

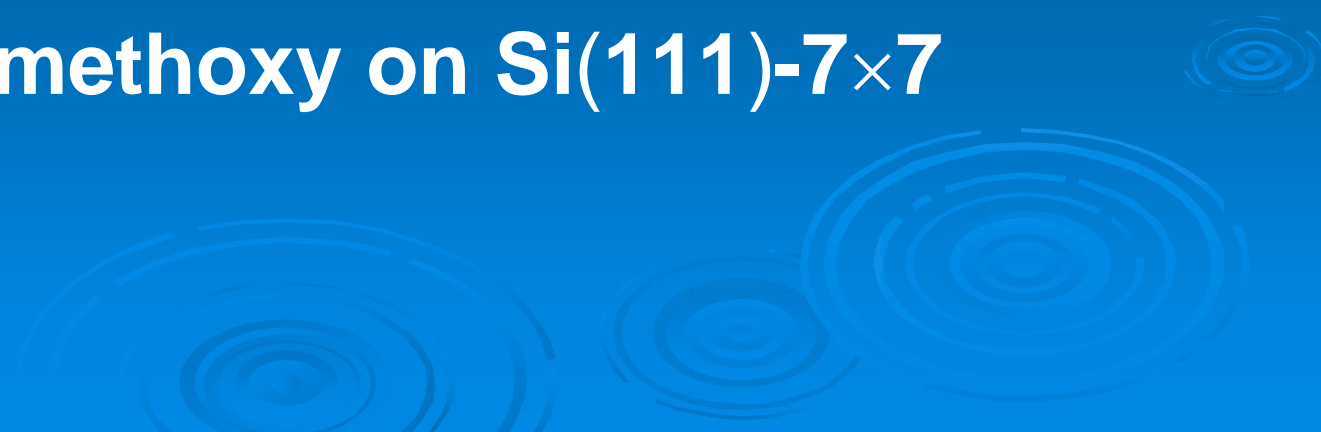
Molecular Adsorption on Semiconductor Surfaces



The surface chemistry of semiconductor surfaces is of fundamental importance in several fields, such as chemical vapor deposition, epitaxial film growth etc. The surface of a silicon crystal projects dangling bonds into the vacuum, and these bonds act as reactive sites for inducing surface chemistry in molecules which adsorb on these sites.

M. N. Piancastelli, J. J. Paggel, Chr. Weindel, M.
Hasselblatt and K. Horn
Phys.Rev.B 56, (1997) R12 737

**Assignment of rest-atom
surface core-level shift through
adsorption-site selectivity
of methoxy on Si(111)-7×7**

A decorative graphic consisting of several sets of concentric circles, resembling ripples in water, is located in the bottom right corner of the slide. The circles are light blue and vary in size and opacity, creating a subtle background pattern.

The formation of the methoxy species on Si(111)- 7×7 upon methanol adsorption leads to a strongly selective extinction of the rest-atom feature in the valence-level photoemission spectrum. The Si 2p surface core level at lowest binding energy is likewise removed in this process, demonstrating that this feature is related to charge distribution around the rest atom, an assignment that has been subject to controversy in the literature.

Here we present a method of analysis of the low binding energy spectral feature by means of adsorption site specificity in order to shed light on the assignment of core-level spectral features. This is based on a comparison of the response of valence-level surface states and surface-related core-level features to adatoms and rest atoms with respect to adsorption of the methoxy species on Si(111)-7×7.



