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Theoretical modeling of photon- and electron-stimulated Na and K desorption from SiO_2

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The mechanism of generation of atomic Na and K from SiO_2 samples has been studied using explicitly correlated wave function and density functional theory cluster calculations. Possible pathways for the photon and electron stimulated desorption of Na and K atoms from silicates are proposed, thus providing new insight on the generation of the tenuous Na and K atmosphere of the Moon.

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I. INTRODUCTION

Neutral alkali vapors (Na, K) are found in the tenuous atmospheres of the planet Mercury, and Earth's Moon.[1–3] Recent laboratory studies provide evidence that photon-stimulated desorption by ultraviolet solar photons is a dominant source process for alkalis in the atmospheres. For a perspective of the phenomena in interplanetary space, see Ref. 4. In particular, experimental results on the photon- and electron-stimulated desorption of Na and K from a lunar basalt surface, and from a model system consisting of a thin film of SiO_2 growth on Re were reported by Yakshinskiy and Madey.[5–7] According to these authors desorption can be initiated by an electronic excitation at about 4 eV, this value being the lowest threshold at which photon absorption results in alkali metals release. It has also been observed that a second excitation in the 8–11 eV energy range further generates nascent alkali atoms. This transition has been tentatively assigned to electronic transitions from valence or band gap states in SiO_2, followed by electron trapping at alkali metal cations which are neutralized in the process and emitted afterwards. A similar interpretation has been previously reported for the emission of hydrogen by electron trapping at protons in silica.[8] In this study we present a theoretical model based on the interaction of Na^+ and Na with regular and defect sites of silica. In particular, we focus on the transition energies associated with the Na species incorporated in the lattice and on the mechanisms that can lead to a release of Na atoms under irradiation. To this end we have performed highly sophisticated *ab initio* quantum chemical calculations for the ground state and excited states of the systems under consideration.

In order to model such a complex system as that represented by Na atoms incorporated at the surface of silica structures one has to make some assumptions about the bonding mode of the Na atoms or ions with the lattice. In particular we have considered two cases, both based on the hypothesis that the active species involves Na^+ but in two different environments in the silica lattice. In the first model, Na^+ is directly interacting with a regular O site. The second one is based on the idea that what is actually incorporated is neutral Na that upon interaction with defect sites of the SiO_2 network also becomes $Na^{\delta+}$. The assumption that the species is $Na^{\delta+}$ is based on previous studies that have shown that the interaction of neutral atomic Na with the SiO_2 regular lattice gives rise only to a weak bonding.[9] On the other hand, a neutral Na atom can interact strongly with point defects present in the structure, like a nonbridging oxygen atom, NBO ($\equiv$Si-O$^\bullet$), or a Si dangling bond ($\equiv$Si$^\bullet$ or E' center). Both these defect centers have been well identified and characterized in crystalline and amorphous silica. A third possibility is that a Na atom is incorporated into the SiO_2 lattice by breaking a Si-O bond, with formation of a $\equiv$Si-O-Na… $^\bullet$Si$\equiv$ structure. This would lead to a Si-O-Na bonding with polar character similar to that formed by a Na atom bound to a NBO center. Thus the problem is restricted to the analysis of essentially two kinds of bonding of sodium to SiO_2: (1) a Na^+ ion interacting with one or more oxygen atoms of the nondefective lattice; (2) a Na atom interacting with a NBO defect center, Si-O-Na; even if other classes of species like a Na atom interacting with a Si$^\bullet$ defect center can exist, we have only briefly considered their effect. The calculations are extended also to K in similar bonding situations.

II. COMPUTATIONAL DETAILS

In order to study the possible generation of atomic Na and K from SiO_2 samples we have employed embedded cluster models together with both wave function and density functional theory methods.

