}_9^+$) and 1490/1430 cm^{-1} ($\text{MgSi}^{18}\text{O}_9^+$), respectively. The frequencies of these bands are indicative for the O-O stretch of an almost unperturbed O_2 unit (compare to 1580 cm^{-1} for free $^{16}\text{O}_2$),¹⁸ and their average frequency reduction by a factor 0.942 upon isotopic substitution is close to the textbook ratio of 0.943 for a diatomic O-O stretch. The double peak structures indicate an isomer with two differently bound O_2 units or two isomeric structures, each with differently bound oxygen molecules. In the structures calculated, either two (isomers (1,1,9)-a,d) or three (isomers (1,1,9)-b,c) O_2 molecules are bound at different positions. As noted above, our PBE0-based DFT calculations systematically overestimate the O_2 stretching frequencies and predict that they are almost unchanged for all O_2 molecules. Tests for the O_2 -based frequencies using PBE-based DFT calculations show an expected downshift of the O-O stretching modes to the experimentally observed range. Moreover, the PBE-based calculations also indicate that symmetrically inequivalent positions for bound O_2 molecules give rise to distinct peaks in good agreement with the experimentally observed double peak (see example for isomer (1,1,9)-d). We note that isomer (1,1,9)-d

has the same silicate core as (1,1,9)-a and may indicate that different positions of relatively “free” O₂ molecules are sampled around this MgSiO₅ core species during the experiment.

Near the blue-edge of the MgSi¹⁶O₉⁺ spectrum, a final unexplained band (labeled i) is observed. This band red-shifts considerably to around 1900 cm⁻¹ upon isotopic labelling. Since this spectral region is neither characteristic for Mg-O and Si-O nor for O-O vibrations, this band cannot arise from a fundamental vibrational motion. We speculate that this band may be assigned to a combination band between the O-O stretch (ii and iii) vibrations and the two bands labeled VIII and IX (cf. Figure 1 in the main text). Both the ii/IX and the iii/VIII combination can lead to the frequency of band i; this frequency coincidence of both combinations may explain the unexpectedly high intensity for a combination band with which this band is observed.

Table S1: Frequencies of the observed bands in the IR-MPD Spectrum of MgSi¹⁶O₉⁺, those of the assigned calculated bands for isomer (1,1,9)-a, and their mode descriptions.

experimental band	experimental frequencies	calculated frequencies for isomer (1,1,9)-a	mode ^(a)
I	1185	1149	O ₃ unit symmetric stretch Si-O stretch (terminal O)
II	1137	1098	OSiO (of MgSiO ₂ ring) asymmetric stretch
III	1060	1053	OSiO (of MgSiO ₂ ring) symmetric stretch
IV	987	987	O ₃ unit asymmetric stretch
V	870	872	O ₃ unit bending
VI	706	651	OSiO (of MgSiO ₂ ring) bending
VII	602	585	OMgO symmetric stretch
VIII	493	489	OMgO asymmetric stretch
shoulder of VIII	468	441	OSiO (of SiO ₃ ring) asymmetric stretch
IX	423	380 ^(b)	MgSiO ₂ out of plane bending / MgSiO ₂ -SiO ₃ symmetric stretch

^(a) Most of the normal modes are coupled modes containing contributions from two or more motions involving several atoms, which makes mode assignments usually difficult. The given mode assignment is based on the most prominent motions, but additional other atoms are typically also involved. ^(b) two modes with almost the same frequency.

Table S2: Frequencies and mode descriptions of the main calculated bands for isomers (1,1,9)-b, (1,1,9)-c, and (1,1,9)-d.

isomer (1,1,9)-b	isomer (1,1,9)-c	isomer (1,1,9)-d	mode ^(a)
--	--	--	
1139	1128	1133	Si-O stretch (terminal O) + OSiO (of MgSiO ₂ ring) symmetric stretch
	1126		OSiO (of MgSiO ₂ ring) asymmetric stretch
1081	--	1060	OSiO (of MgSiO ₂ ring) asymmetric stretch
--	--	--	
873 ^(a)	836	868	OSiO (of MgSiO ₂ ring) symmetric stretch + Si-O (terminal O) stretch
--	--	--	

606	557	626	OMgO symmetric stretch
499		515	OMgO asymmetric stretch
486 ^(b)	460	498 ^(a)	Mg-Si stretch
420	412	409	MgSiO ₂ out of plane bending
392		395	O-O ₂ stretch
	422		OMgO asym stretch

^(a) Most of the normal modes are coupled modes containing contributions from two or more motions involving several atoms, which makes mode assignments usually difficult. The given mode assignment is based on the most prominent motions but additional other atoms are typically also involved. ^(b) combined with OMgO asymmetric stretch

S3.2 IR-MPD spectra of MgSiO_z⁺ (z = 7,9)

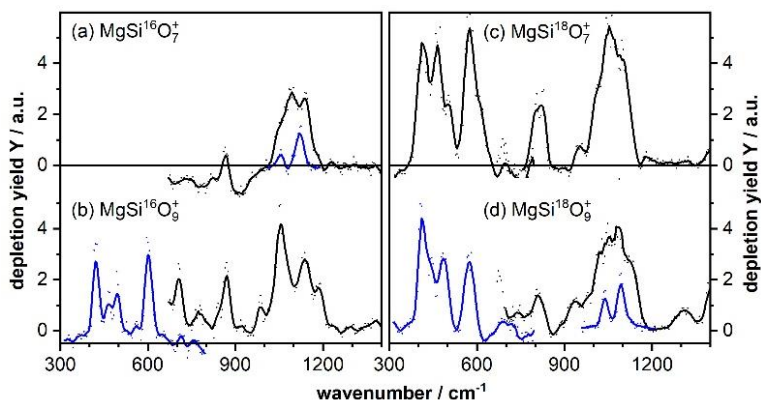


Figure S8: IR-MPD spectra of (a) MgSi¹⁶O₇⁺, (b) MgSi¹⁶O₉⁺ as well as the isotopically labelled counterparts (c) MgSi¹⁸O₇⁺ and (d) MgSi¹⁸O₉⁺. The spectra of MgSi¹⁶O₉⁺ and MgSi¹⁸O₉⁺ are discussed in detail in the main text. The IR-MPD spectra of MgSi¹⁶O₇⁺ and MgSi¹⁸O₇⁺ show similar modes as the spectra of MgSi¹⁶O₉⁺ and MgSi¹⁸O₉⁺ indicating a similar cluster core. The low wavenumber region of the IR-MPD spectrum of MgSi¹⁶O₇⁺ is dominated by signal gain and is thus not shown here. The blue parts of the spectra have been obtained at reduced IR macro-pulse intensity. The dots of the experimental spectra represent the sum of typically four to five spectra and the solid lines are obtained by a five-point average.

S3.3.1 IR-MPD spectra of Mg₂SiO₉⁺: alternative isomers.

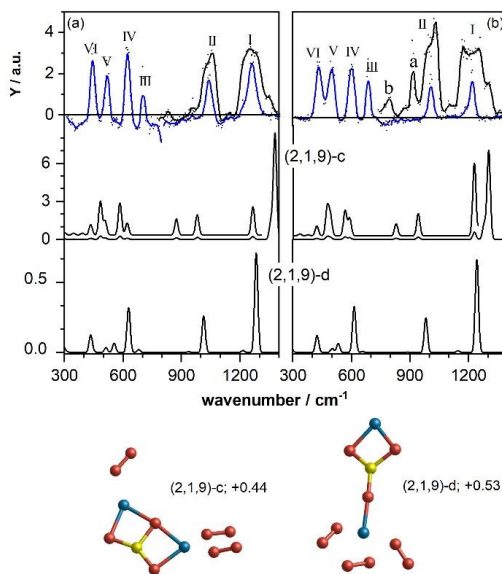


Figure S9: IR-MPD spectra of (a) $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ and (b) $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$ shown in the 2000-1300 cm^{-1} spectral region together with the calculated vibrational spectra of isomers (2,1,9)-c and (2,1,9)-d. The spectra of other isomeric structures are shown in the main text. The labels (x,y,z) correspond to $\text{Mg}_x\text{Si}_y\text{O}_z^+$. The dots of the experimental spectra represent the sum of typically four to five spectra and the solid lines are obtained by a five-point average. Mg, Si, and O atoms are depicted as cyan, yellow, and red spheres, respectively.

S3.3.2 IR-MPD spectra of $\text{Mg}_2\text{SiO}_9^+$: alternative isomers in the high-frequency range.

The IR-MPD spectra of $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ and (b) $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$ in the 2000-1300 cm^{-1} spectral region are shown in Figure S10. Both spectra show one intense band (labeled ii) around 1560/1480 cm^{-1} (for $\text{Mg}_2\text{Si}^{16}\text{O}_9^+/\text{Mg}_2\text{Si}^{18}\text{O}_9^+$), and one lower intensity band (i) around 1970/1900 cm^{-1} . The high intensity bands are indicative for the O-O stretch of an almost unperturbed O_2 unit (compared to 1580 cm^{-1} for free $^{16}\text{O}_2$).¹⁸ The geometry of the calculated isomers (2,1,9)-a and (2,1,9)-d are very similar with the O_2 units bound at different positions. However, due to the rather large distance of the O_2 to the cluster core (> 2.1 Å), the position hardly effects the frequency of the O-O stretch mode, which is calculated to be between 1715 and 1700 cm^{-1} for both isomers. In contrast, isomer (2,1,9)-b contains two non-identical O_2 units. The distance between the Si atom and the O_2 is with 2.4 Å rather large leading to a very low intensity mode at 1695 cm^{-1} . The distance between the Mg atom and the second O_2 is considerably shorter (2.04 Å), which results in a red-shift of the mode to 1561 cm^{-1} and a considerably increased intensity. Finally, in isomer (2,1,9)-c the two additional oxygen atoms are almost identical and are both bound to the same Mg atom. This leads to a very low intensity mode at 1552 cm^{-1} . The intense mode predicted at 1379 cm^{-1} corresponds to the O-O stretch of the third O_2 unit η^1 -bound to the Mg atom. All

the discussed O-O bands (except for the 1379 cm^{-1} mode of isomer (2,1,9)-c) can account for the experimentally observed band (ii). The mode labeled (i) can, similarly to the above discussed case of MgSiO_9^+ , not be explained by fundamental vibrational modes but must instead be assigned to a combination band.

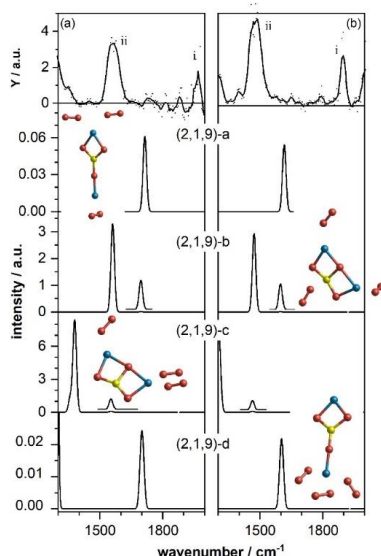


Figure S10: IR-MPD spectra of (a) $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ and (b) $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$ shown in the 2000-1300 cm^{-1} spectral region together with the calculated vibrational spectra of several isomeric structures. The spectra in the 1400-300 cm^{-1} region are discussed in the main text. The labels (x,y,z) correspond to $\text{Mg}_x\text{Si}_y\text{O}_z^+$. The insets in the calculated spectra of isomer (2,1,9)-c are magnified by a factor of 10, those of isomer (2,1,9)-b by a factor of 100. The dots of the experimental spectra represent the sum of typically four to five spectra and the solid lines are obtained by a five-point average. Mg, Si, and O atoms are depicted as cyan, yellow, and red spheres, respectively.

