

Electronic structure and screening dynamics of ethene on single-domain Si(001) from resonant inelastic x-ray scattering

A. Föhlisch,¹ F. Hennies,¹ W. Wurth,¹ N. Witkowski,² M. Nagasono,³ M. N. Piancastelli,⁴ L. V. Moskaleva,⁵ K. M. Neyman,^{5,6} and N. Rösch⁵

¹*Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany*

²*Laboratoire d'Optique des Solides, Case 80, 4 Place Jussieu, 75252 Paris 05, France*

³*Kyoto University, Sakyo-ku, 6068501 Kyoto, Japan*

⁴*Department of Chemical Sciences and Technologies and INFM, University "Tor Vergata," 00133 Rome, Italy*

⁵*Department Chemie, Technische Universität München, 85747 Garching, Germany*

⁶*ICREA and Departament de Química Física, Universitat de Barcelona, 08028 Barcelona, Spain*

(Received 30 January 2004; published 20 April 2004)

We present a resonant inelastic x-ray scattering (RIXS) study of a strongly bound adsorbate on a semiconductor surface, C₂H₄/Si(001). The valence electronic structure as well as the photon energy dependence in RIXS can be studied without the dominating effect of dynamic metallic screening. We demonstrate that for this strongly coupled system the RIXS spectrum resulting from a selective excitation into the unoccupied σ_{CSi}^* resonance can be interpreted with the help of density-functional calculations. In addition, we show how excitation into different resonances leads to a significant photon energy dependence of the RIXS spectral features, not seen in strongly coupled adsorbate systems on metals.

DOI: 10.1103/PhysRevB.69.153408

PACS number(s): 73.20.Hb, 78.70.En

The investigation of resonant inelastic scattering in the soft x-ray spectral range using third-generation synchrotron radiation sources has recently attracted great interest as a powerful method for detailed electronic structure determination.¹ The inelastic-scattering process can be described as a transition from the electronic ground state of a system via an intermediate resonant core-excited state into a final state which is electronically and/or vibrationally excited. This event can be studied by either detecting scattered photons or secondary Auger electrons. The former case involving photons in the incoming as well as the outgoing channel has the advantage of being almost independent of the sample environment, thus enabling even electronic structure studies of complex interfaces and liquids. Resonant inelastic x-ray scattering (RIXS) is governed by the dipole operator, and therefore has a well-defined polarization dependence and anisotropy, which provides insight into spatial orientation and symmetry properties of the systems studied.² Furthermore, due to the element specificity of the resonant excitation process, one is able to probe the electronic structure of complex heteronuclear systems for selected states.^{1,3} In crystalline solids, momentum conservation in RIXS can be used to access the k -resolved band structure.⁴ In adsorption systems, RIXS effectively suppresses contributions from the much larger number of substrate atoms and thus permits to access the atom-specific valence electronic structure of the adsorbate,^{2,3,5} allowing significantly improved understanding of the surface chemical bond.^{3,5}

In free molecules, RIXS depends strongly on the energy of the incoming photon as a result of the interference of degenerate or near-degenerate intermediate states in the scattering process.⁶ Furthermore, excitation to different resonances leads to significant differences in the spectral shape of the scattering spectra because of strong symmetry selection rules.⁶ For adsorbed molecules, this situation changes because coupling to the substrate, which modifies the dy-

namic response of the core-hole RIXS intermediate state, has to be taken into account. To date only adsorbates on metallic substrates have been investigated with RIXS. For these adsorbates, dynamic metallic screening leads to a significant loss of coherence in the scattering process. Fully angle-resolved RIXS investigations were performed for weakly coupled C₂H₄ (Refs. 7 and 8) and C₆H₆ (Refs. 7 and 9) on Cu(110). In case of C₂H₄/Cu(110), the excitation to two different resonances is reflected only weakly in the spectral shape, which was attributed to the highly efficient screening in the core-hole intermediate state.^{7,8} For C₆H₆/Cu(110) a stronger photon energy dependence was observed, most likely due to the weaker coupling of the aromatic C₆H₆ which preserves the localized, molecular nature of the adsorbate.^{7,9}