Cluster models were cut from the α-quartz structure where the O-Si dangling bonds are further saturated with H atoms, which provides a simple embedding representing the mechanical constraints associated with the presence of the rest of the solid matrix. This kind of embedding and the clusters themselves have been found to be reasonable models when compared to larger structures and quantum mechanic–molecular mechanics (QM/MM) calculations.[10] Two models have been explored: the first one represents the regular surface while the second one is representative of one of the most common point defects in silica samples when produced in O_2 excess atmospheres, the nonbridging oxygen NBO center, where a Si-O link is lost. The models employed are

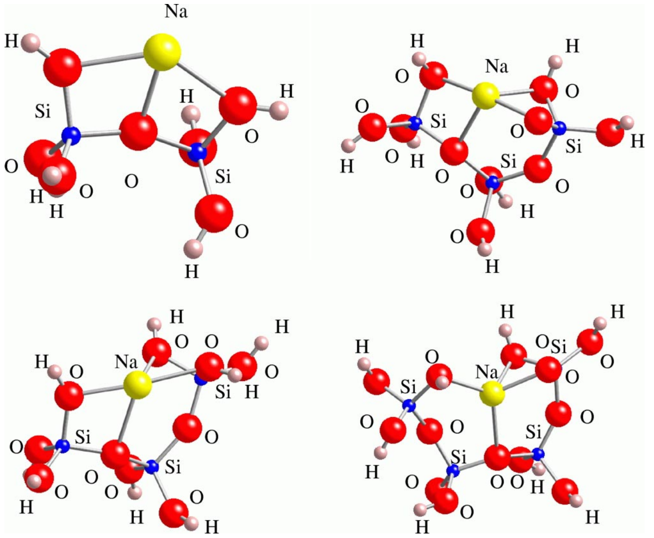

FIG. 1. (Color online) Adsorption of alkalis at regular and defect sites of SiO_2. Regular sites, on the left column, are represented by a two tetrahedra (top) and three tetrahedra (bottom) model. The nonbridging oxygen (NBO) defect models are shown on the right column with three and four tetrahedra (top and bottom) models.

the same as in previous papers,[9] a 2-tetrahedra model to represent the regular surface and a 3-tetrahedra cluster to model the NBO defect.[11] In both cases these models have been further complemented by a 3-tetrahedra model (for the regular surface) and a 4-tetrahedra model for the NBO defect, to carefully analyze the effect of the embedding employed and the fact that the metal atom can interact with several oxygens on the substrate, see below. The optimization of different structures has been carried out within the density functional theory (DFT) employing B3LYP as the exchange-correlation functional.[12,13] During the optimizations the terminal H atoms are kept fixed to simulate the existence of the solid matrix. The basis set employed has been 6-31G* for all atoms in the model. The structures for the alkali-NBO and alkali-regular surface are shown in Fig. 1.

The study of stimulated desorption has been performed with two different methods: Time dependent density functional theory (TDDFT) (B3LYP functional) and a method derived from second order perturbation theory applied to a complete active space self-consistent field wave function (CASPT2). These techniques were previously employed to study spectroscopic features of defects in SiO_2.[15,16] The electronic transition between the ground and the first singlet excited state has been studied at the state average CASSCF (SA-CASSCF)/multistate CASPT2 (MS-CASPT2)[17] level. MS-CASPT2 method is an extension of the CASPT2 treatment, able to correctly treat quasi-degeneracy situations. In these calculations, atomic natural orbital (ANO) basis sets[18,19] have been used with the following contraction scheme: $[4s/2s]$ for H, $[14s9p4d/4s3p1d]$ for O and $[17s12p5d/5s4p1d]$ for Na and Si, and finally $[17s12p4d/6s5p2d]$ for K. The active space contains the ns alkali orbital $[n=3(4)$ for Na $(K)]$, the occupied $2p$ orbitals of the nearest oxygen atom to the alkali and their corresponding virtual p and d counterparts. Therefore, the active space contains 4 electrons and 10 molecular orbitals, with a total of 825 configuration state functions. For the TDDFT calculations we have employed the same basis set as in the optimization processes and we have determined the lowest roots (or energy transitions) with the proper character.

III. RESULTS

The results for a series of cluster models of SiO_2 containing different alkali atoms and cations are presented as follows. First, we consider the properties of the ground state and we discuss in particular the bonding mode and the stability of the models described above. In a second step we consider the local excitation energies associated to these systems. Finally, we describe possible mechanisms which can lead to the release of Na or K atoms under the effect of irradiation. This has been done by studying the potential energy curves for the interaction of the alkali atom with a given bonding site in the ground and in the excited states. From the shape of the potential energy curves one can deduce the efficiency of the process for alkali detachment from the silica lattice.