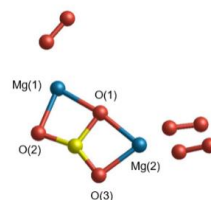
Table S3: Assignment of bands (labeled I–VI) observed in the IR-MPD Spectrum of $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ shown in Figure 2a of the main text and S9. The bands are assigned based on calculated vibrational spectra of isomers (2,1,9)-a and (2,1,9)-b.

experimental band	experimental frequencies	calculated frequencies for isomer (2,1,9)-a	calculated frequencies for isomer (2,1,9)-d	mode ^(a)
I	1261	1268 1208	1283 1215	Si-O stretch O-O (of η^2 -bound O_2) stretch
II	1041	1054	1014	OSiO (of MgSiO_2 ring) asymmetric stretch
III	704	780	--	OSiO (of MgSiO_2 ring) + Mg- O_2 symmetric stretch
IV	624	624	680,628	OMgO (of MgSiO_2 ring) symmetric stretch + Mg- O_2 symmetric stretch
V	518	521 517 488	555 513 --	OMgO (of MgSiO_2 ring) asymmetric stretch Mg-Si stretch Mg- O_2 asymmetric stretch
VI	445	435	434 451	MgSiO ₂ out of plane bend Mg- O_2 asymmetric stretch
a		960	935	OSiO (of MgSiO_2 ring) symmetric stretch
b				

^(a) Most of the normal modes are coupled modes containing contributions from two or more motions involving several atoms, which makes mode assignments usually difficult. The given mode assignment is based on the most prominent motions, but additional other atoms are typically also involved.

Table S4: Assignment of bands (labeled I–VI) observed in the IR-MPD Spectrum of $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ shown in Figure S9. The bands are assigned based on the calculated vibrational spectrum of isomer (2,1,9)-c.

experimental band	isomer (2,1,9)-c	mode ^(a)
I	1379	O-O (of η^1 -bound O_2) stretch
	1358	O-O (of two Mg η^1 -bound O_2) stretch
	1266	O(2)SiO(3) asymmetric stretch
II	--	
III	--	
IV	621	O(2)Mg(1)O(1) symmetric stretch
	585	O(3)Mg(2)O(1) symmetric stretch
V	509	O(2)SiO(3) bend + Mg(1)- O_2 symmetric stretch
	485	Mg-Si stretch
VI	435	Mg_2SiO_3 out of plane bend
a	981	O(2)SiO(3) symmetric stretch
b	874	Si-O(1) stretch



^(a) Most of the normal modes are coupled modes containing contributions from two or more motions involving several atoms, which makes mode assignments usually difficult. The given mode assignment is based on the most prominent motions but additional other atoms are typically also involved. ^(b) two modes with almost the same frequency

S3.4 Vibrational Spectra of $\text{Mg}_2\text{SiO}_z^+$ ($z = 7,9$)

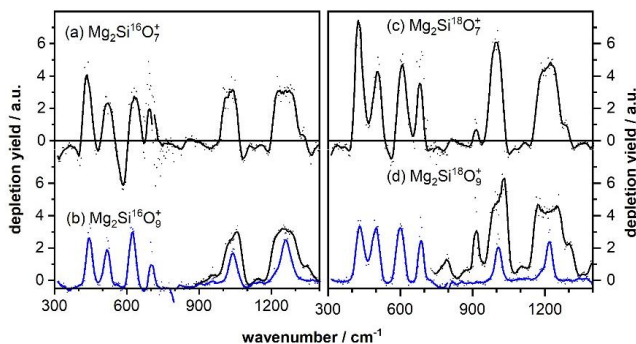


Figure S11: IR-MPD of (a) $\text{Mg}_2\text{Si}^{16}\text{O}_7^+$, (b) $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ as well as the isotopically counterparts (c) $\text{Mg}_2\text{Si}^{18}\text{O}_7^+$ and (d) $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$. The spectra of $\text{Mg}_2\text{Si}^{16}\text{O}_9^+$ and $\text{Mg}_2\text{Si}^{18}\text{O}_9^+$ are discussed in detail in the main text. The IR-MPD spectra of $\text{Mg}_2\text{Si}^{16}\text{O}_7^+$ and $\text{Mg}_2\text{Si}^{18}\text{O}_7^+$ show similar modes as the spectra of $\text{MgSi}^{16}\text{O}_9^+$ and $\text{MgSi}^{18}\text{O}_9^+$ indicating a similar cluster core. The blue parts of the spectra have been obtained at reduced IR macropulse intensity. The dots of the experimental spectra represent the sum of typically four to five spectra and the solid lines are obtained by a five-point average.

S4 Structures and charge/spin populations of selected low energy clusters

S4.1 MgSiO_3^+ cluster core

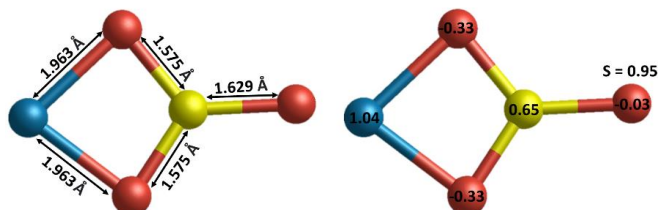


Figure S12: Structure and charge/spin populations of MgSiO_3^+ . The numbers in left structure denote bond lengths and the numbers in the right structure denote charges. Also given is the spin (S) on the terminal oxygen atom. Mg, Si, and O atoms are depicted as blue, yellow, and red spheres, respectively.

S4.2 Isomer (1,1,9)-a of the MgSiO_9^+ cluster

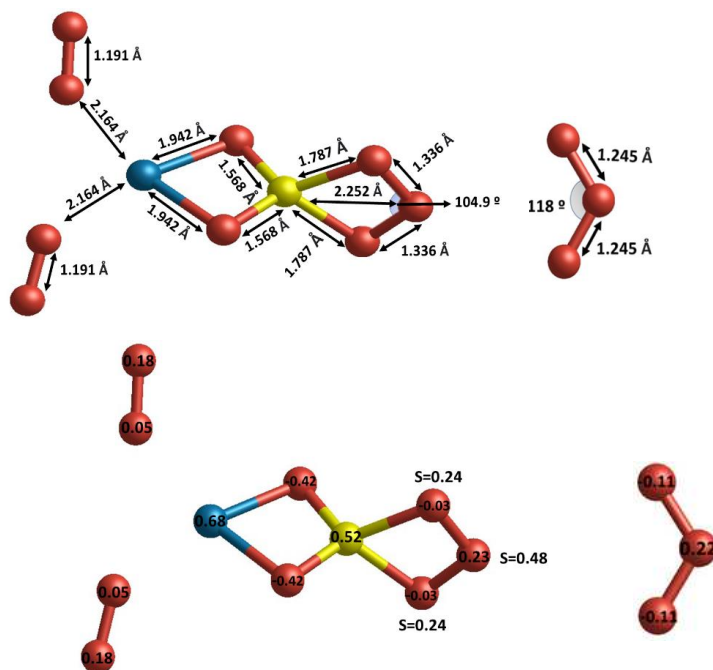


Figure S13: Structure and charge/spin populations of MgSiO_9^+ (left) in comparison with free ozone O_3 (right). The numbers in the top structure denote bond lengths and the numbers in bottom structures denote charges. We also provide the atomically partitioned spin populations (S) on the oxygen atoms of the bound O_3 unit. Mg, Si, and O atoms are depicted as blue, yellow, and red spheres, respectively.

S4.3 Isomer (2,1,9)-a of the $\text{Mg}_2\text{SiO}_9^+$ cluster

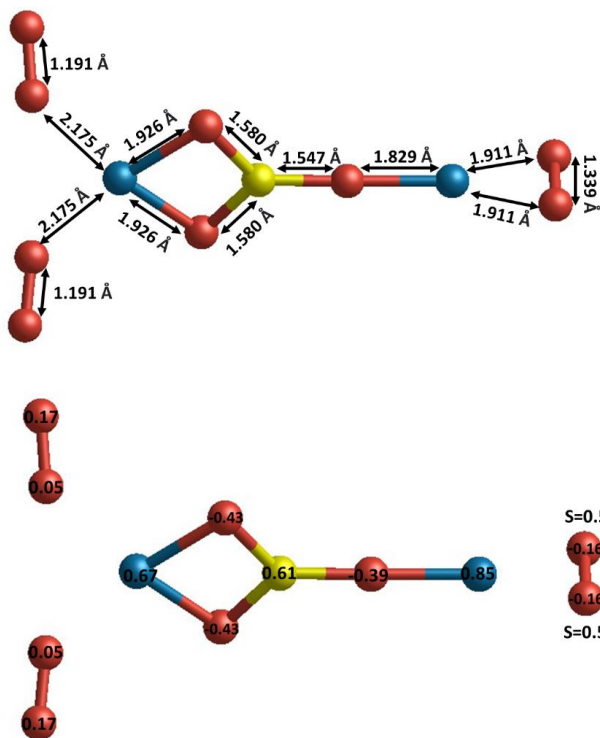


Figure S14: Structure and charge/spin populations of $\text{Mg}_2\text{SiO}_9^+$. The numbers in the top structure denote bond lengths and the numbers in the bottom structure denote charges. We also provide the atomically partitioned spin populations (S) on the oxygen atoms of the O_2 molecule bound to the terminal Mn atom. Mg, Si, and O atoms are depicted as blue, yellow, and red spheres, respectively.

S4.4 Cartesian coordinates of MgSiO^+ and $\text{Mg}_2\text{SiO}_9^+$ clusters.

Below we include the cartesian coordinates of a selection of low energy clusters from our DFT calculations. The data is given using the xyz file format where the first line gives the number of atoms in the system, the second line gives the relative total energy with respect to the respective lowest energy and the remaining lines provide the optimized cartesian coordinates of each atom.

(1,1,9)-a

11

0 eV

Mg	-1.93284741	2.99401786	1.28533342
O	-0.29591504	3.91841519	0.79644574
O	-0.65696986	1.57039482	1.63041566
Si	0.44393573	2.58677278	1.16824778
O	1.9669517	2.68631486	2.09692686
O	2.66163727	2.20976175	1.05991453
O	1.7532948	2.00514873	0.10148242
O	-3.6671923	2.24623932	0.23051686
O	-3.99460305	1.22050613	-0.27807524
O	-3.19619987	4.26048074	2.50364762
O	-3.08876195	5.31752783	3.04152435

(1,1,9)-b

11

0.16 eV

Mg	-2.83758391	2.68252166	0.37347008
O	-1.58187134	4.06834407	-0.13778206
O	-1.36099991	2.20424879	1.54167524
Si	-0.59990307	3.42879545	0.9097142
O	0.87064301	3.93745406	1.24710188
O	1.62736195	2.75330997	2.63410995
O	-4.81653672	3.51139366	0.65495712
O	-3.66978865	0.95318192	-0.62807551
O	-3.37839431	-0.19284522	-0.76721175
O	-5.28961783	4.60317171	0.70166484
O	2.72258078	3.08288395	2.84725601

(1,1,9)-c

11

0.20 eV

Mg	-1.80140211	2.50174372	0.51703798
O	-0.28284108	1.3462982	-0.00017021
O	-0.26761506	3.63108084	1.08309009
Si	0.63828665	2.47648543	0.55467435
O	2.25631427	2.45672234	0.57771774
O	-2.82448551	3.11238021	3.42528978
O	-2.97510658	2.56472373	2.37825958
O	-2.95288473	4.05493575	-0.53716558
O	-2.78558875	5.22289201	-0.70102084
O	-3.2903986	0.03734609	-0.72079237
O	-3.35502853	1.11484167	-0.21717049