This is in line with the present understanding of the femtosecond dynamics of the adsorbate/substrate charge transfer in the intermediate core excited state, achieved in resonant inelastic-scattering studies with Auger electrons^{10–12} where a direct correspondence between coupling strength and charge-transfer probability was found.¹¹

In the following we will present a RIXS study for an adsorbate on a semiconductor surface, where for a strongly bound adsorbate the valence electronic structure as well as the photon energy dependence in RIXS can be studied without the dominating effect of dynamic metallic screening. As a model system for the early stages of the formation of Si-C layers, we investigated an ordered C₂H₄ adsorbate layer on a single-domain Si(001) surface. This system has been thoroughly characterized experimentally and theoretically.^{13–15} We demonstrate that for this strongly coupled surface complex, the RIXS spectrum resulting from selective excitation into the unoccupied σ_{CSi}^* resonance can be interpreted with the help of density-functional (DF) calculations. In addition, we show how excitation into different resonances leads to a

significant photon energy dependence of the RIXS spectral features, even though the molecule is strongly perturbed upon interaction with the substrate.

The experiments were performed at beamline I511 at Max-Lab, Sweden. The bandwidth of the exciting radiation was set to 0.2 eV for the C K edge. The x-ray emission spectrometer¹⁶ can be rotated around the optical axis of the exciting synchrotron radiation and was operated at 0.5 eV bandwidth. Switching the direction of observation relative to the surface of the sample results in the detection of valence molecular orbitals (MO's) of different orientation. In normal emission, valence states in plane are probed while in grazing emission in-plane and out-of-plane orbitals contribute to the spectrum.² Assuming a linear superposition of these contributions, a subtraction procedure allows us to separate the spatial contributions to the valence states.² The quality of the sample was assured through repeated x-ray photoelectron spectroscopy (XPS) measurements and the spectra were collected by scanning the sample in front of the spectrometer to minimize beam damage. We used p -doped Si(001) surfaces, 5° miscut towards the [110] direction, yielding a single (2×1) domain orientation over the whole Si surface,¹⁷ as verified by low energy electron diffraction. Two of these single-domain crystals were mounted at 7° grazing incidence rotated 90° around the surface normal, permitting to excite and detect in the direction parallel to the surface (along and perpendicular to the Si-dimer rows) as well as perpendicular to the surface.

The molecule C_2H_4 belongs to symmetry group D_{2h} with the electronic configuration $(1a_g)^2 (1b_{3u})^2 (2a_g)^2 (2b_{3u})^2 (1b_{2u})^2 (3a_g)^2 (1b_{1g})^2 (1b_{1u})^2$ (Ref. 18), where the MO $1b_{1u}$ is denoted as π orbital; the lowest unoccupied MO is $1b_{2g}$ (π^*). The adsorption system of C_2H_4 on Si(001)-(2×1) exhibits local C_2 symmetry according to angle-resolved UV photoemission spectroscopy (ARUPS).^{14,15} In combination with first-principles calculations, C_2H_4 was shown to be adsorbed on top of a Si(001)-(2×1) dimer, with the C-C bond axis rotated in the surface plane by 11.4° relative to the Si-Si dimer axis.^{14,15} This rotation, originally attributed to the spatial overlap of valence MO's between neighboring C_2H_4 adsorbates, leads to the formation of a one-dimensional band-like dispersion of the $1b_{2u}$ - and $1b_{1g}$ -derived C-H bonding states along the dimer rows of the Si(001)-(2×1) surface. Our recent polarization-dependent near-edge x-ray-absorption fine-structure investigation of the unoccupied adsorbate states¹³ confirms the picture of the surface chemical bond derived in those earlier studies. In absorption with the electric-field vector oriented normal to the surface, two equally strong absorption resonances were observed below the ionization threshold at 285.3 eV and 286.5 eV. Assuming sp^3 hybridized carbon atoms^{13,14,15} with tetrahedrally oriented bonds, the resonance at 285.3 eV was assigned to the π^* -derived states related to C-Si (σ_{CSi}^*) bonds. The resonance at 286.5 eV was assigned to a state that results from the coupling to a C-H antibonding state involving CH_2 moieties which are bent away from the surface.¹³