A. Geometries and binding energies

In Table I, we report the structures and geometries for different Na(K)-SiO_2 models. The bonding of Na^+ and K^+ to the clusters is on the order of 3 eV (Na^+) and 2 eV (K^+), where the different stability is essentially connected to the larger dimension of K (see for instance the longer K-O distance, 2.6–2.7 Å, compared to the Na-O distance, 2.2 Å). For both ions, the interaction is not restricted to a single O atom, but involves 2 or 3 bridging oxygens in the structure; see Fig. 1. The bonding is largely due to the polarizing effect of the cations on the lone pair orbitals of the O atoms, with little charge transfer from oxygen to the alkali cation. The interaction of neutral Na or K with a NBO center arises largely from the coupling of the unpaired electrons, one in the $O(2p)$ states and one in the alkali *ns* orbital. The bonding is largely localized, and a substantial polarization of the electrons towards oxygen allows one to classify the bonding as $\equiv$Si-$O^{\delta-}$-$M^{\delta+}$. This charging can be seen from the values of the Weinhold charges.[23] The reason to select Weinhold charges instead of the standard Mulliken charges is that the former are more stable with respect to the atomic coordination number and the extension of the basis set, two key issues in the present calculations. As shown in the Table I, charges on the alkalis are in all cases positive and large, more than 0.8, showing that in both models the alkalis are present on the surface as cations.

Very similar results have been obtained with the $2T$, $3T$ cluster models of the regular surface and the $3T$, $4T$ model of the defective surface. Therefore we have employed only the simplest models to perform the CASPT2 calculations, which are much more time consuming than the TDDFT ones. A final technical aspect is that since the strength of the bond is large we have not included basis set superposition error effects since they will not change our description.

TABLE I. Geometries for Na and K adsorbed on $2T$ and $3T$ clusters (regular surface), and $3T$ and $4T$ (defective surfaces) and the corresponding binding energies. d_O stands for the distance in Å to the nearest O atoms. Binding energies, in eV, for detaching Na^+ (K^+) and Na (K) from the models are included. q_M stands for the Weinhold charges on the alkali metals. (BE^i stands for ionic asymptote: regular$+$alkali$^+$ or NBO$^-$ $+$alkali$^+$; BE^n stands for the neutral: NBO$+$alkali asymptote.)

	$2T$ regular Na^+	$2T$ regular K^+	$3T$ regular Na^+	$3T$ regular K^+	$3T$ NBO Na	$3T$ NBO K	$4T$ NBO Na	$4T$ NBO K
d_O	2.212	2.693	2.196	2.595	2.208	2.461	2.199	2.448
d_O	2.381	2.736	2.348	2.671	2.260	2.704	2.242	2.673
d_O	2.448	2.796	2.462	2.681	2.304	2.791	2.393	2.883
d_O			2.472	2.747	2.392	2.796	2.462	3.013
BE^i	2.92	1.96	3.19	2.27	7.55	6.38	7.10	5.92
BE^n					5.25	5.00	4.56	4.31
q_M	0.96	0.98	0.93	0.97	0.88	0.95	0.87	0.95

B. Transition energies and excited state profiles

In the experiments there are two strong bands associated with the stimulated desorption of alkali atoms adsorbed on the silica network. One of the bands is alkali dependent and the onset for desorption arises at about 3.5 to 4 eV for K and Na, respectively, while the second one seems to be less dependent on the nature of the metal and maximizes at energies of about 9 eV; this is in the same region where the conduction band is placed for these materials. In fact, this second band has been suggested to be related to internal conversions in the material in the sense that a transition across the band gap can deactivate through the desorption of an alkali atom.

To better assess the reliability of the present theoretical models we have computed some test values as reported in Table II. In particular we considered the ionization potential (IP) of Na and K, the first $ns \rightarrow np$ excitation energy, T_e, and the estimate of the band gap in SiO_2 computed as the first singlet to singlet transition in our cluster model constituted by two tetrahedra. The results are generally satisfactory, showing that both TDDFT and CASPT2 provide values close to the experimental ones. The band gap is underestimated in TDDFT, a feature which is not surprising given the well known problems caused by electron self-interactions. Furthermore, the small clusters used do not allow a proper description of the valence and conduction bands of the system. Due to the use of cluster models our estimation of the band gap is done through the calculation of the self-trapped exciton (STE). The results are close to the band gap for CASPT2 and less accurate for TDDFT showing how well silica properties can be reproduced with the present approach. It should be kept in mind that CASPT2 results have been obtained with the smallest possible CAS and therefore could be further improved if necessary.