(1,1,9)-d

11

0.39 eV

Mg	-1.48324688	2.30055321	1.14412419
O	-0.11098692	3.13614015	0.08042807
O	0.05608934	1.49203499	1.97324465
Si	0.91361021	2.32369511	0.95224169
O	2.38739255	3.14925546	1.52415040
O	3.15311907	2.36218111	0.76360203
O	2.29687110	1.54656637	0.14078684
O	-4.54723559	2.95174385	0.73306551
O	-3.59577379	2.43479197	1.22819919
O	2.98013873	0.32448356	3.14318612
O	2.39980219	-0.35168578	3.93437234

(2,1,9)-a

12

0 eV

O	-0.84486215	5.15311159	-0.10506699
O	-1.29469365	3.41902408	1.65157813
O	1.30505707	3.50011438	0.60701055
Si	-0.16021639	3.98474234	0.70859529
Mg	-2.45378611	4.74568577	0.87288489
Mg	3.03516706	2.91510293	0.50829379
O	-3.63980886	5.71966294	2.41360306
O	-3.67030728	5.69679339	3.60377969
O	-4.18104363	4.72242801	-0.44729602
O	-4.35193573	4.77610124	-1.62454014
O	4.91083853	2.80536645	0.86032574
O	4.5431211	1.86649689	-0.020898

(2,1,9)-b

12

0.43 eV

O	-0.46312124	5.73848497	0.94198145
O	-2.32663145	4.0580926	0.68539056
O	-0.34735961	4.79286619	-1.42392764
Si	-1.06251298	4.59283325	-0.06735
Mg	-1.957149	5.29871587	2.10894376
Mg	0.69117235	6.30919875	-0.69324248
O	-2.67247542	5.92401964	3.91317617
O	-2.44043902	6.79540577	4.71556983
O	1.40610635	8.09844665	-1.00236521
O	2.37537517	7.28966059	-0.63738633
O	0.32058806	2.76240887	0.58843087
O	0.56504678	1.82902687	-0.11114095

(2,1,9)-c

12

0.44 eV

O	-0.57158568	5.89975424	0.62996597
O	-1.28686722	3.48630857	1.00859467
O	0.17136523	4.54609965	-1.37411093
Si	-0.56438777	4.39537909	-0.01184288
Mg	-1.56985903	5.03373809	2.20546483
Mg	0.39529724	6.44740664	-1.01508208
O	-3.35664345	5.83708919	2.72297956
O	-3.62720555	6.28208493	3.83325159
O	-0.76711581	5.27044697	4.0503336
O	-1.34385337	5.77993588	5.00514957
O	1.12047614	8.13590105	-1.72417823
O	1.07492925	9.2364357	-1.16398566

(2,1,9)-d

12

0.53 eV

O	-1.3666696	5.52063565	0.68656727
O	-1.82049919	3.06937762	0.45915748
O	0.86993539	3.86505334	0.2853398
Si	-0.63427319	4.12803544	0.45991802
Mg	-2.98843272	4.53843929	0.72487403
Mg	2.59352917	3.4068972	-0.23133565
O	3.16340288	2.52422408	1.85089539
O	4.05296115	1.83279386	2.23959231
O	3.45237865	3.21216154	-1.95750943
O	3.87198243	2.26575837	-1.11736849
O	3.84018256	5.20637377	0.37087969
O	4.81547245	5.70739984	-0.09423044

¹ Bakker, J. M.; Lapoutre, V. J. F.; Redlich, B.; Oomens, J.; Sartakov, B. G.; Fielicke, A.; von Helden, G.; Meijer, G.; van der Meer, A. F. G., Intensity-Resolved Ir Multiple Photon Ionization and Fragmentation of C₆₀. *J. Chem. Phys.* 2010, 132, 074305.

² Haertelt, M.; Lapoutre, V. J. F.; Bakker, J. M.; Redlich, B.; Harding, D. J.; Fielicke, A.; Meijer, G., Structure Determination of Anionic Metal Clusters Via Infrared Resonance Enhanced Multiple Photon Electron Detachment Spectroscopy. *J. Phys. Chem. Lett.* 2011, 2, 1720-1724.

³ Meng Wang, G. Audi, F.G. Kondev, W.J. Huang, S. Naimi, Xing Xu, *Chinese Physics C* Vol. 41, No. 3 (2017) 030003

⁴ Meng Wang, G. Audi, F.G. Kondev, W.J. Huang, S. Naimi, Xing Xu, *Chinese Physics C* Vol. 41, No. 3 (2017) 030003

⁵ D. J. Wales, J. P. K. Doye, Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms. *J. Phys. Chem. A* 1997, 101, 5111–5116.

-
- ⁶ A. Macià Escatllar, T. Lazaukas, S. M. Woodley, S. T. Bromley, Structure and Properties of Nanosilicates with Olivine (Mg_2SiO_4) N and Pyroxene (MgSiO_3) N Compositions. *ACS Earth Sp. Chem.* **2019**, *3*, 2390–2403.
- ⁷ C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- ⁸ Jensen, S. R.; Saha, S.; Flores-Livas, J. A.; Huhn, W.; Blum, V.; Goedecker, S.; Frediani, L. The Elephant in the Room of Density Functional Theory Calculations. *J. Phys. Chem. Lett.* **2017**, *8*, 1449–1457.
- ⁹ A. Tkatchenko, M. Scheffler, Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data, *Phys. Rev. Lett.* **102**, 073005.
- ¹⁰ Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. Ab initio molecular simulations with numeric atom-centered orbitals. *Comput. Phys. Commun.* **2009**, *180*, 2175–2196.
- ¹¹ S. Bhattacharya, S. V. Levchenko, L. M. Ghiringhelli, M. Scheffler, Stability and Metastability of Clusters in a Reactive Atmosphere: Theoretical Evidence for Unexpected Stoichiometries of Mg_mO_x , *Phys. Rev. Lett.* **2013**, *111*, 135501.
- ¹² B. E. Krisyuka, A. V. Maiorovb, Quantum Chemical Study of the Primary Step of Ozone Addition at the Double Bond of Ethylene, *Kinet. Catal.*, **2011**, *52*, 798.
- ¹³ Valencia, E. M.; Worth, C. J.; Fortenberry, R. C. Enstatite (MgSiO_3) and forsterite (Mg_2SiO_4) monomers and dimers: highly detectable infrared and radioastronomical molecular building blocks. *Mon. Not. R. Astron. Soc.* **2020**, *492*, 276–282.
- ¹⁴ de la Pierre, M.; Orlando, R.; Maschio, L.; Doll, K.; Ugliengo, P.; Dovesi, R. Performance of Six Functionals (LDA, PBE, PBESOL, B3LYP, PBE0, and WC1LYP) in the Simulation of Vibrational and Dielectric Properties of Crystalline Compounds. The Case of Forsterite Mg_2SiO_4 . *J. Comput. Chem.* **2011**, *32*, 1775–1784.
- ¹⁵ Demichelis, R.; Suto, H.; Nöel, Y.; Sogawa, H.; Naoi, T.; Koike, C.; Chihara, H.; Shimobayashi, N.; Ferabone, M.; Dovesi, R. The infrared spectrum of ortho-enstatite from reflectance experiments and first-principle simulations. *Mon. Not. R. Astron. Soc.* **2012**, *420*, 147–154.
- ¹⁶ Mariñoso Guíu, J.; Macià Escatllar, A.; Bromley, S. T. How Does Temperature Affect the Infrared Vibrational Spectra of Nanosized Silicate Dust? *ACS Earth Space Chem.* **2021**, *5*, 4, 812–823.
- ¹⁷ J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.*, **1996**, *77*, 3865–3868.
- ¹⁸ K. P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure Iv. Constants of Diatomic Molecules; Van Nostrand, New York, 1979

APPENDIX D

Supporting Information for:
Oxygen-rich Anionic Metal Silicate
Clusters as Nucleation Seeds for
Noctilucent Clouds

Oxygen-rich Anionic Metal Silicate Clusters as Nucleation Seeds for Noctilucent Clouds

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S1 Assignment of Mass Peaks

Laser ablation of a binary MgSi target in the presence of a O₂/He pulse results in unusually rich mass spectra due to the natural isotope distributions of magnesium and silicon, which leads to multiple mass peaks for each cluster size formed. Due to (1) the natural isotope distribution of Mg and Si which results in partially overlapping isotope distributions of different clusters and (2) the similar masses of Si₂ and MgO₂ units ($m(^{28}\text{Si}_2) = 55.95 \text{ u}$ and $m(^{24}\text{Mg}^{16}\text{O}_2) = 55.97 \text{ u}$)¹ as well as O₃ and Mg₂ units ($m(^{16}\text{O}_3) = 47.98 \text{ u}$ and $m(^{24}\text{Mg}_2) = 47.97 \text{ u}$), a mass difference that cannot be resolved in the TOF mass spectrometer)¹ an unambiguous assignment of the individual mass peaks is not straightforward and must be done with particular care. Therefore, the experiments have been performed with ¹⁶O₂/He and ¹⁸O₂/He mixtures. The shift of individual mass signals upon isotopic labeling together with the calculated mass distributions arising from the natural abundance of the Mg and Si isotope allows for a reliable assignment of the mass peaks. Furthermore, clusters of the same stoichiometry but produced with ¹⁶O₂ and ¹⁸O₂, respectively, are expected to exhibit similar patterns in the IR-MPD spectra with some spectral shifts due to the different masses of the oxygen isotopes. In addition, we obtained mass spectra of silicon oxide and magnesium oxide clusters produced from bare Si and Mg targets, respectively. In the following, we will restrict our discussion to the clusters further studied in the main manuscript.

S1.1 Assignment of mass $m = 148 \text{ amu}$

The upper panel of Figure S1a shows the mass spectrum (black curve) around 148 amu. This mass can in principle be assigned to several different cluster stoichiometries such as Si₃¹⁶O₄⁻, MgSi¹⁶O₆⁻, Mg₂Si₃¹⁶O⁻, and Mg₃Si¹⁶O₃⁻. To determine the most likely stoichiometry, the experimentally detected isotope distribution is compared with the isotope distribution of these clusters calculated on the basis of the natural abundance of Mg and Si (red curves). The best agreement between the experimental and the calculated isotope distribution is given for MgSi¹⁶O₆⁻, however, the match for Si₃O₄⁻ is only slightly worse. For an unambiguous assignment, the experiment has been repeated with isotopically labeled oxygen, ¹⁸O₂ (bottom panel). The mass peak at $m = 160 \text{ amu}$, corresponding to MgSi¹⁸O₆⁻, is comparable in intensity to the $m = 148 \text{ amu}$ signal in the ¹⁶O₂ experiment, whereas the mass peak at $m = 156 \text{ amu}$, corresponding to Si₃¹⁸O₄⁻, is considerably lower in intensity supporting the assumption that the $m = 148 \text{ amu}$ peak corresponds to MgSi¹⁶O₆⁻. In addition, the theoretically obtained isotope distributions for Si₃¹⁸O₄⁻, MgSi¹⁸O₆⁻, Mg₂Si₃¹⁸O⁻, and Mg₃Si¹⁸O₃⁻ (green curves) confirm the assignment to MgSiO₆⁻.

In addition, production of Si₃O₄⁻ is rather unlikely since this cluster has not been observed in the mass spectrum obtained via laser ablation of a pure silicon oxide target under similar experimental conditions. Finally, the assignment of $m = 148 \text{ amu}$ peak to MgSi¹⁶O₆⁻ is further substantiated by the similarity of the IR-MPD spectra recorded at $m = 148 \text{ amu}$ (with ¹⁶O₂) and $m = 160 \text{ amu}$ (with ¹⁸O₂), which show very similar patterns and spectral shifts consistent with the different masses of the oxygen isotopes (cf. Figure S1b below). Due to the low mass peak intensity of Si₃¹⁸O₄⁻ no IR-MPD spectrum could be obtained for comparison.