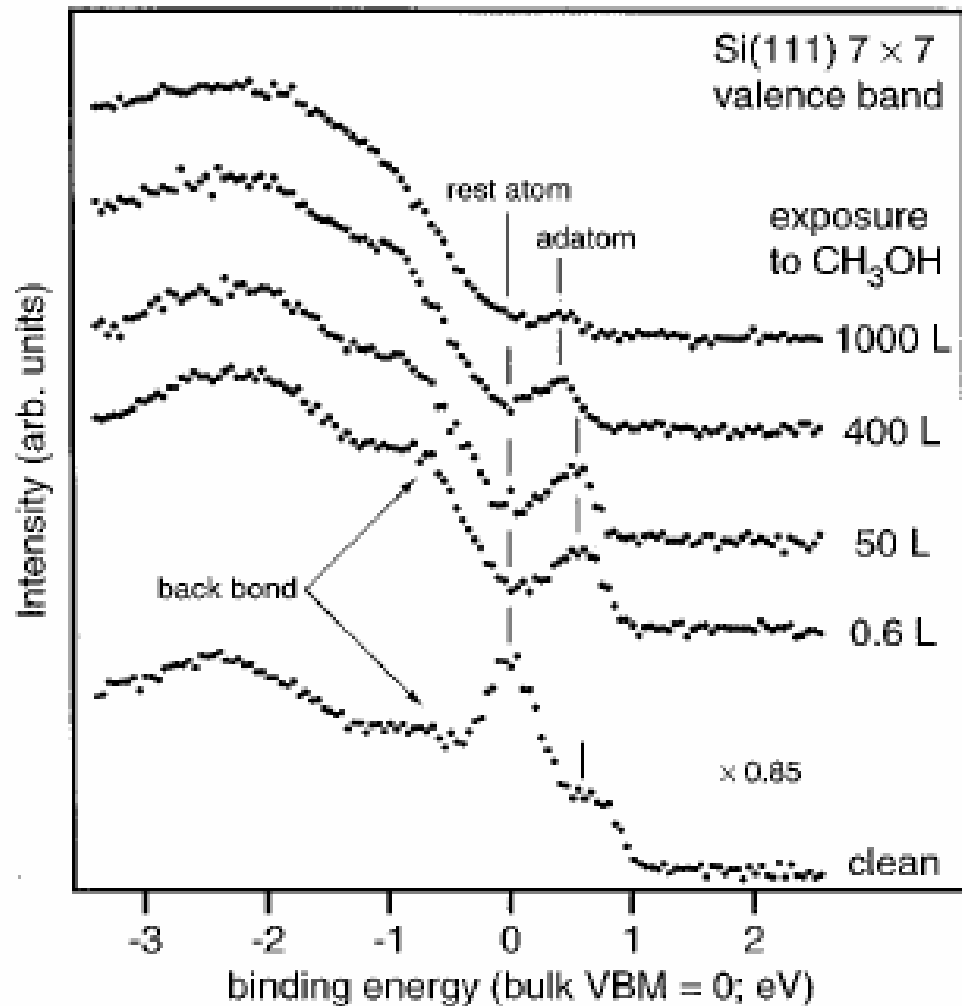


FIG. 1. Series of Si(111)- 7×7 valence-level spectra, recorded after different amounts of exposure to CH_3OH as indicated. Note the suppression of the rest-atom surface state upon 0.6-L exposure, while the adatom feature is only partially extinguished even after 1000-L exposure.

Methanol, CH_3OH , is known to adsorb on $\text{Si}(111)\text{-}7\times 7$ dissociatively at room temperature, by converting into a methoxy species in which the O-H molecular bond is broken and an O-Si bond is formed with a Si surface atom. From previous high-resolution photoemission studies of the valence band, it has been demonstrated that at low methanol exposures (below 0.6 Langmuirs) the surface reaction quenches the rest-atom-related spectral features, while the peak related to adatoms is only quenched for exposures several orders of magnitude higher.