TABLE II. Ionization potentials (IP), first transition energies, T_e, and band gap energies, E_g; all the results are in eV.

System	TDDFT (B3LYP)	CASPT2	Experiment
IP (Na)	5.40	4.97	5.14[a]
IP (K)	4.48	4.08	4.34[a]
T_e (Na)	2.26	1.99	2.10[a]
T_e (K)	1.67	1.48	1.61[a]
E_g	7.4	8.15	8.6–8.8[b]

[a] Reference 20.

[b] Experimental band gap, Refs. 21 and 22.

In Table III we report the transition energies for the metals adsorbed on different SiO_2 sites. Together with the energy required to reach the excited state, denoted as T_e, we report the oscillator strength between ground and excited state, f. Clearly, the intensity of the photon adsorption, and consequently of alkali emission, is proportional to this oscillator strength.

Our calculations seem to indicate that the first absorption band observed in the lower energy range could originate from electron transfer from the NBO oxygen to the alkali metal when this is bonded to a defect on the material. As shown by the experiments this transition depends strongly on the alkali atom and it is lower for K. When comparing both types of calculations, TDDFT and CASPT2 values, the transition energies differ by about 1–1.5 eV (see Table IV). These energy differences have several origins. One is the limited inclusion of correlation effects in CASPT2, due to both a limited active space and the need for larger basis sets when massively including correlation. On the other hand, TDDFT may suffer from typical underestimation of high-energy transitions due to the too low prediction of the band gap in the material.[14] Again this problem is connected to the Coulomb self-interaction energy.

With respect to the second band, observed in the energy range of the band gap of the material,[5–7] it has been assigned to the transference of an electron from the valence band of silica to the conduction band that afterwards can result in Na emission. The calculations show that the high energy band involves a transition from any O($2p$) nonbonding state to the adsorbed Na^+ or K^+ species. According to the values in Table III the energy needed for the transition is quite independent of the nature of the metal atom and appears at much higher energies than for defects, close to the band gap values. Again TDDFT estimates are much lower than CASPT2 val-

TABLE III. Vertical transition energies, T_e in eV, and oscillator strengths, *f*, for $2T$ and $3T$ models of Na^+ bound to the regular SiO_2 surface and for $3T$ and $4T$ models of neutral Na bound to a NBO defect center of SiO_2. Only transitions bearing enough intensity are reported. For TDDFT the lowest two transitions are reported, T_{e1} and T_{e2}, together with the corresponding oscillator strengths, f_1 and f_2. (For a Si dangling bond the onset of adsorption is at 2.8 eV with an oscillator strength of $f = 0.0390$ for Na, and 2.4 eV and $f = 0.0544$ for K.)

	$2T$ reg. Na^+	$2T$ reg. K^+	$3T$ reg. Na^+	$3T$ reg. K^+	$3T$ NBO Na	$3T$ NBO K	$4T$ NBO Na	$4T$ NBO K
CASPT2								
T_e, eV	8.7	8.9			5.6	5.3		
$f(10^{-2})$	3.53	3.79			4.16	2.26		
TDDFT (B3LYP)								
T_{e1}, eV	7.1	7.1	7.2	7.3	4.4	3.8	4.5	3.9
$f_1(10^{-2})$	1.41	1.45	1.16	1.53	1.69	2.22	1.11	1.70
T_{e2}, eV	7.3	7.4	7.6	7.4	5.5	5.2	5.2	5.2
$f_2(10^{-2})$	4.35	1.89	2.87	1.49	1.69	1.40	1.76	1.11

ues. Still, they suggest that the second band can be associated with a band gap excitation which transfers one electron to the adsorbed cation. Even more, it has been shown before that the ability to determine excited states through TDDFT schemes depends on the transition energy and the quality of results decays when considering higher excited states, in that case both the excitation and the self-trapped exciton appear at very similar energies.[24] It should be mentioned that this transition corresponds to the creation of a localized hole in a $2p$ nonbonding orbital of a bridging oxygen atom. The resulting paramagnetic center is known as a self-trapped hole, STH ($\equiv$Si-O$^\bullet$-SiO$\equiv$), and has been carefully characterized by both EPR experiments and theoretical calculations.[25,26]