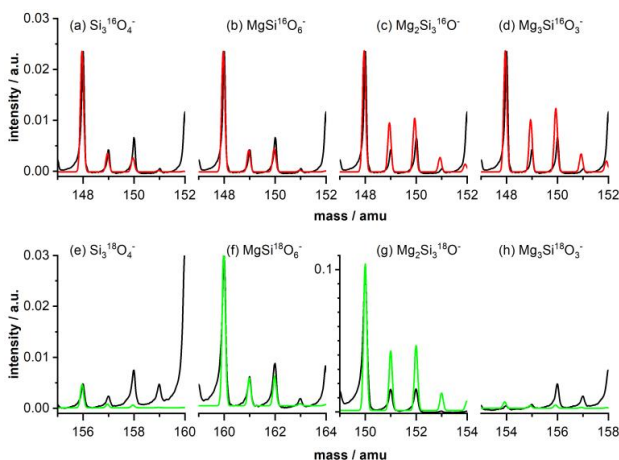


Figure S1a: (top row) Experimentally obtained mass spectrum (black curves) around 148 amu. The red curves show theoretical isotope distributions obtained on basis of the natural abundance of Mg and Si for several stoichiometries corresponding to a mass of 148 amu. (bottom row) Theoretical isotope distributions for the same clusters but with isotopically labeled $^{18}\text{O}_2$ (green curves) together with the experimental mass spectra in the corresponding mass regions.

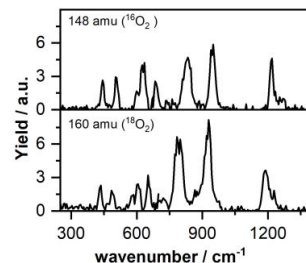


Figure S1b: IR-MPD spectra obtained on the mass (top row) $m = 148$ amu with $^{16}\text{O}_2$ and on the mass (bottom row) $m = 160$ amu with $^{18}\text{O}_2$ in the carrier gas. Both spectra are similar, mainly differing by the expected isotopic shifts.

S1.2 Assignment of mass $m = 172$ amu

For the mass peak $m = 172$ amu we have performed a similar data evaluation as described above for $m = 148$ amu. Figure 2a shows that the experimental spectrum is best described by the calculated isotope distributions of $\text{MgSi}_3^{16}\text{O}_4^-$ and $\text{Mg}_2\text{Si}^{16}\text{O}_6^-$. However, in the experiments with $^{18}\text{O}_2$ only mass $m = 184$ amu (potentially corresponding to $\text{Mg}_2\text{Si}^{18}\text{O}_6^-$) is produced in comparable amount whereas $m = 180$ amu (potentially corresponding to $\text{MgSi}_3^{18}\text{O}_4^-$) is only produced in very small amount. In case of $^{18}\text{O}_2$ the calculated isotope distribution of $\text{Mg}_2\text{Si}^{18}\text{O}_6^-$ nicely fits the intensity of the peaks at 184 and 185 amu, but underestimates the peak at 186 amu. This discrepancy can arise from the mass overlap at 186 amu in the experimental spectrum with a different cluster distribution, which demonstrates the complexity of the experimental mass spectrum. The assignment of $m = 172$ amu to $\text{Mg}_2\text{Si}^{16}\text{O}_6^-$ is further supported by the similarity of the IR-MPD spectra recorded at $m = 172$ amu (with $^{16}\text{O}_2$) and $m = 184$ amu (with $^{18}\text{O}_2$), which show very similar patterns and spectral shifts consistent with the different masses of the oxygen isotopes (cf. Figure 2b). Due to the low mass peak intensity of $\text{MgSi}_3^{18}\text{O}_4^-$ no IR-MPD spectrum could be obtained for comparison.

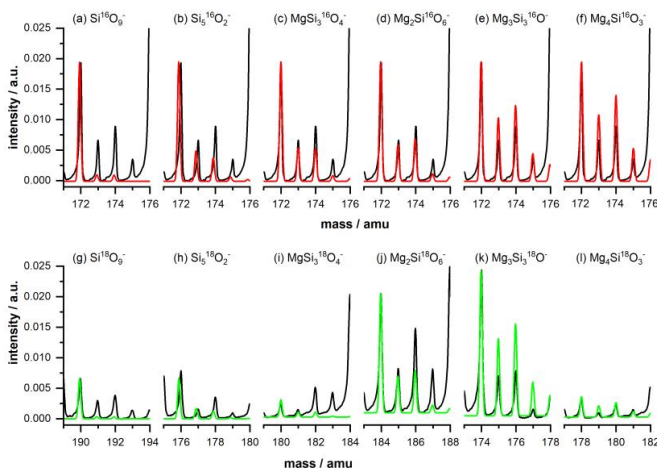


Figure S2a: Same as Figure S1a but for $m = 172$.

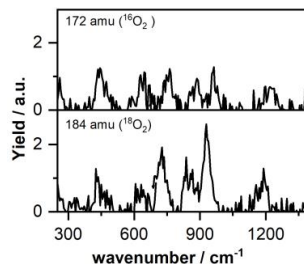


Figure 2b: Same as Figure S1b but for $m = 172$ amu and $m = 184$ amu.

S1.3 Assignment of mass $m = 188$ amu

Comparison of experimental and simulated isotope distributions around mass $m = 188$ amu shows that this mass might correspond to $\text{MgSi}_3^{16}\text{O}_5^-$ or $\text{Mg}_2\text{Si}^{16}\text{O}_7^-$ with the latter giving a slightly better fit (cf. Figure S3a). However, cluster production with $^{18}\text{O}_2$ in the He carrier gas results in a very low intensity of $m = 198$ amu (potentially corresponding to $\text{MgSi}_3^{18}\text{O}_5^-$) but an intensity comparable to the one in the $^{16}\text{O}_2$ spectrum for $m = 202$ amu (potentially corresponding to $\text{Mg}_2\text{Si}^{18}\text{O}_7^-$). The assignment of $m = 188$ amu to $\text{Mg}_2\text{Si}^{18}\text{O}_7^-$ is further supported by the IR-MPD spectra recorded on the masses $m = 188$ amu (with $^{16}\text{O}_2$) and $m = 202$ amu (with $^{18}\text{O}_2$) showing very similar patterns with the expected isotopic shifts. Although the spectrum obtained at $m = 198$ amu (with $^{18}\text{O}_2$) exhibits some features also visible in the $m = 188$ amu spectrum, it misses some parts. Thus, we unambiguously assign mass $m = 188$ amu to $\text{Mg}_2\text{Si}^{16}\text{O}_7^-$.

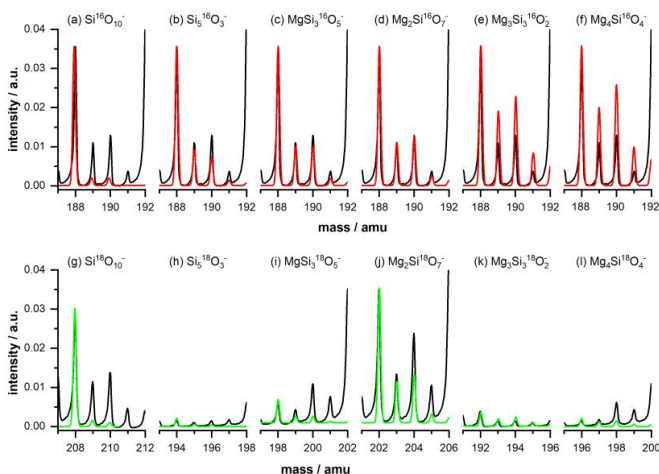


Figure S3a: Same as Figure S1 but for $m = 188$ amu.

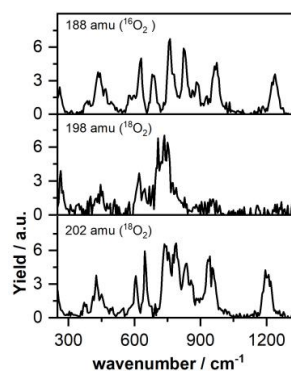


Figure 3b: Same as Figure S1b but for $m = 188$ amu (with $^{16}\text{O}_2$) as well $m = 198$ amu and 202 amu (both with $^{18}\text{O}_2$).

S1.4 Assignment of mass $m = 192$ amu

In case of $m = 192$ amu, the simulated isotope distributions provide satisfactory fits for Mg_2O_9^- , $\text{MgSi}_2\text{SiO}_7^-$, and Si_4O_5^- (cf. Figure S4a). However, the existence of Mg_2O_9^- and Si_4O_5^- is rather unlikely since these clusters were not produced in sufficient amount via laser ablation of a mono-elemental magnesium or silicon target, respectively, under similar production conditions. In addition, the IR-MPD spectra recorded (cf. Figure S4b) at $m = 192$ amu (with $^{16}\text{O}_2$) and $m = 206$ amu (with $^{18}\text{O}_2$ potentially corresponding to $\text{MgSi}_2^{18}\text{O}_7^-$) show very similar patterns while the spectra recorded at 202 amu (potentially corresponding to $\text{Si}_4^{18}\text{O}_5^-$) and 210 amu (potentially corresponding to $\text{Mg}_2^{18}\text{O}_9^-$) are

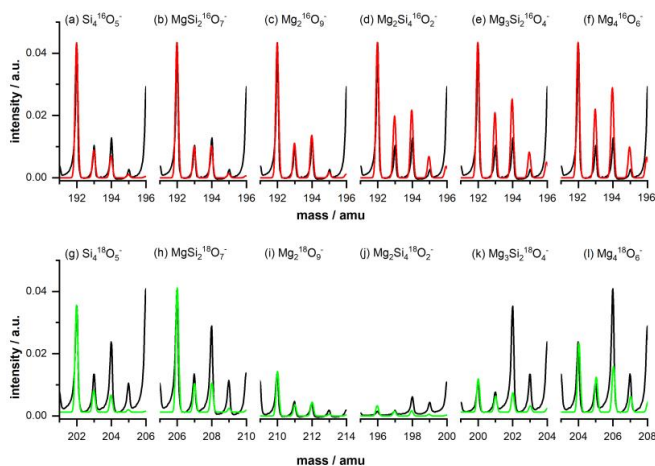


Figure S4a: Same as Figure S1 but for $m = 192$ amu.

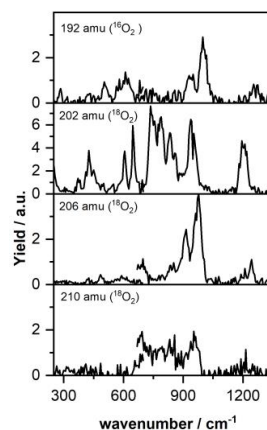


Figure S4b: Same as Figure S1b but for $m = 192$ amu (with $^{16}\text{O}_2$) as well $m = 202$ amu, 206 amu, and 210 amu (all with $^{18}\text{O}_2$).

considerably different. It should be noted that the masses 202 amu and 210 amu can potentially also arise from other cluster stoichiometries than those given in the lower panel of Figure S4a and thus the mass spectrum shown in Figure S4a is not in disagreement with the lack of these clusters in the spectra produced with the mono-elemental targets. Therefore, we assign the mass peak at 192 amu to $\text{MgSi}_2\text{SiO}_7^-$.