To interpret the present RIXS spectra, all-electron DF calculations, using a local-density approximation, were carried out^{19,20} for the substrate model cluster Si_9H_{12} . The same

basis set as in Ref. 21 was employed. The Si_9H_{12} cluster was derived from a previously used model²¹ by reducing the top layer representation to six Si atoms. First, a C_{2v} symmetry constraint was applied to the cluster C_2H_4/Si_9H_{12} , with the C-C bond of ethene oriented along the Si-Si dimer bond (x direction) nearest to the adsorbate and with the C_2H_4 moiety parallel to the (001) surface. The geometry of ethene as well as the dimer Si-Si and Si-C distances were allowed to relax (within C_{2v} constraints). This cluster model was also considered in reduced (C_2) symmetry, but calculated spectral features showed only minor differences, despite the resulting noncollinearity of C-C and Si-Si bonds (see below). For clarity, we discuss the C_{2v} data.

The RIXS spectra were modeled invoking the commonly used ground-state approximation,^{2,5,7,22} which is believed to furnish a sufficiently accurate description of experimental x-ray data. Thus, the dipole matrix elements for transitions between the C $1s$ levels and valence MO's of the adsorption complex were calculated using ground-state orbitals. The transition energies were approximated by differences between the Kohn-Sham energies of the valence orbitals and C $1s$ a_1 and b_1 symmetry-adapted orbitals. Within the dipole approach, the intensity $I(\epsilon)$ of a transition from a valence

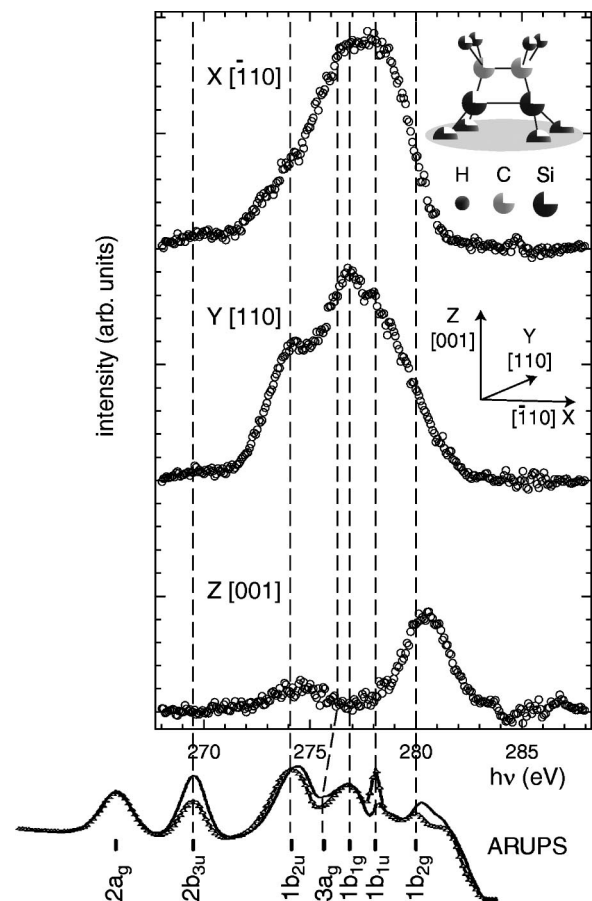


FIG. 1. Angle-resolved carbon K -edge RIXS excited at the σ_{CSi}^* resonance (285.3 eV) on single-domain $C_2H_4/Si(001)$, resolving the adsorbate valence electronic structure along the crystallographic axes. Below ARUPS spectra recorded in s and p symmetries (Ref. 14).