A key problem is to determine if photon absorption in the process described above can cause the release of free Na or K atoms. This can be done by exploring the potential energy surfaces, or a suitable section, of all the different states involved. For these studies TDDFT is not well suited since it has problems in the description of the asymptotes when calculated as supermolecule, because of the use of a single determinant in the Kohn-Sham formulation. Therefore, in order to study the shape of the excited states we have employed the CASPT2 description of the potential energy surfaces for the ground and excited states of the models described before, which depend only on the coordinate that controls the separation between the SiO_2 and the alkali metal atom. For singly-coordinated adsorbates, the initial force ejecting the desorbing ion or atom is along the bond direction. In the case of multiply coordinated sites the situation is somewhat more complicated and one should explore the potential energy surfaces in the excited state. However, from the preceeding discussion one can assume that the nature of these potential energy surfaces is repulsive for all directions representing a motion of the alkali atom outwards from the surface.

TABLE IV. Tentative assignment of observed bands; all the energies are in eV.

Experiment	Assignation	TDDFT	CASPT2
4	Na-NBO	4.4	5.62
3.5	K-NBO	3.8	5.30
10	Na^+ regular O	7.2	8.7
9	K^+ regular O	7.3	8.9

We start by considering the high energy process corresponding to release of alkali metals for energies about 9 eV. We have seen before that this process involves a charge transfer from the O($2p$) band to the Na^+ with formation of a STH and a neutral Na atom. These curves are reported in Fig. 2 as calculated for the interaction of Na^+ with the regular surface studied with the 2-T model. The ground state shows a bonding character, and can be described as $(SiO_2)\times(Na^+)$; the excited state, schematically $(SiO_2^+)(Na)$, is purely repulsive and lies about 8 eV above the ground state. Thus, the excited state $(Na^0)+(SiO_2^+)$ is such to generate nascent Na^0 atoms by adsorbing photons of about 8–9 eV. This is quite similar to the observed structure for the H^+

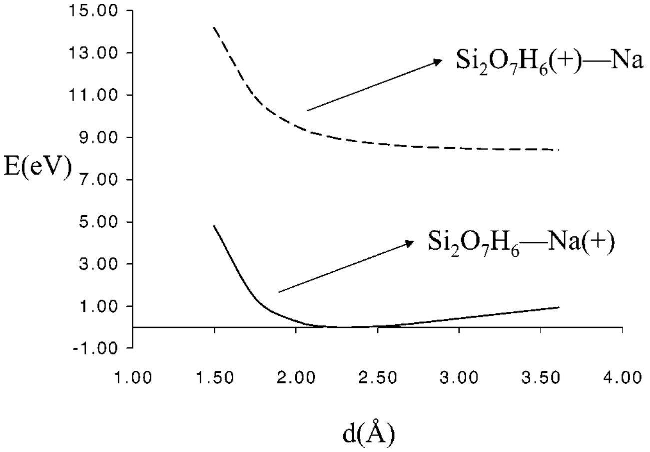

FIG. 2. Potential energy curves (CASPT2) for the ground and first excited states of a Na^+ cation bound to a regular site of the SiO_2 surface.