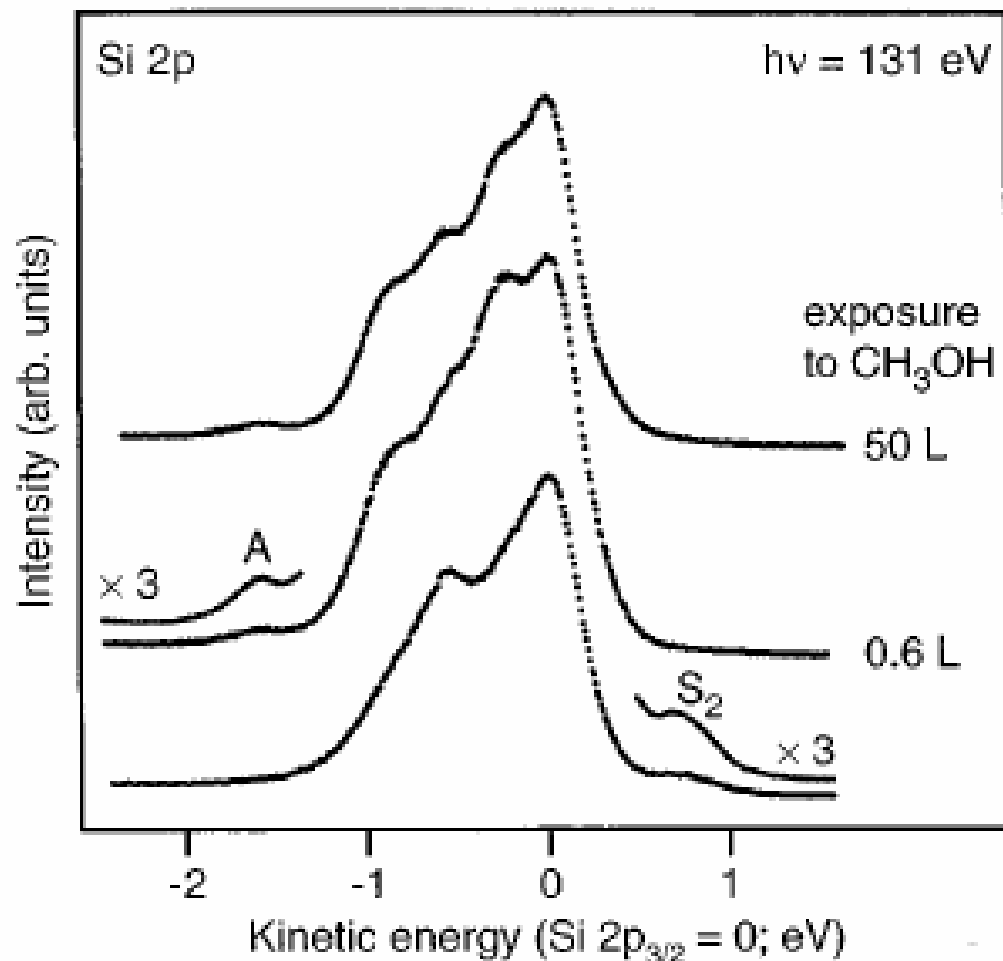


FIG. 2. Series of Si 2p spectra from Si(111)-7×7, clean surface (bottom) and after exposure to different amounts of CH₃OH as indicated. Note the suppression of the S₂ surface core level at low binding energy, and the emergence of a new line (marked A) after the lowest exposure.

By comparing the spectrum for the clean surface (bottom) with the one at 0.6-L CH₃OH exposure, several significant differences are evident.

The most important one is the disappearance of the low binding-energy feature (*S2*) and the simultaneous appearance of another feature (*A*) on the high-binding-energy side of the Si 2*p* line. The behavior of the low-binding-energy spectral feature is similar to that of the *S2* peak in the valence spectrum shown in

Fig.1.

This must be regarded as strong evidence for the origin of this feature on the rest atoms, even though intensity changes of core- and valence-level features upon adsorption are due to different physical processes.



A loss of surface-state emission in the valence region must be ascribed to a redistribution of its intensity in energy and momentum space, since the emission may lose its directional nature when a substrate-adsorbate bond is formed; this is the basis of the frequently observed suppression of surface-state intensity upon adsorption. Shifts in energy are related, in a simple two-center molecular-orbital picture, as due to the formation of bonding and antibonding levels between the substrate atom and the adsorbate.

In the core-level region, a peak may be shifted by adsorption through a change of the valence charge distribution around a particular surface atom; this “chemical shift” model may be put on a semiquantitative basis through the difference in electronegativity. Thus the corresponding appearance of a high-binding-energy feature with the removal of the S_2 component can be explained by a change in charge transfer induced by the formation of Si-O direct bonds, and therefore a surface-reaction-induced chemical shift for the Si atoms directly involved in the chemisorption bond with the methoxy species.