S1.5 Assignment of mass $m = 208$ amu

For $m = 208$ amu the simulated isotope distributions provide satisfactory fits for $\text{Mg}_2\text{O}_{10}^-$, $\text{MgSi}_2\text{SiO}_8^-$, and Si_4O_6^- (cf. Figure S5a). Similar to $m = 192$ amu, the existence of the mono-elemental oxides $\text{Mg}_2\text{O}_{10}^-$ and Si_4O_6^- is rather unlikely since they were not produced in sufficient amount via laser ablation of a mono-elemental magnesium or silicon target, respectively, under similar production conditions. Moreover, the IR-MPD spectra recorded at $m = 208$ amu (with $^{16}\text{O}_2$) and $m = 224$ amu (with $^{18}\text{O}_2$ potentially corresponding to $\text{MgSi}_2^{18}\text{O}_8^-$) show very similar patterns while the spectra recorded at 220 amu (potentially corresponding to $\text{Si}_4^{18}\text{O}_6^-$) and 210 amu (potentially corresponding to $\text{Mg}_2^{18}\text{O}_{10}^-$) are considerably different. Therefore, we assign the mass peak at 192 amu to $\text{MgSi}_2\text{SiO}_7^-$.

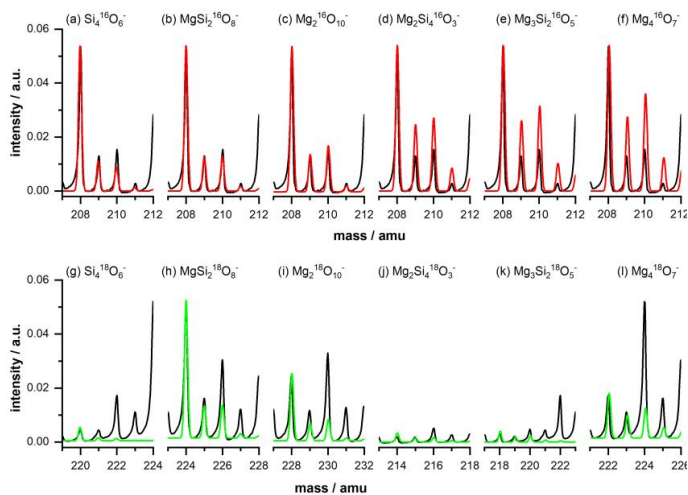


Figure S5a: Same as Figure S1 but for $m = 208$ amu.

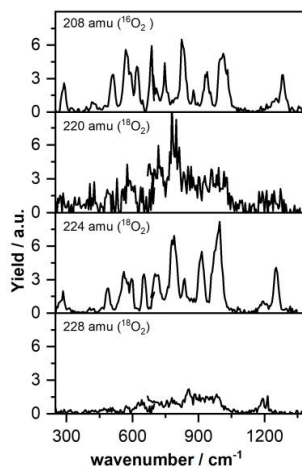


Figure S5b: Same as Figure S1b but for $m = 208$ amu (with $^{16}\text{O}_2$) as well $m = 220$ amu, 224 amu, and 228 amu (all with $^{18}\text{O}_2$).

S2 Infrared Spectra and Mode Assignments

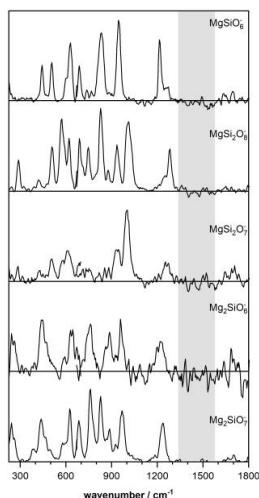


Figure S6: IR-MPD spectra of all investigated anionic $\text{Mg}_x\text{Si}_y\text{O}_z^-$ clusters in the extended spectral region between 1800 cm^{-1} and 225 cm^{-1} . The gray highlighted region represents the characteristic region of the O-O stretching mode of weakly bound and hardly activated O_2 units. The lack of any modes in this spectral region indicates the absence of any loosely bound O_2 .

S2.1 IR-MPD Spectra of $\text{MgSi}^{16}\text{O}_6^-$ and $\text{MgSi}^{18}\text{O}_6^-$

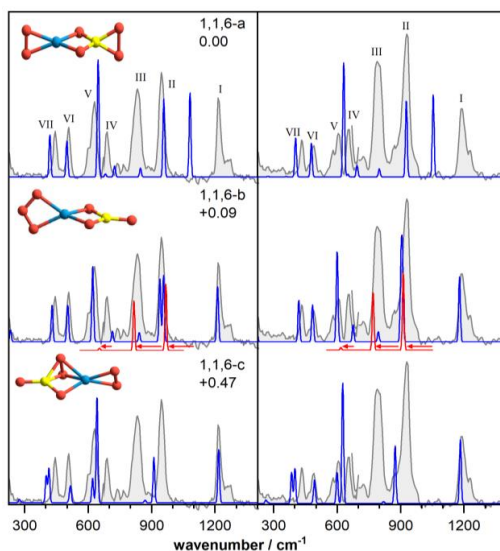


Figure S7: IR-MPD spectra (in grey) and calculated vibrational spectra (in blue) of (left column) $\text{MgSi}^{16}\text{O}_6^-$ and (right column) $\text{MgSi}^{18}\text{O}_6^-$. The IR-MPD spectra with ^{16}O represent the average of five ($650\text{--}1800\text{ cm}^{-1}$) and six ($225\text{--}700\text{ cm}^{-1}$) individual spectra, respectively, and a 3 point average of the individual data points. The IR-MPD spectra with ^{18}O represent an average of three ($650\text{--}1500\text{ cm}^{-1}$) and five ($225\text{--}700\text{ cm}^{-1}$) individual spectra, respectively, and a 3 point average of the individual points. To achieve intensity match of the two spectra, the spectrum in the high wavenumber range was multiplied with a factor of 3.9 for ^{16}O and 2.5 for ^{18}O . The calculated spectra in blue were obtained with the PBE0 functional (relative energies in eV) and the red curves represent the O_3 modes of the shown structures obtained with the PBE functional. Mg, Si, and O atoms are depicted as blue, yellow, and red balls, respectively.

Besides the isomers 1,1,6-a and 1,1,6-b discussed in the main text, we found a third isomer (1,1,6-c at 0.47 eV) without an O₃ unit but instead a superoxide-like O₂ unit (total charge ~ -0.5), which shows an inferior agreement with the IR-MPD spectrum, particularly failing to match bands II-IV.

Table S1: Assignment of experimental bands of MgSi¹⁶O₆⁻ to the vibrational modes of isomer 1,1,6-b (cf. Figure S7).

band	mode (1,1,6-b)	frequency / cm ⁻¹ (PBE0)	frequency / cm ⁻¹ (PBE)	band
I	SiO stretching (terminal oxygen)	1212		
n.v.	O ₃ symmetric stretching	1192	966	II
	O ₃ asymmetric stretching	956	816	III
II	OSiO asymmetric stretching (MgSiO ₂ ring)	939		
III	SiO ₃ symmetric stretching	841		
IV	O ₃ bending	714	653	IV
V	OMgO symmetric stretch (MgSiO ₂ ring)	621		
VI	OMgO asymmetric stretching (MgSiO ₂ ring)	504		
	Mg-O ₃ stretching + SiO ₂ bending (MgSiO ₂ ring)	501		
VII	MgSiO ₂ ring out of plane bending	429		

n.v. = not visible

S2.2 IR-MPD Spectra of MgSi₂¹⁶O₈⁻ and MgSi₂¹⁸O₈⁻

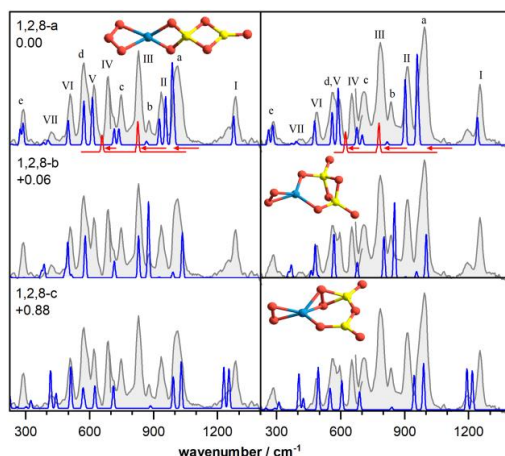


Figure S8: IR-MPD spectrum and calculated vibrational spectra of (left column) MgSi₂¹⁶O₈⁻ and (right column) MgSi₂¹⁸O₈⁻. Further details are given in the caption of Figure S7.

Adding a SiO₂ unit to MgSiO₆⁻, yielding MgSi₂O₈⁻, leads to a rather complex IR-MPD spectrum. Besides the bands I-VII, additional bands (labelled *a-e*) are observed, indicating a cluster structure similar to 1,1,6-b. Indeed, the lowest energy isomer 1,2,8-a is very similar to isomer 1,1,6-a as discussed in the man text. The calculated vibrational spectrum can explain most of the experimentally found features and the new bands *a-e* can be attributed to vibrations of the additional SiO₂ unit as well as shifts and/or splitting of bands already obtained for MgSiO₆⁻ (for a detailed mode analysis see Table S2 below). The only exceptions are bands III and IV, which, however, can be nicely explained by O₃ vibrational modes when calculating the spectrum with the PBE functional (red curve).

In addition, we found a second almost isoenergetic isomer (+ 0.06 eV, isomer 1,2,8-b) that consists of a more compact $\text{MgSi}_2\text{O}_4^-$ core with two terminal O atoms and a superperoxo-like O_2 unit (total charge ~ -0.5). This isomer can clearly not explain bands I, II, c, V, and e and strongly overestimates the intensity of band b. A further isomer is 0.88 eV higher in energy. Although this isomer provides a reasonable match in the spectral region below 650 cm^{-1} , it misses several bands in the $700\text{--}1000\text{ cm}^{-1}$ region.

Table S2: Assignment of experimental bands of $\text{MgSi}_2^{16}\text{O}_8^-$ to the vibrational modes of isomer 1,2,8-a (cf. Figure S8).

band	mode (1,2,8-a)	frequency / cm^{-1} (PBE0)	frequency / cm^{-1} (PBE)	band
I	SiO stretching (terminal oxygen)	1275		
n.v.	O_3 symmetric stretching	1117	1006	a
a	OSiO asymmetric stretching (MgSiO_2 ring)	994		
	OSiO symmetric stretching (MgSiO_2 ring)	986		
II	O_3 asymmetric stretching	956	826	III
	OSiO asymmetric stretching (Si_2O_2 ring)	927		
b	SiO_3 symmetric stretching (terminal oxygen)	866		
III	--	--		
c	OSiO symmetric stretching (Si_2O_2 ring)	737		
IV	O_3 bending	715	658	IV
V	OMgO symmetric stretch (MgSiO_2 ring)	613		
	OSiO asymmetric stretching (Si_2O_2 ring)	610		
d	Mg- O_3 stretching	573		
VI	OMgO asymmetric stretching (MgSiO_2 ring)	499		
	Si_2O_2 ring out of plane bending	411		
VII	MgSiO_2 ring out of plane bending	404		
	$\text{SiO}_2\text{Mg-O}_3$ stretching	383		
e	SiO_3 out of plane bending (terminal oxygen)	287		
	OSiO bending (terminal oxygen)	274		

n.v. = not visible

S2.3 IR-MPD Spectra of $\text{MgSi}_2^{16}\text{O}_7^-$ and $\text{MgSi}_2^{18}\text{O}_7^-$

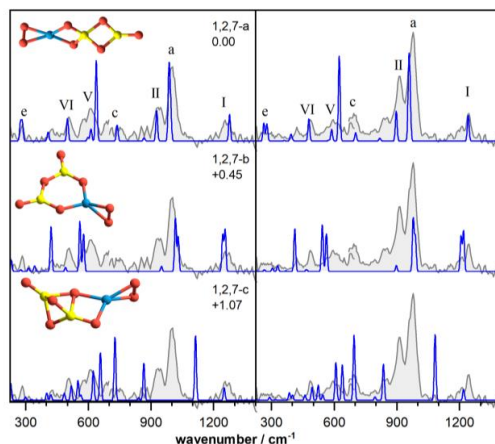


Figure S9: IR-MPD spectrum and calculated vibrational spectra of (left column) $\text{MgSi}_2^{16}\text{O}_7^-$ and (right column) $\text{MgSi}_2^{18}\text{O}_7^-$. Further details are given in the caption of Figure S7.