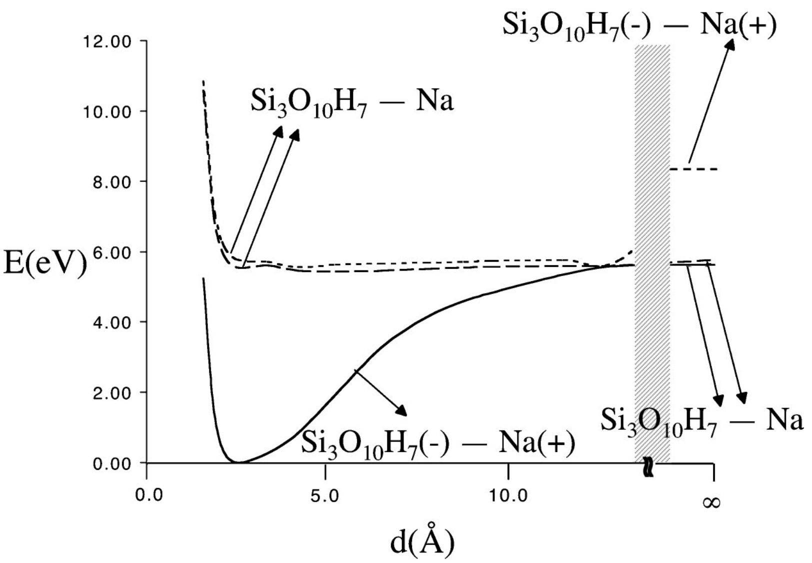

FIG. 3. Potential energy curves (CASPT2) for the ground and lowest excited states of a Na atom bound to a NBO defect center of the SiO_2 surface.

$+SiO_2$ system; however in that case, due to the high value of the hydrogen ionization potential, the two diabatic curves cross.[8]

The second process is that involving a Na atom bound to a defect like the NBO center, ≡Si-O-Na. Here the situation is more complicated. The ground state has a significant polar character and can be described as Si-$O^{\delta-}$-$Na^{\delta+}$. There are several transitions associated to this center, but only transitions which correspond to a charge transfer from oxygen to Na (or K) have sufficient intensity. Therefore, in the following discussion we concentrate on the ground state and on the charge-transfer exited states which lead to a (≡Si-$O^{\bullet}$) $+(Na^0)$ structure. These two excited states correspond to charge transfer processes to the Na ($3s$) empty state from two different p orbitals of the same oxygen defective center. The curves are shown in Fig. 3. At low Na-SiO_2 distances where the minimum occurs for the ground state the transition to the excited state takes place. The excited state is repulsive in nature thus pushing the neutral metal atom far away from the lattice. At larger distances, about 10 Å, a complex area exists with (at least) two avoided crossings between the excited states and the ground state. The coupling constants at this point are quite small since the energy difference between the curves is very small in this region. Therefore, at infinite distances the metal is neutral. The irregularities in the excited state curves in the range from 2 to 4 Å in Fig. 3 observed for the excited states are due to the fact that an avoided crossing occurs between the two excited states. In fact, this kind of profile could be quite general since several states might lay in the same energetic region because similar O atoms exist in the network. These avoided crossings may introduce small wells and tiny barriers in the excited states. However, our accuracy prevents us from being more definitive at this point.

The final aspect that needs some clarification is related to the dynamics of the system, that is, the possibility of releasing Na or K after photon or electron irradiation. This would imply that the nuclear relaxation following the vertical excitation is extremely fast (nonradiative decay), and can lead to bond breaking before decay from the excited state to the ground state. In fact, from measurements of electron-stimulated desorption, the desorbing Na and K atoms are thermally "hot," with kinetic energies of order 0.1 eV,[5,6] qualitatively this is consistent with the profiles reported in Fig. 2 and Fig. 3. This means that the excited state lives enough time so Na with 0.1 eV kinetic energy can travel far enough for the adsorbate-surface bond to break (1 Å) in approximately 0.1 ps. Thus, an excited state lifetime longer than 0.1 ps is adequate for desorption to occur. Of course, the detailed shape of the potential energy curves in the Franck Condon region will determine the exact dynamics.

The lifetime of the excited state, τ, depends on the oscillator strength as follows:

$$\tau = 1.499/[\Delta E^2 * f], \tag{1}$$

where ΔE is the energy difference between ground and excited state in cm^{-1}, and $f(r)$ is the oscillator strength.[27] Using for $\Delta E = 7.3$ eV (58881 cm^{-1}) and $f = 1.53\times 10^{-2}$, see Table III, one obtains a lifetime of 28 ns. Moreover, the order of magnitude of the lifetime of the excited state is more or less the same with various methods and clusters. Therefore, our data support the view of an excited state which lives long enough to allow the Na atom to dissociate.