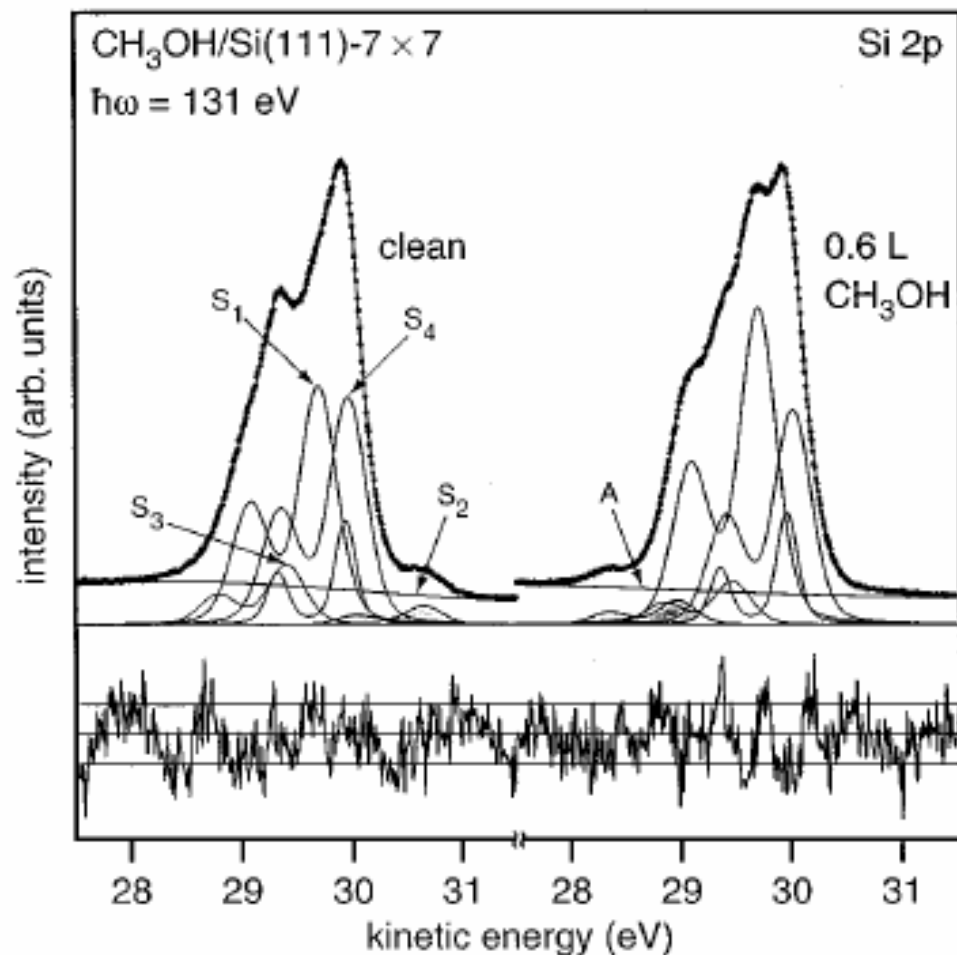


FIG. 3. Line-shape analysis of Si 2*p* spectra for the clean surface (left) and 0.6-L exposure to methanol (right). Also shown are the separate contributions, as well as the residual, where the upper and lower straight line indicate the deviation expected from the counting statistics; for the line designations see text. The rest-atom derived line *S*₂ in the clean surface spectrum, and the adsorbate-induced line *A* (right-hand side) are shaded in gray.

The chemical behavior of the Si(111)-7×7 surface with respect to methanol is intriguing, since the higher reactivity of rest atoms towards adatoms is not obvious on the grounds of simple chemical arguments. Since the O-H molecular bond in methanol is broken, chemical intuition would suggest that the methoxy species should preferentially be formed at the more acidic adatom sites, which an electron-rich species such as methanol should be more likely to occupy in the first stages of the surface reaction. This is at variance with the present observation.

However, that this simple argument may not describe the situation on the Si(111)-7×7 surface is shown by the analogous case concerning ammonia dissociative adsorption on the same surface. Both scanning tunneling microscope and photoemission data show that the adsorption of the NH₂ fragment occurs preferentially on rest-atom sites. A similar behavior of the spectral structure in the low-binding-energy site of the Si 2*p* line has been reported.




The experimental findings that rest-atom sites appear much more affected by methoxy formation can be explained by the coordination number of adatoms vs rest atoms. The line of reasoning is as follows: rest atoms are triply coordinated surface atoms, while adatoms form a fourth weak bond with a subsurface atom. Therefore at rest-atom sites the interaction with a foreign species is a simple saturation of a dangling bond, while a similar reaction at an adatom site implies the formation of a fivefold coordinated surface atom.