Figure S9 shows the IR-MPD spectrum of $\text{MgSi}_2\text{O}_7^-$ that is formed by adding a SiO unit to MgSiO_6^- . It should be noted that the depletion yield of $\text{MgSi}_2\text{O}_7^-$ is only half of the depletion yield of the clusters discussed earlier, leading to a reduced signal-to-noise ratio and consequently, low intensity bands might be hidden in the background noise. Similar to $\text{MgSi}_2\text{O}_8^-$, bands I, II, V, and VI as well as bands *a*, *c*, and *e* are clearly observed, while e.g. bands III (assigned to O_3 asymmetric stretching for MgSiO_6^- and $\text{MgSi}_2\text{O}_8^-$) and IV (assigned to O_3 bending for MgSiO_6^- and $\text{MgSi}_2\text{O}_8^-$) are not visible. This indicates again a similar structural motif, but with the absence of an ozone-like O_3 species. Indeed, the minimum energy structure found (1,2,7-a) is similar to the chain-like structure of $\text{MgSi}_2\text{O}_8^-$; however, the removal of one oxygen atom leads to the disappearance of the O_3 unit and instead a superoxo-like O_2 (total charge $\sim -0.5\text{eV}$) is bound to the Mg atom ($d(\text{O}-\text{O}) = 1.33 \text{ \AA}$; $\text{O}-\text{O}$ stretching mode at 1194 cm^{-1} with such a low intensity that it cannot be seen in the vibrational spectrum). The corresponding vibrational spectrum is in favourable agreement with the IR-MPD spectrum and can account for all experimentally observed bands, also in the isotopically labelled experiments. In contrast, the higher energy isomers 1,2,7-b (+0.45 eV) and 1,2,7-c (+1.07 eV) clearly provide inferior agreement.

Table S3: Assignment of experimental bands of $\text{MgSi}_2^{16}\text{O}_7^-$ to the vibrational modes of isomer 1,2,7-a (cf. Figure S9).

band	mode (1,2,7-a)	frequency / cm^{-1}
I	SiO stretching (terminal oxygen)	1275
a	OSiO asymmetric stretching (MgSiO_2 ring)	993
	OSiO symmetric stretching (MgSiO_2 ring)	985
II	OSiO asymmetric stretching (Si_2O_2 ring)	926
n.v.	SiO_3 symmetric stretching	866
c	OSiO symmetric stretching (Si_2O_2 ring)	737
	Mg-O ₂ stretching	637
V	OSiO asymmetric stretching (Si_2O_2 ring)	612
	OMgO + OSiO bending (MgSiO_2 ring)	597
VI	OMgO asymmetric stretching (MgSiO_2 ring)	500
n.v.	Si_2O_2 ring out of plane bending + OMgO asymmetric stretching (MgSiO_2 ring)	411
	MgSiO_2 ring out of plane bending	406
e	SiO_3 out of plane bending	283
	OSiO bending (terminal oxygen)	274

n.v. = not visible

S2.4 IR-MPD Spectrum of $\text{Mg}_2\text{Si}^{16}\text{O}_6^-$ and $\text{Mg}_2\text{Si}^{18}\text{O}_6^-$

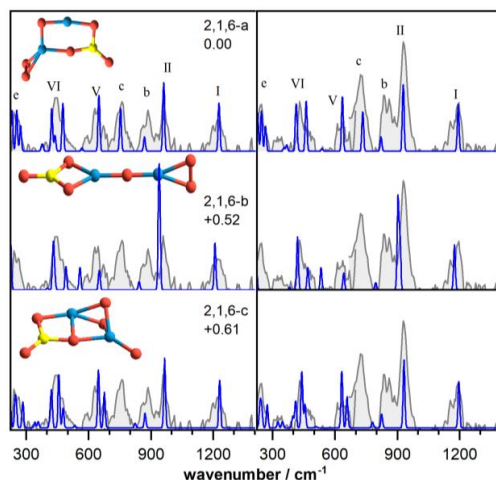


Figure S10: IR-MPD spectrum and calculated vibrational spectra of (left column) $\text{Mg}_2\text{Si}^{16}\text{O}_6^-$ and (right column) $\text{Mg}_2\text{Si}^{18}\text{O}_6^-$. Further details are given in the caption of Figure S7.

Besides the isomer 2,1,6-a discussed in the main text, we found isomers based on a four-membered MgSiO_2 -ring (0.52 eV higher in energy) and one on a six-membered MgSiO_3 -ring (+0.61 eV), which both provide a much poorer comparison.

Table S4: Assignment of experimental bands of $\text{MgSi}_2^{16}\text{O}_6^-$ to the vibrational modes of isomer 2,1,6-a (cf. Figure S10).

band	mode (2,1,6-a)	frequency / cm^{-1}
I	SiO stretching (terminal oxygen)	1227
II	OSiO asymmetric stretching (ring)	961
b	SiO ₃ symmetric stretching	869
c	OMgO asymmetric stretching	753
V	MgO stretching	650
	OSiO bending (ring)	567
	OMgO asymmetric stretching	476
	OSiO bending (including terminal O)	438
VII	SiO ₃ out of plane bending	422
	SiO-Mg stretching	378
	Mg-O ₂ asymmetric stretching	372
	MgO stretching + SiO ₂ bending (terminal O)	272
e	Mg ₂ O ₂ out of plane bending (Mg ₂ SiO ₃ ring)	254
	MgOMg asymmetric stretching	231

S2.5 IR-MPD Spectra of $\text{Mg}_2\text{Si}^{16}\text{O}_7^-$ and $\text{Mg}_2\text{Si}^{18}\text{O}_7^-$

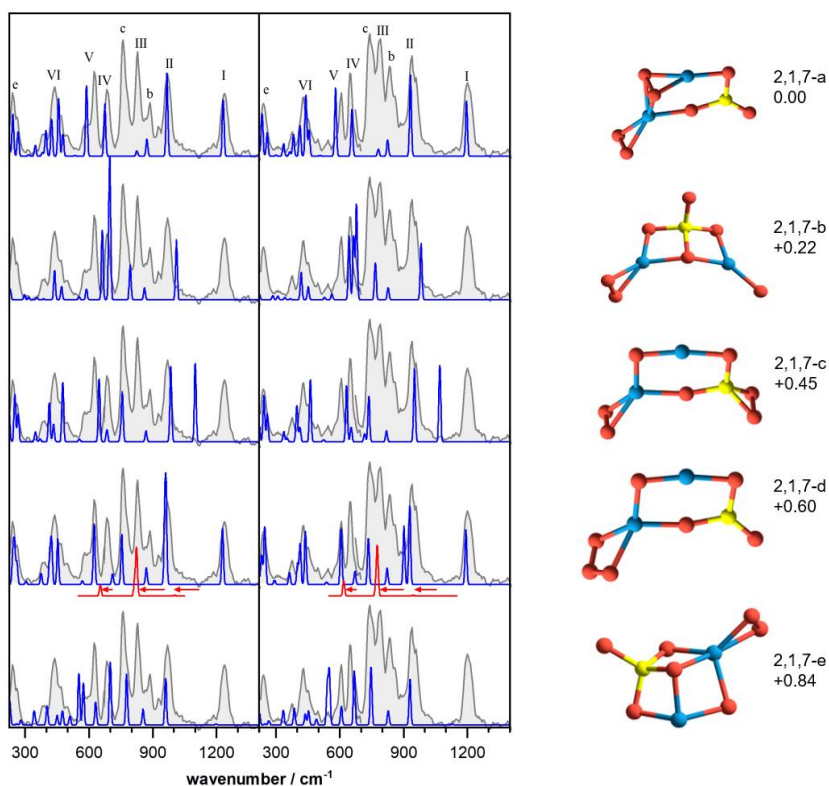


Figure S11: IR-MPD spectrum and calculated vibrational spectra of (left column) $\text{Mg}_2\text{Si}^{16}\text{O}_7^-$ and (right column) $\text{Mg}_2\text{Si}^{18}\text{O}_7^-$. Further details are given in the caption of Figure S7.

The IR-MPD spectrum of $\text{Mg}_2\text{SiO}_7^-$ exhibits g features similar to bands I-V and VII of MgSiO_6^- and three more bands at frequencies comparable to bands *b*, *c*, and *e* of $\text{MgSi}_2\text{O}_8^-$. Similar to $\text{Mg}_2\text{SiO}_6^-$, the minimum energy structure consists of a six-membered Mg_2SiO_3 ring with a terminal O and a superoxo-like O_2 ($d(\text{O}-\text{O})=1.33\text{\AA}$, 1197 cm^{-1} with intensity too low to be visible). The additional oxygen atom bridges the two Mg atoms and forms with $1.54\text{\AA}$ a long O-O bond (O-O stretching at 824 cm^{-1}). This isomer can account for all experimentally observed features, except for bands III and *c*. Three more isomers, both based on a six-membered Mg_2SiO_3 -ring but with different binding of the remaining oxygen atoms are found to be 0.22 eV (2,1,7-b), 0.49 eV (2,1,7-c), and 0.60 eV (2,1,7-d) higher in energy, respectively. Isomer 2,1,7-b shows a feature in the spectral region of band *c* (SiO stretching of terminal O), however, cannot account for band I. Isomer 2,1,7-c also shows a mode in the region of band, however, this isomer can be excluded due to the strong band at around 1100 cm^{-1} (Si-O2 stretching mode) that is not visible in the IR-MPD spectrum. Isomer 2,1,7-d is in very good agreement with the IR-MPD spectrum and is discussed in more detail in the main text. A further isomer has a cubic structure and is 0.84 eV higher in energy. This isomer cannot account for band I.

Table S5: Assignment of experimental bands of $\text{MgSi}_2^{16}\text{O}_7^-$ to the vibrational modes of isomer 2,1,7-d (cf. Figure S11).

band	mode (2,1,7-d)	frequency / cm^{-1} (PBE0)	frequency / cm^{-1} (PBE)	band
I	SiO stretching (terminal oxygen)	1227		
n.v.	O_3 symmetric stretching	1116	1003	II
II	OSiO asymmetric stretching (ring)	962		
b	SiO_3 symmetric stretching	869		
III	O_3 asymmetric stretching	956	823	III
c	OMgO asymmetric stretching (Mg in the center of the ring)	754		
IV	O_3 bending	710	653	IV
V	MgO stretching (Mg close to O_3)	624		
	OSiO bending (ring) + OMgO bending	568		
	OSiO bending (terminal O and O in center of ring)	453		
VI	OSiO bending (ring)	423		
	Mg- O_3 stretching + OSiO bending (terminal O and O in center of ring)	414		
	Mg-Si stretching	374		
	Mg- O_2 asymmetric stretching (terminal oxygens in O_3)	303		
e	O_3 out of plane bending	260		
	Mg-O stretching (center Mg and O in ring)	249		
	Mg_2O_2 ring out of plane bending	241		

S3 Calculated Properties of Selected Neutral and Anionic Clusters

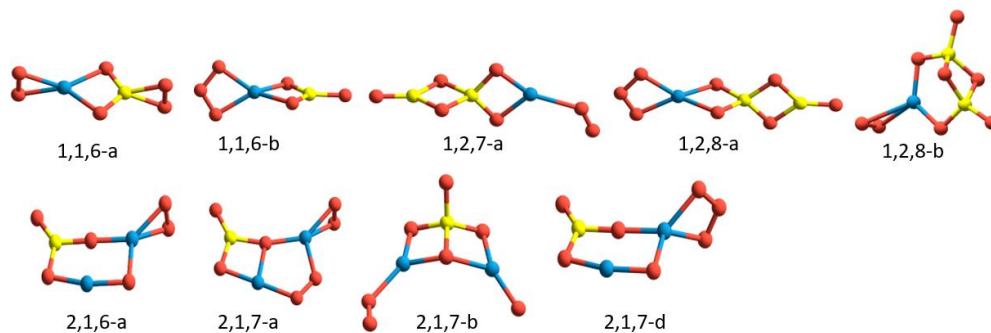


Figure S12: Structure of neutral clusters used for calculating the electron affinities (Table 1 of the main text) as well as the properties given in Tables S6-S8. The structures of the neutral clusters were obtained by full relaxation of the structures of the anions with one electron less.