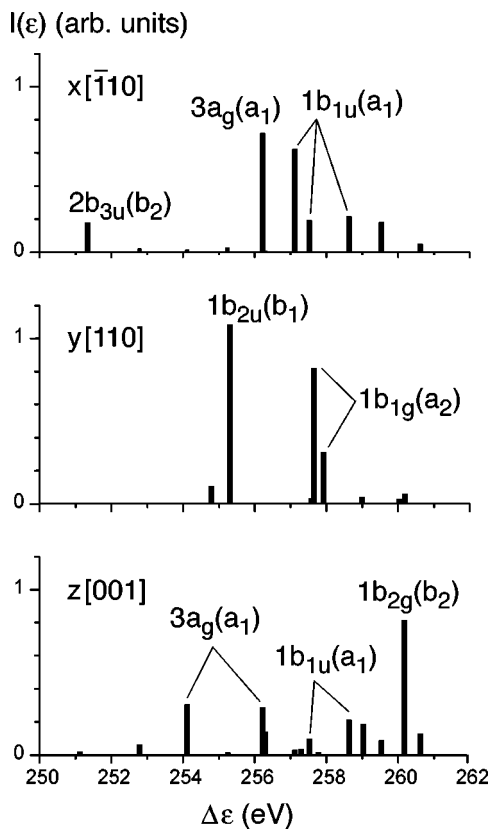


FIG. 2. Simulated carbon K -edge RIXS spectra from a C_{2v} model of the $C_2H_4/Si(001)$ adsorption complex. $\Delta\epsilon$ is the energy difference between valence and core (C $1s$) Kohn-Sham levels. The labels give the dominant ethylene contributions to the respective orbitals (symmetry shown in parentheses) of the adsorbate-substrate complex.

orbital $|f\rangle$ of energy ϵ_f to a previously generated hole in the core state $|i\rangle$ of energy ϵ_i is $I(\epsilon) \propto (\epsilon_i - \epsilon_f)^4 \langle i | \mathbf{r} | f \rangle^2$.^{2,5,7,22}

In Fig. 1, we show the anisotropy of our angle-resolved spectra for scattering into the σ_{CSi}^* excitation resonance at 285.3 eV. Due to symmetry selection rules for scattering off the C $1s$ core level, the RIXS spectral features with the electric-field vector in a given direction stem from C $2p$ -type valence orbitals oriented in the same direction. Using the known ultraviolet photoemission spectroscopy (UPS) binding energies¹⁴ and the results of our calculations, we can assign the spectral features to the adsorbate valence level structure. MO's of free ethene are invoked to assign the UPS spectrum of the adsorption system, assuming that they contribute preferentially to the corresponding states of the coupled system. For direct comparison, Fig. 2 shows simulated RIXS spectra for the C_{2v} cluster model; they exhibit the same strong polarization dependence as the experimental results, yielding very similar overall profiles. To elucidate this, we illustrate the relationship between MO symmetry and angular anisotropy for a few examples. For the $1b_{2g}$ (π^*) derived MO (b_2 character in C_{2v} symmetry), which becomes occupied upon interaction with the Si substrate, we experimentally observe a strong RIXS signal for z polarization, but only weak contributions for the polarization vector along x and y directions. This is also found in the simulated

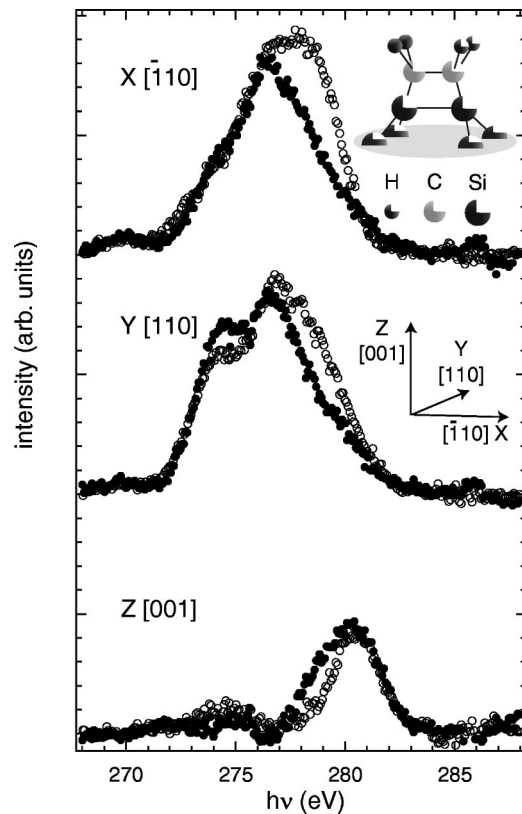


FIG. 3. Excitation energy dependence of RIXS on single-domain $C_2H_4/Si(001)$ for scattering into the σ_{CSi}^* (285.3 eV) (open circles) and the CH_2^* (286.5 eV) (full circles) excitation resonances.