As a consequence, the activation barrier for a reaction at adatom sites could be larger than at rest-atom sites, and it could counterbalance the chemical effect of acidic vs basic sites. Since both fragments of methoxy formation (CH_3O and hydrogen atoms) may stick to the surface, most likely on adjacent adatom-rest atom sites, the fact that the adatom surface states are much more difficult to quench by methanol adsorption may be ascribed to a slow kinetics of Si-H bond formation and a competitive H-H recombination with subsequent molecular hydrogen desorption, for which evidence has been found in water adsorption and dissociation on Si.

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Piancastelli, L. Aballe, K. Weiss, and K. Horn
Phys.Rev.B 62, (2000) 17128

**Ethylene adsorption on
Si(100)2×1: A high-resolution
photoemission study**

The background of the slide features several sets of concentric circles in a lighter shade of blue, resembling ripples on water. These circles are positioned in the lower right and bottom center areas of the slide.

The adsorption of ethylene on Si(100)2×1 has been investigated at room temperature by high-resolution synchrotron radiation photoemission in the exposure range: 1–1000 L. A consistent picture in favor of molecularly di-σ bonded ethylene is obtained from the analysis of the photoemission spectral features, which shows the progressive decreasing of the surface states in the valence band and the Si 2*p* features related to the surface dimers upon adsorption. By careful fitting of the Si 2*p* complex envelope, the appearance of a component in the Si 2*p* core-level spectrum is evidenced already after 1 L exposure to ethylene.

This component, which grows with exposure, is assigned to the formation of two Si-C bonds per dimer as a result of ethylene adsorption. The line-shape analysis by model functions permits us to follow the symmetrization of Si-Si dimers, which are known to be asymmetric on the clean surface, and the growth of a Si-C related spectral component upon adsorption. Relative quantitative analysis of the various peak components suggests that the intensity increase of the new component almost completely parallels the progressive decrease of the surface dimer components.