Table S6. Calculated polarizabilities and dipole moments of some neutral clusters as shown in Figure S12 obtained from DFT calculations.

Cluster	Polarizability / m^3	Dipole moment / Debye
MgSi_2O_7 (1,2,7-a)	$2.02781 \cdot 10^{-29}$	9.16
Mg_2SiO_7 (2,1,7-a)	$2.27381 \cdot 10^{-29}$	5.88
Mg_2SiO_7 (2,1,7-b)	$2.21077 \cdot 10^{-29}$	3.585

Table 7. Vibrational frequencies (cm^{-1}) for MgSi_2O_7 (isomer 1,2,7-a), Mg_2SiO_7 (isomer 2,1,7-a), Mg_2SiO_7 (isomer 2,1,7-b), and FeSi_2O_7 and their respective anions obtained through DFT calculations. The corresponding structures are given in Figure 1 of the main text as well as Figure S12. Fe-containing isomers have the same structure as Mg-containing isomers but with Mg atoms exchanged by Fe.

MgSi_2O_7	Mg_2SiO_7 (a)	Mg_2SiO_7 (b)	$\text{MgSi}_2\text{O}_7^-$	$\text{Mg}_2\text{SiO}_7^-$ (a)	$\text{Mg}_2\text{SiO}_7^-$ (b)	FeSi_2O_7	$\text{FeSi}_2\text{O}_7^-$
16.3	53.2	16.6	51.1	57.8	51.1	17.34	50.97
18.2	64.5	29.9	68.8	73.7	62.5	46.18	68.80
58.6	83.4	48.5	78.0	90.8	76.7	89.09	99.57
85.1	88.6	58.9	131.5	92.2	108.1	90.54	119.03
120.3	109.6	100.1	164.1	161.4	133.3	95.54	129.16
129.7	164.7	117.6	224.3	229.5	139.4	167.31	220.35
188.7	167.2	123.4	242.9	248.1	194.7	209.89	235.95
218.1	201.4	181.8	282.8	249.4	227.3	259.77	266.28
280.1	207.4	193.9	291.9	274.0	236.3	274.33	280.81
289.9	240.2	233.7	390.8	326.4	305.3	274.54	398.49
356.8	333.0	246.9	419.0	357.7	325.6	393.59	400.90
411.7	352.7	312.6	423.4	392.7	365.1	426.99	461.93
446.4	401.6	359.8	434.6	409.1	398.3	434.42	500.99
593.5	424.6	440.9	515.5	436.7	451.2	561.23	534.55
612.1	459.1	469.1	616.1	470.7	484.8	570.35	578.06
689.0	495.6	536.0	631.1	491.4	569.2	713.38	634.43
705.4	551.9	620.2	657.3	549.0	605.5	717.46	648.96
788.5	633.2	659.1	760.5	605.9	682.2	789.08	761.42
877.8	704.4	699.4	893.1	694.8	715.6	868.49	888.95
925.1	918.2	718.7	955.4	849.9	719.6	882.03	928.15
928.5	952.6	812.3	1015.8	898.5	817.7	921.29	946.99
995.4	1218.6	898.0	1023.6	996.0	886.9	1002.83	996.76
1334.4	1313.9	1049.0	1231.7	1234.4	1041.9	1274.01	1021.27
1708.8	1320.2	1572.7	1314.8	1268.2	1230.7	1344.27	1319.71

Table 8: Rotational constants (MHz) for MgSi_2O_7 (isomer 1,2,7-a), Mg_2SiO_7 (isomer 2,1,7-a), Mg_2SiO_7 (isomer 2,1,7-b), and FeSi_2O_7 and their respective anions obtained through DFT calculations. The corresponding structures are given in Figures 1 of the main text as well as Figure S12. Fe-containing isomers have the same structure as Mg-containing isomers but with Mg atoms exchanged by Fe.

MgSi_2O_7	Mg_2SiO_7 (a)	Mg_2SiO_7 (b)	$\text{MgSi}_2\text{O}_7^-$	$\text{Mg}_2\text{SiO}_7^-$ (a)	$\text{Mg}_2\text{SiO}_7^-$ (b)	FeSi_2O_7	$\text{FeSi}_2\text{O}_7^-$
4151.03	1562.65	1541.42	4604.53	1576.97	1286.80	5145.23	4551.51
370.670	643.769	584.563	401.857	662.919	650.819	339.30	371.93
361.765	473.095	447.952	399.459	497.116	474.384	336.95	369.09

References

1. Meng, W.; Audi, G.; Kondev, F. G.; Huang, W. J.; Naimi, S.; Sing, X., *Chinese Phys. C* **2017**, *41*, 030003.

APPENDIX E

Supporting Information for:
Understanding the Size-dependent
Structural Properties and Infrared
Spectra of Silicate Dust Grains via
Atomistic Nucleated Growth
Simulations

Force Field Parameters

In the following tables, the different parameters of the FF used in the MD simulation of the nucleated nanosilicate growth are shown.

Element	Charge
Si	2.7226
Mg	1.3613
O _{Core}	1.91981
O _{Shell}	-3.28111

Table 1: Charges of the Force Field used in the MD Simulations

Interacting atoms	A (eV)	P (Å)	C (eV/Å ⁶)
Si- O _{Shell}	8166.2632	0.193884	0.0
O _{Shell} - O _{Core}	15039.909	0.227708	0.0
Mg - O _{Shell}	2014.61	0.247732	10.1938

Table 2: Buckingham parameters of the Force Field used in the MD Simulations

Interacting atoms	Spring constant (Å ⁻²)
O _{Core} - O _{Shell}	2.7226

Table 3: Core-Shell Spring Constant of the Force Field used in the MD Simulations

DFT vs FF energetic stability

To validate the ability of the FF described in Tables 1–3 to accurately sample nanosilicate structures during MD simulations, the set of nanosilicate structures used in Chapter 6 was employed as a reference. Each structure in this set was optimized using both DFT-PBE0 and the aforementioned FF. Figure 1 presents the relative energy per unit (MgSiO_3 and Mg_2SiO_4 , depending on the stoichiometry) obtained from both optimization methods. As shown in the figure, there is an almost linear correlation between the relative energies computed with DFT and FF. This suggests that the FF effectively reproduces the relative energy trends obtained from high-accuracy DFT calculations, confirming its suitability for use in MD simulations.

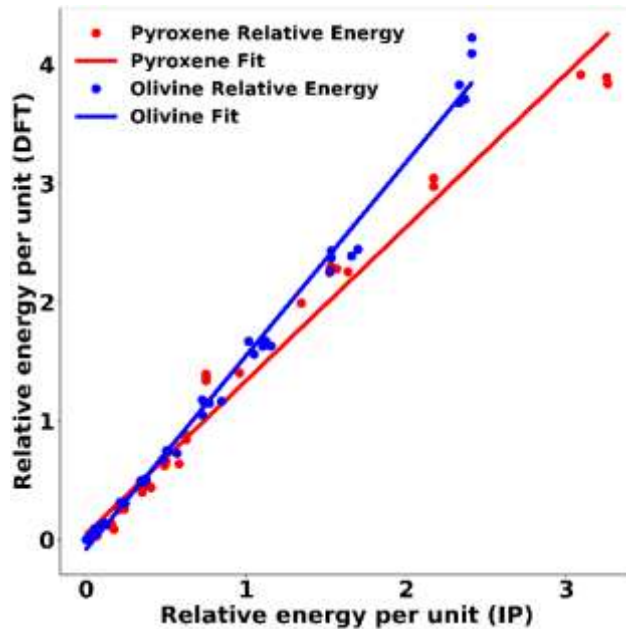


Figure 1: Relationship between the relative energies of the optimized structures of all grains in the nanosilicate set used in Chapter 6, using DFT-PBE0 and the FF previously described.

DFT vs FF IR spectra

To evaluate the accuracy of the FF used to compute the harmonic spectra of nanosilicate grains, we computed the harmonic spectra of a nanosilicate population consisting of the 92 grains modelled in Chapter 6 using DFT-PBE0 and the FF. Figure 2, presents a comparison of these spectra, considering different signal broadenings.

The results indicate that, in terms of vibrational mode wavelengths, the FF performs remarkably well, as the overall shape of both spectra is nearly identical. However, the FF systematically overestimates the intensity of signals corresponding to the 11 and 16-micron nanosilicate features. To correct this intensity excess, we derived an intensity ratio by comparing DFT and FF intensities across the entire reference spectrum and applied this correction to the remaining FF-computed harmonic spectra. To minimize spectral noise, we used the ratio obtained from spectra broadened with Gaussian functions featuring FWHM of 100 cm^{-1} for which the signals are smoother.

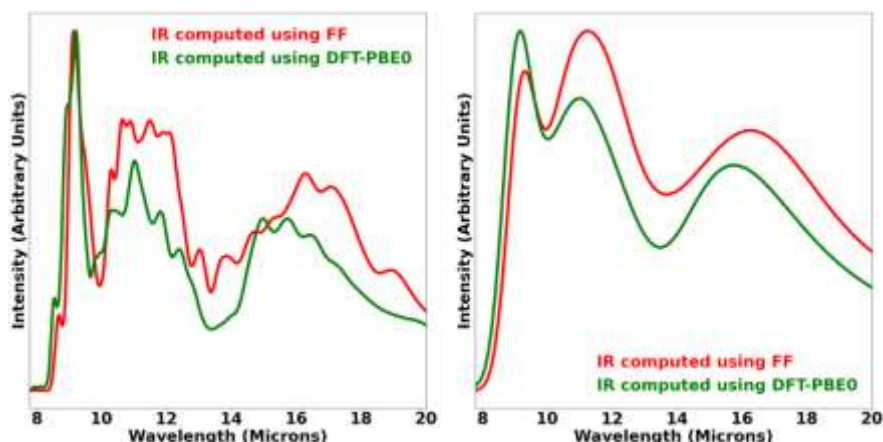


Figure 2: Comparison between the harmonic spectra obtained using DFT-PBE0 (green) and the previously described FF (red), broadening each signal using Gaussian functions with 20 cm^{-1} (left) and 100 cm^{-1} (right) FWHM.

Physical properties obtained at 600 K

In this section, the plots with the results of the simulations carried out at 600 K are presented. Overall, the trends are the same as in the simulations at 1100 K.