From the calculations above it seems as two different alkali related structures, both involving $Na^{\delta+}$, are responsible for each transition. The threshold feature, at 3–4 eV, is likely to be due to NBO but the band at 9 to 11 eV is due to the transition from O($2p$) valence band orbitals to $Na^{\delta+}(3s)$. In the case of adsorption on the regular site the lowest transition is from the O($2p$) valence band to the $Na^{\delta+}(3s)$ empty state, and after the transition Na can desorb; this happens at roughly 7 eV for TDDFT and 9 eV for CASPT2. For the NBO there is a local charge transfer from O of NBO to $Na^{\delta+}(3s)$ also leading to desorption. However, in the NBO case this is only the first transition since at higher energies an extra band with the characteristics of the band at 7–9 eV should also be present. We have computed these transitions and found that the onset of the second band appears at 6.7 eV, which is rather close to the 7.1 eV value found with the regular model. For this peak at high energy a larger intensity is observed.[5–7] Interestingly enough, for the high energy peak there are many possible excitations with O$(2p)$ to Na^+ character in this range of energy, all with transition probability similar to that found for the Na^+-NBO case. All these excitations would contribute to the intensity observed for the high energy peak; they outnumber the possibilities leading to the energy peak at 4 eV because there are more regular O sites coordinated to Na, at least 3 O atoms, than the single O coming from NBO. In practice, what we call NBO, $SiO^{\delta-}Na^{\delta+}$, is the same kind of bonding one can find in silicates. In this respect, the model of NBO is valid both for a point defect of SiO_2 as well as for the presence of $[SiO_4]^{4-}$ tetrahedra bound to Na^+ ions. In this case in fact the excitation will take place from the SiO^- unit, and will occur at a lower energy than transitions involving the O$(2p)$ valence band states. The reason why both transitions have been calculated with two different models was just for computational convenience. Actually, the same $Na^{\delta+}$ can be responsible for both transitions, and depending on the local environment, alkalis can be desorbed starting at 3 eV or at 9 to 11 eV.

IV. DISCUSSION AND CONCLUSIONS

From the ESD and PSD experiments it is seen that Na^0 can be produced from charge transfer excitations from SiO_2 to the unoccupied Na $3s$ orbital. In fact, calculations show that the first transition is found at energies around 4 eV. This excitation is local, and involves a Na atom bound to a defect center like a NBO. The bonding of Na to NBO is strongly polarized towards the terminal O atom, and Na can be described as a nearly full cation. The local charge transfer from the O$(2p)$ nonbonding orbitals to Na leads to the formation of Na^0 which is released from the system. A problem with this model is that it is based on the presence of a considerable number of NBO centers to explain the observed emission. On the other hand, neutral Na atoms can become incorporated into the Si-O-Si linkage with relatively low energy cost, leading to the formation of Si-O-Na bonds in the nondefective material. The problem does not exist if instead of pure silica we assume the presence of silicate structures where a large number of $(\text{Si-O}^-)(\text{Na}^+)$ interactions are present.

We have explored also the features of other defects, for instance, a Si dangling bond (E' center). For a $3T$ model the first absorption band appears at somewhat lower energies than for NBO, 2.8 and 3.2 eV for K and Na, respectively. The transitions are very intense (only TDDFT data). Also in this case the key question is the number of these centers present on the as-grown material. The model system consists of stoichiometric SiO_2 and it is less likely that E' centers play an important role in the process.

Assuming that the concentration of NBO defects is sufficiently large or that Na^+ is in the form of a silicate, the present calculations predict a threshold for alkali emission in agreement with experiment. This is because no excitations with lower energy than approximately 3 eV for K and 4 eV for Na are observed.

The resonantlike peak at 9–11 eV can be related to a direct or indirect excitation from the O$(2p)$ band to interstitial cations. Notice that since there are several of these oxygens around the alkali atom a larger intensity is expected. For both Na^+ at a regular site, and for alkali cations bonded to NBO we have found a transition which is rather close to this value (considering the problems of TDDFT with band gap).

In summary, for the band at high energy, a O$(2p)$ to $Na^+(3s)$ (or K) transition is involved. This transition is independent of the alkali in agreement with experiment. Notice that this transition is found for the two models considered in the present work: Na^+ interacting with a regular O site of the lattice and for Na trapped at a NBO site. In the second case, the trapped Na species is also strongly positively charged and due to the undercoordinated O atom (the NBO center) a local excitation of similar characteristics appears at rather lower energy and is associated with the threshold found in the experiments. Finally, the lifetime of excited states is large enough to allow the desorption of ‘‘hot’’ Na and K atoms.

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