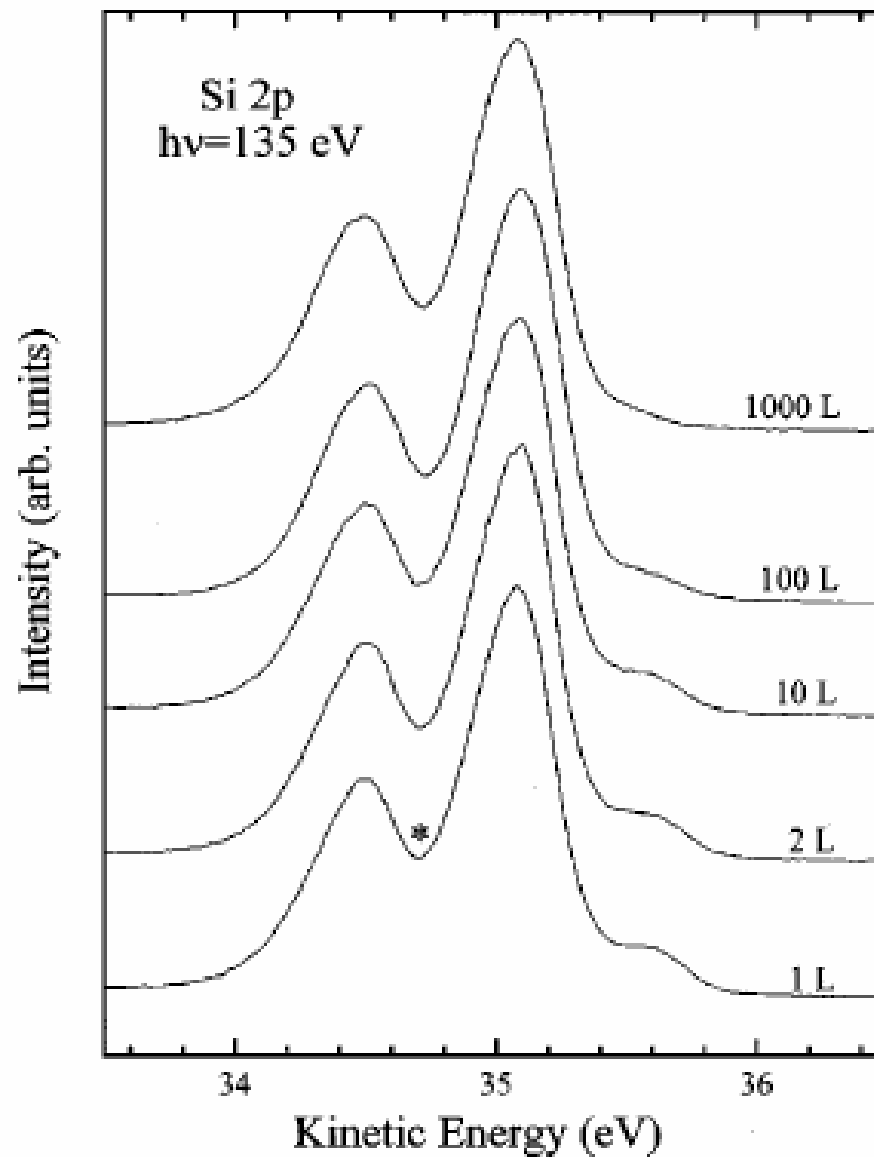


FIG. 1. Si 2p spectra as a function of ethylene exposure at room temperature. The photon energy is 135 eV. The star * indicates the region of the trough depth.

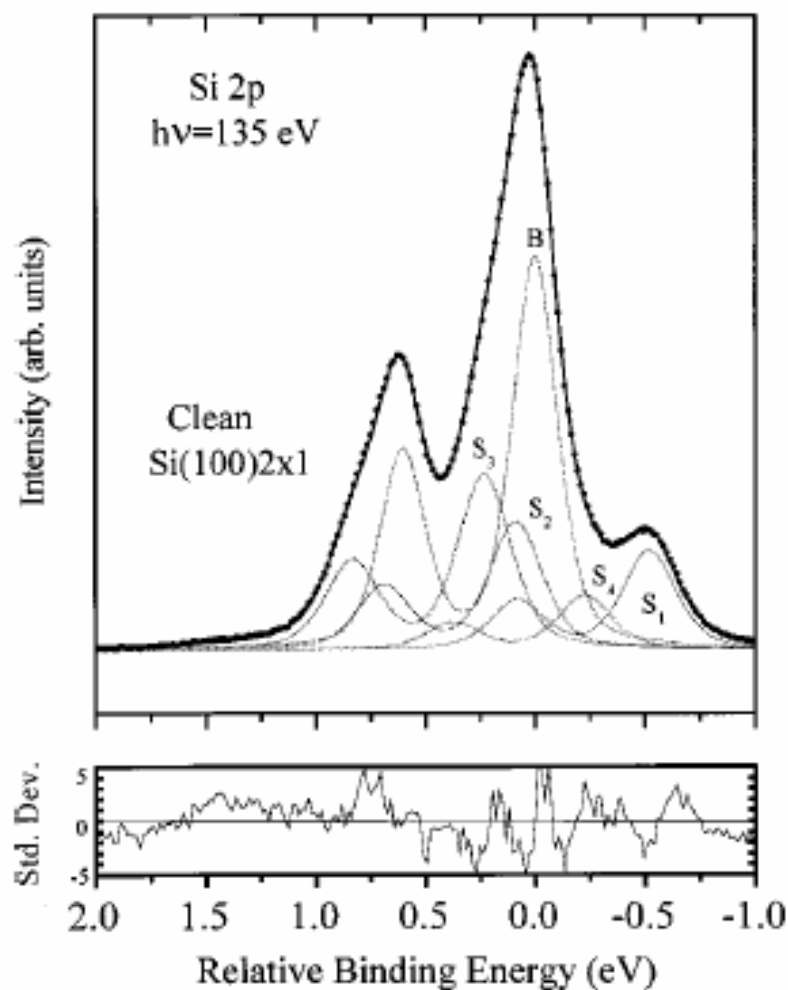


FIG. 2. Line-shape analysis of the Si 2p spectrum for the clean Si(100)2 \times 1 surface at room temperature. The photon energy is 135 eV. The scattered curve refers to the raw data, while the solid line to the fitting results. B, S_1, S_2, S_3, S_4 dotted curves denote emission from bulk, up and down atoms in a dimer, second layer and subsurface, respectively. The bottom line refers to the residual of the fitting procedure.