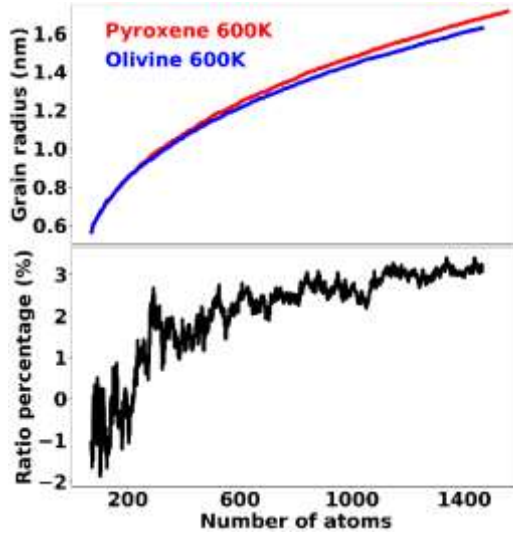


Figure 3: Evolution of silicate grain radius (top) of pyroxene (red) and olivine (blue) grains at 600K with respect to the number of atoms in the grain. Bottom panel shows the corresponding ratio (as a percentage) of the radii of pyroxene to olivine grains. The results for each grain composition are obtained from averages over ten nucleated growth simulations.

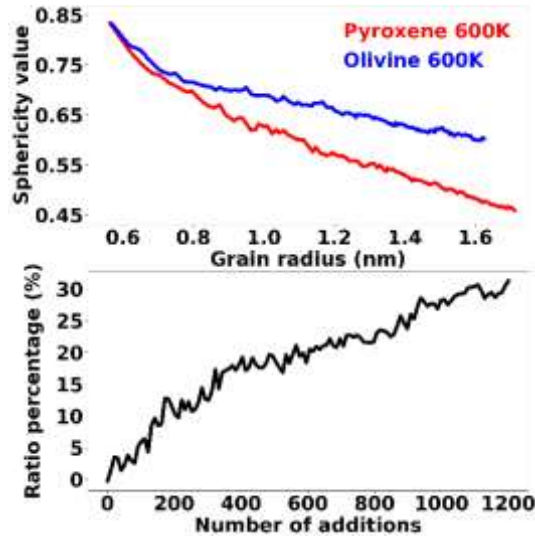


Figure 4: Top: Silicate grain sphericity evolution with respect to increasing grain radius for pyroxene (red) and olivine (blue) grains at 600 K. Bottom: the ratio (as a percentage) of pyroxene sphericity to olivine sphericity. The results are obtained from averages over ten nucleated growth simulations.

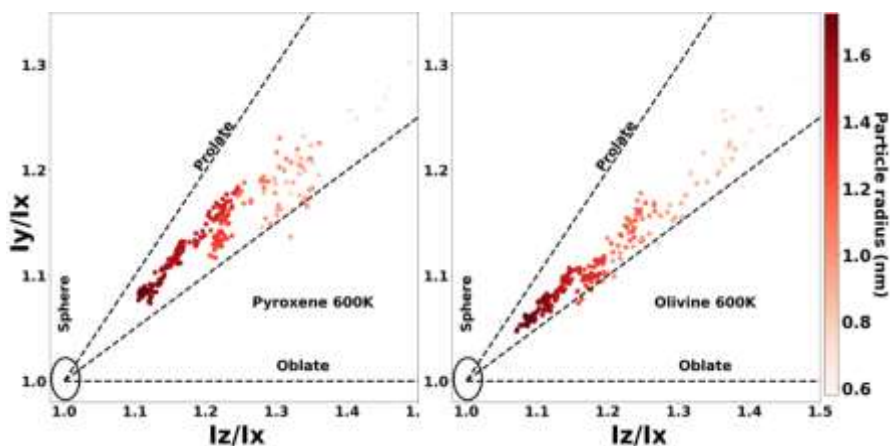


Figure 5: Silicate grain shape evolution for simulations of pyroxenic (left) and olivinic (right) grains at 1100K. The results are obtained from averages over ten nucleated growth simulations.

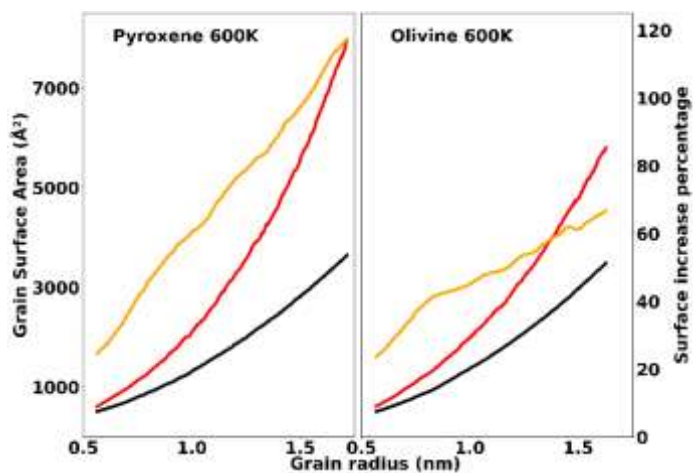


Figure 6: Surface area of growing grains (red line) and of a sphere with same radius as the grain (black line) referred to left y-axis. The orange line shows the percentage of excess surface area of the grains with respect to the corresponding sphere. Results are shown for pyroxenic (left) and olivinic (right) grains at 600 K. The results are obtained from averages over ten nucleated growth simulations.

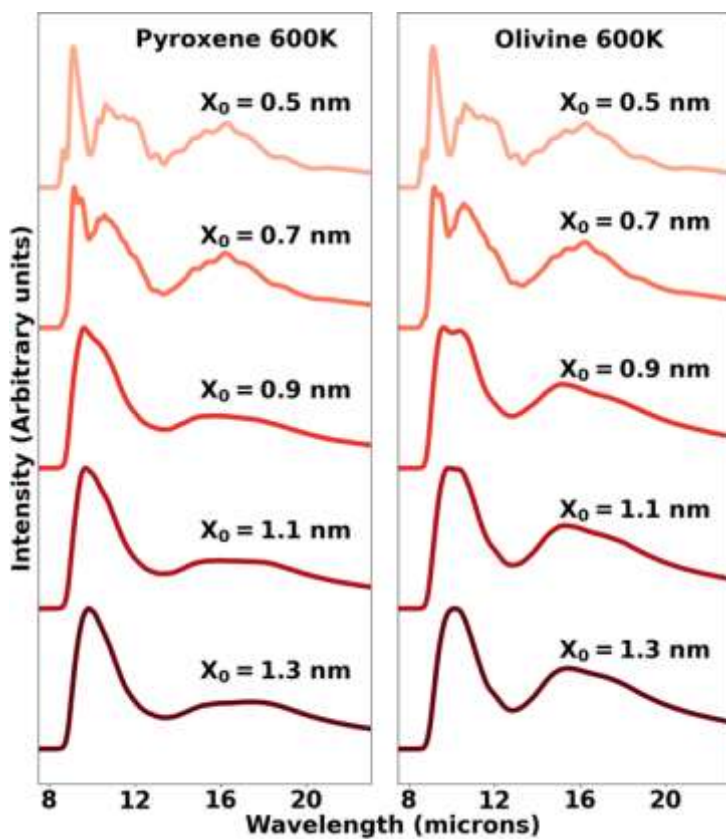


Figure 7: Evolution of IR spectra of different grain size populations containing pyroxene (left) and olivine (right) grains at 600 K. X_0 values indicate the average radius of the grain in the population.

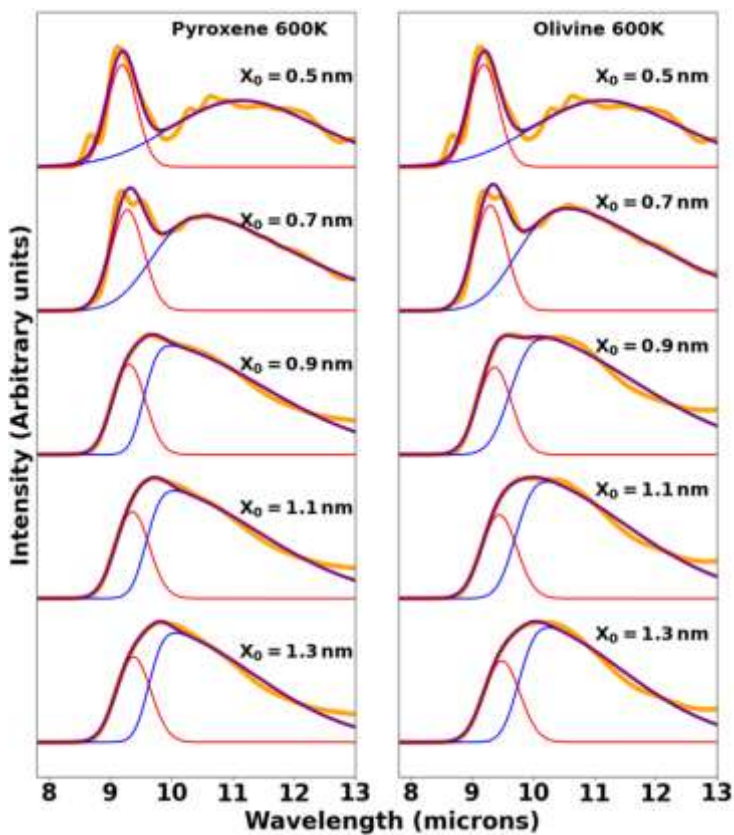


Figure 8: Fitting (purple) of the IR spectra of grain populations in Figure 7 (Orange) using a Gaussian function (red) and a skewed Gaussian function (blue).

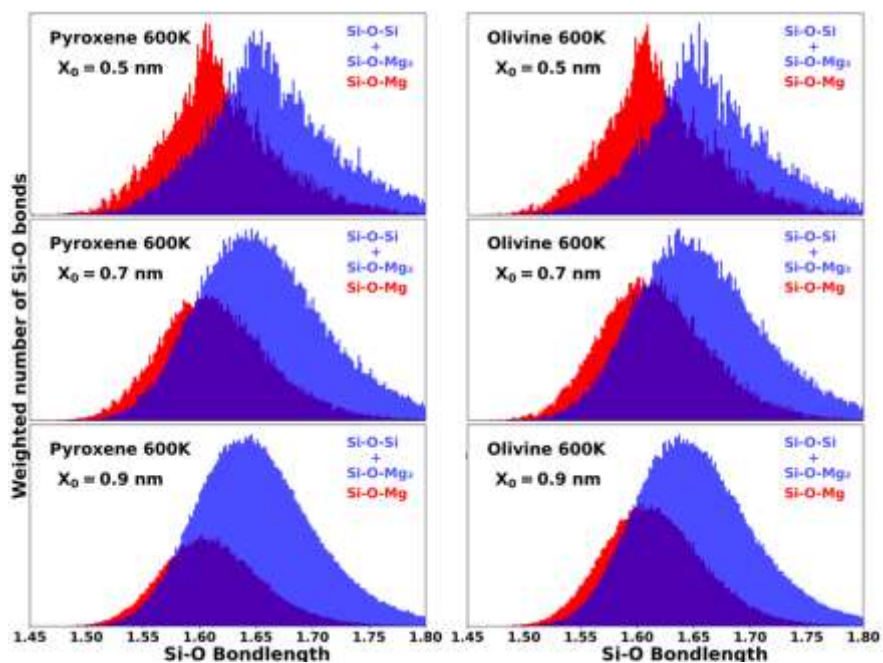


Figure 9: Histograms showing the weighted number of Si-O bonds with a given bond length, for different Si-O environments, for a population of grains with average radii of 0.5 (top), 0.7 (middle) and 0.9 nm (bottom). The grain populations are the same as in the spectra of Figure 7.