RIXS spectra, which reflect the fact that only the C $2p_z$ orbitals contribute to this state. The spectral assignment is more difficult for the x - and y -polarized cases because here several states, closely spaced in energy, contribute. With the computational model, we assign the two strong bands, observed only for y polarization, to contributions derived from the $1b_{2u}$ (b_1) and $1b_{1g}$ (a_2) MO's. These bands directly reflect C-H bonding MO's which are antisymmetric with respect to the C-C bond; these MO's are only moderately perturbed upon adsorption, thus keeping their dominant C $2p_y$ character. In contrast, the former $\sigma(CC)$ and $\pi(CC)$ MO's, $3a_g$ and $1b_{1u}$, respectively, undergo strong mixing of C $2p_x$ and C $2p_z$ components (a_1 in C_{2v} symmetry) due to chemisorption and therefore appear with different intensities under z and x polarizations. Thus, we can directly observe how strongly the valence electronic structure of ethene is modified upon adsorption. The optimized nonplanar geometry of the adsorbed C_2H_4 moiety manifests a considerable sp^3 character of the carbon atoms. Thus, the RIXS anisotropy directly reflects the spatial orientation of particular C $2p$ orbitals.

In view of earlier findings,^{14,15} we reoptimized the adsorption cluster model in C_2 symmetry, allowing a rotation of the ethene moiety about the Si surface normal. The resulting structure features two methylene groups twisted with respect to one another. The C-C axis is rotated relative to the Si-Si bond by 15.4° , in satisfactory agreement with the result of periodic calculations.¹⁵ This suggests that the symmetry re-

duction is an inherent feature of the ethene adsorption complex, which distorts from an energetically unfavorable collinear conformation; interadsorbate repulsion at high coverage may enhance this effect.

We also performed angle-resolved RIXS for scattering into the CH_2^* excitation resonance at 286.5 eV, which we compare in Fig. 3 directly to RIXS results from the lower lying σ_{CSi}^* excitation resonance. The two RIXS spectral distributions vary significantly. In the picture of femtosecond charge transfer on the time scale of the core-hole lifetime, spectral features which change with the photon energy are related to the coherent RIXS process, whereas spectral features independent of excitation energy are related to radiative decay processes associated with loss of coherence in the core-excited intermediate state. Thus we conclude that ethene on Si falls into the former category where a significant contribution of coherent scattering processes is observed for a strongly coupled adsorbate, which shows notable electronic rehybridization in the ground state as discussed above. In particular, the spectral intensities of some of the valence states vary significantly, whereas energetic shifts are less pronounced. Comparing with our assignment given above, the

most prominent effects occur in the spectral region of the $1b_{1g}$ and $1b_{1u}$ derived MO's. This may reflect the fact that those states couple most efficiently to the respective core excited states, but a more elaborate theoretical description is needed to elucidate this problem.

In summary, we demonstrated that the valence electronic structure, and hence the chemisorption of a strongly bound adsorbate on a semiconductor surface [$\text{C}_2\text{H}_4/\text{Si}(001)$], can be studied in detail with the help of RIXS experiments and DF calculations. In addition, we showed how excitation into different resonances leads to a significant photon energy dependence of the RIXS spectral features, not seen in strongly coupled adsorbate systems on metals. This indicates a very different dynamic screening response for strongly coupled adsorbates on semiconductors as compared to metal surfaces.

This work was supported by Access to Research Infrastructure (ARI) Program, Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and the "Grant-in-Aid for Japan Society for the promotion of Science Fellows." Valuable support from Max-lab staff is gratefully acknowledged. L.V.M. thanks the Alexander von Humboldt foundation for financial support.