TABLE I. Curve-fitting parameters for the clean Si(100)2×1 surface. The surface core-level shift (SCLS) of each component is reported in relative binding energy (RBE).

Component	SCLS (eV)	FWHM (eV)	Branching (eV)	Spin-orbit (eV)
B	0	0.2410	0.50	0.602
S_1	-0.523	0.2876	0.50	0.602
S_2	+0.087	0.2876	0.50	0.602
S_3	+0.231	0.2876	0.50	0.602
S_4	-0.227	0.2876	0.50	0.602

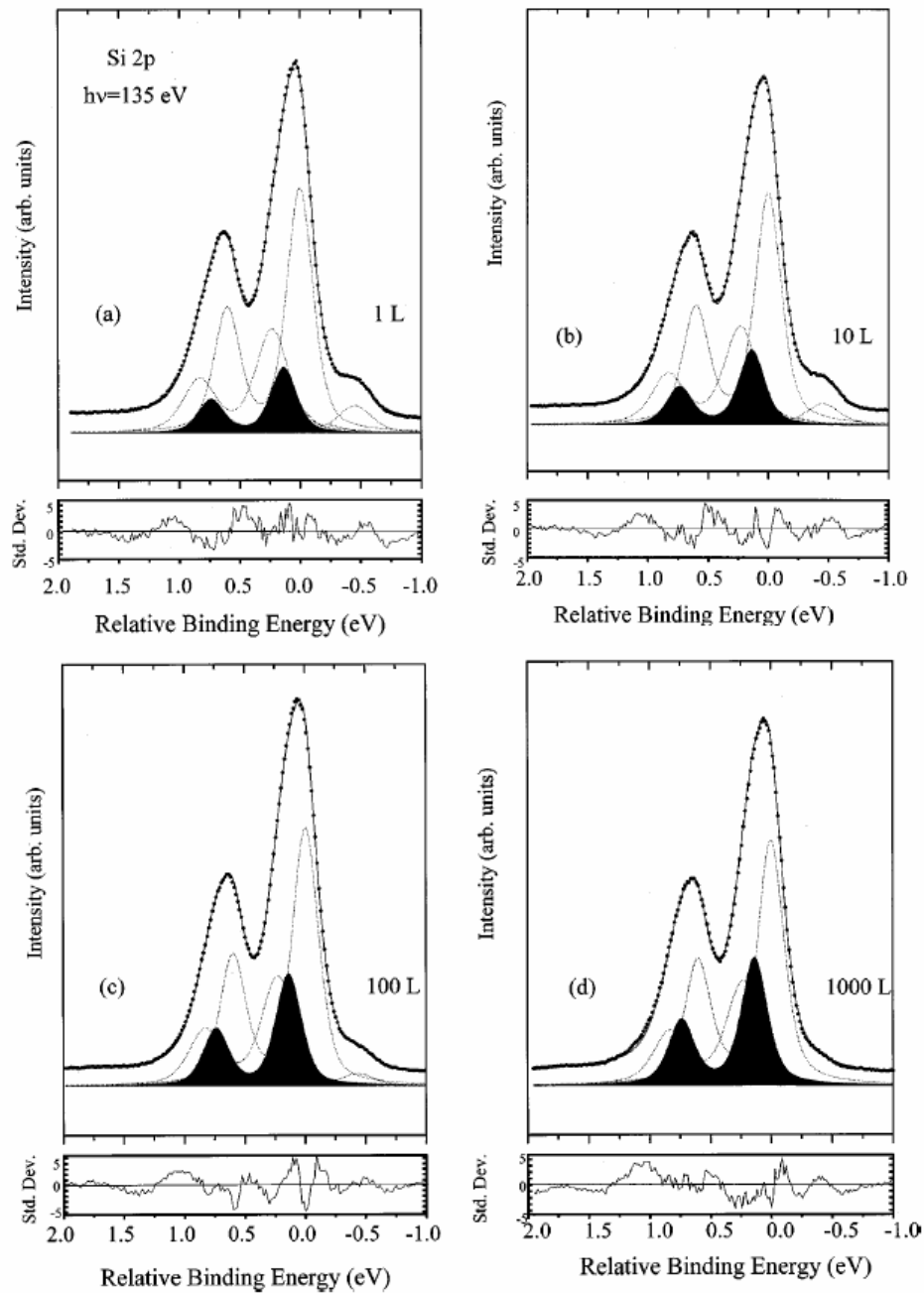


FIG. 3. Line-shape analysis of the Si 2p spectra as a function of ethylene exposure at room temperature. The photon energy is 135 eV. Spectra in (a), (b), (c), and (d) refer to 1, 10, 100, and 1000 L ethylene exposures, respectively. The scattered curve refers to the raw data, while the solid line to the fitting results. The single components are plotted as dotted curves and the filled areas show the new Si-C component. The bottom curve represents the residual of the fitting procedure.

A major result of the line-shape analysis is the energy location of the component at +0.128 eV SCLS, which can be assigned to the formation of Si-C bonds. This is the first high-resolution photoemission evidence of Si-C bonds arising from ethylene adsorption on Si (100) 2×1 . The presence of such a component in the Si $2p$ spectrum already after 1 L exposure to ethylene is also confirmed in the valence-band region, showing the typical spectral features related to the adsorbate.

TABLE II. Curve-fitting parameters for the ethylene-exposed Si(100)2 \times 1 surface. The surface core-level shift (SCLS) of each component is reported in relative binding energy (RBE).

Component	SCLS (eV)	FWHM (eV)	Branching ratio	Spin-orbit (eV)
B	0	0.2562	0.50	0.602
S_1	-0.450	0.3231	0.50	0.602
S_2	+0.083	0.3231	0.50	0.602
S_3	+0.231	0.3231	0.50	0.602
S_4	-0.227	0.3231	0.50	0.602
Si-C	+0.128	0.2537	0.50	0.602

TABLE III. Intensity ratio of all the surface components relative to the bulk as a function of ethylene exposure. $\Delta S_1 + \Delta S_2$ denotes the total intensity decrease of the Si dimer atoms upon adsorption.

	S_1	S_2	S_3	S_4	Si-C	$\Delta S_1 + \Delta S_2$
Clean	0.30	0.42	0.53	0.17		
1 L	0.14	0.17	0.53	0.05	0.26	-0.41