-
- ¹J. Nordgren, *J. Electron Spectrosc. Relat. Phenom.* **110-111**, 1 (2000), and references therein.
- ²A. Föhlisch, J. Hasselström, P. Bennich, N. Wassdahl, O. Karis, A. Nilsson, L. Triguero, M. Nyberg, and L.G.M. Pettersson, *Phys. Rev. B* **61**, 16 229 (2000).
- ³A. Föhlisch, M. Nyberg, J. Hasselström, O. Karis, L.G.M. Pettersson, and A. Nilsson, *Phys. Rev. Lett.* **85**, 3309 (2000).
- ⁴Y. Ma, N. Wassdahl, P. Skytt, J.-H. Guo, J. Nordgren, P.D. Johnson, J.-E. Rubensson, T. Böske, W. Eberhardt, and S.D. Kevan, *Phys. Rev. Lett.* **69**, 2598 (1992).
- ⁵A. Föhlisch, M. Nyberg, P. Bennich, L. Triguero, J. Hasselström, O. Karis, L.G.M. Pettersson, and A. Nilsson, *J. Chem. Phys.* **112**, 1946 (2000).
- ⁶F. Gel'mukhanov and H. Ågren, *Phys. Rep.* **312**, 87 (1999), and references therein.
- ⁷L. Triguero, A. Föhlisch, P. Väterlein, J. Hasselström, M. Weinelt, L.G.M. Pettersson, Y. Luo, H. Ågren, and A. Nilsson, *J. Am. Chem. Soc.* **122**, 12 310 (2000).
- ⁸L. Triguero, Y. Luo, L.G.M. Pettersson, H. Ågren, P. Väterlein, M. Weinelt, A. Föhlisch, J. Hasselström, O. Karis, and A. Nilsson, *Phys. Rev. B* **59**, 5189 (1999).
- ⁹M. Weinelt, N. Wassdahl, T. Wiell, O. Karis, J. Hasselström, P. Bennich, A. Nilsson, J. Stöhr, and M. Samant, *Phys. Rev. B* **58**, 7351 (1998).
- ¹⁰C. Keller, M. Stichler, G. Comelli, F. Esch, S. Lizzit, W. Wurth, and D. Menzel, *Phys. Rev. Lett.* **80**, 1774 (1998).
- ¹¹W. Wurth and D. Menzel, *Chem. Phys.* **251**, 141 (2000).
- ¹²P. Brühwiler, O. Karis, and N. Mårtensson, *Rev. Mod. Phys.* **74**, 703 (2002).
- ¹³F. Hennies, A. Föhlisch, W. Wurth, N. Witkowski, M. Nagasono, and M. N. Piancastelli, *Surf. Sci.* **529**, 144 (2003).
- ¹⁴W. Widdra, A. Fink, S. Gokhale, P. Trischberger, D. Menzel, U. Birkenheuer, U. Gutdeutsch, and N. Rösch, *Phys. Rev. Lett.* **80**, 4269 (1998).
- ¹⁵U. Birkenheuer, U. Gutdeutsch, N. Rösch, A. Fink, S. Gokhale, P. Trischberger, D. Menzel, and W. Widdra, *J. Chem. Phys.* **108**, 9868 (1998).
- ¹⁶J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.-E. Rubensson, and N. Wassdahl, *Rev. Sci. Instrum.* **60**, 1690 (1989).
- ¹⁷S. van Dijken, H.J.W. Zandvliet, and B. Poelsema, *Surf. Rev. Lett.* **5**, 15 (1998).
- ¹⁸The notation reflects the choice of axes shown in Figs. 1 and 3, which differs from the conventional choice for ethene molecule, see A.J. Merer and R.S. Mulliken, *Chem. Rev. (Washington, D.C.)* **69**, 639 (1969).
- ¹⁹T. Belling, T. Grauschopf, S. Krüger, F. Nörtemann, M. Staufer, M. Mayer, V.A. Nasluzov, U. Birkenheuer, and N. Rösch, *PARAGAUSS, version 2.1*, Technische Universität München (2000).
- ²⁰T. Belling, T. Grauschopf, S. Krüger, M. Mayer, F. Nörtemann, M. Staufer, C. Zenger, and N. Rösch, in *High Performance Scientific and Engineering Computing*, edited by H.-J. Bungartz, F. Durst, and C. Zenger, Lecture Notes in Computational Science and Engineering, Vol. 8 (Springer, Heidelberg, 1999), p. 439.
- ²¹M. Staufer, U. Birkenheuer, T. Belling, F. Nörtemann, N. Rösch, W. Widdra, K.L. Kostov, T. Moritz, and D. Menzel, *J. Chem. Phys.* **112**, 2498 (2000).
- ²²M. Staufer, U. Birkenheuer, T. Belling, F. Nörtemann, N. Rösch, M. Stichler, C. Keller, W. Wurth, D. Menzel, L.G.M. Pettersson, A. Föhlisch, and A. Nilsson, *J. Chem. Phys.* **111**, 4704 (1999).