10 L	0.12	0.15	0.53	0.04	0.31	-0.45
100 L	0.06	0.07	0.53	0.02	0.43	-0.59
1000 L			0.53		0.52	-0.72

Analysis of the photoemission spectral features confirms that ethylene is molecularly di- σ bonded to the surface and shows the progressive decreasing of the surface states intensity and the appearance of a component in the Si 2p core spectrum. Line-shape analysis by model functions allows following the symmetrization of the Si-Si dimers and the progressive growth of a new component as a function of ethylene adsorption. This component exhibits a very small SCLS and can be assigned to the formation of two Si-C bonds per dimer. The intensity increase of the Si-C related component closely parallels the progressive decrease of the surface dimer components.

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Piancastelli, L. Aballe, K. Weiss and K. Horn
Surface Science 505 (2002) 251

**Methanol adsorption on Si(100) 2×1
investigated by
high-resolution photoemission**

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The adsorption of methanol on Si(1 0 0)21 has been investigated at room temperature by high-resolution synchrotron radiation photoemission in the exposure range: 0.01–0.15 L. A combined evidence for a dissociative mechanism has been obtained from the analysis of the photoemission spectral features, which shows the absence of the ionization peak mainly based on the σ_{OH} bond in the valence band and the identification of a Si–O related component in the Si 2p core spectrum after adsorption.

The line-shape analysis of the Si 2p core level shows the rising of two surface-related components upon adsorption. Their energy location allows for the assignment to Si–H and Si–OCH₃ bonds, as resulting from the interaction of the molecular fragments (H atom and methoxy group) with the surface. The growth of the Si–H and Si–OCH₃ related spectral components upon adsorption has been followed by a careful curve fitting of the Si 2p line.

The analysis of the C1s photoemission core-line suggests that no C–O bond rupture occurs at low exposure. A further fragmentation of the CH₃O– group occurs at higher exposure (>20 L).

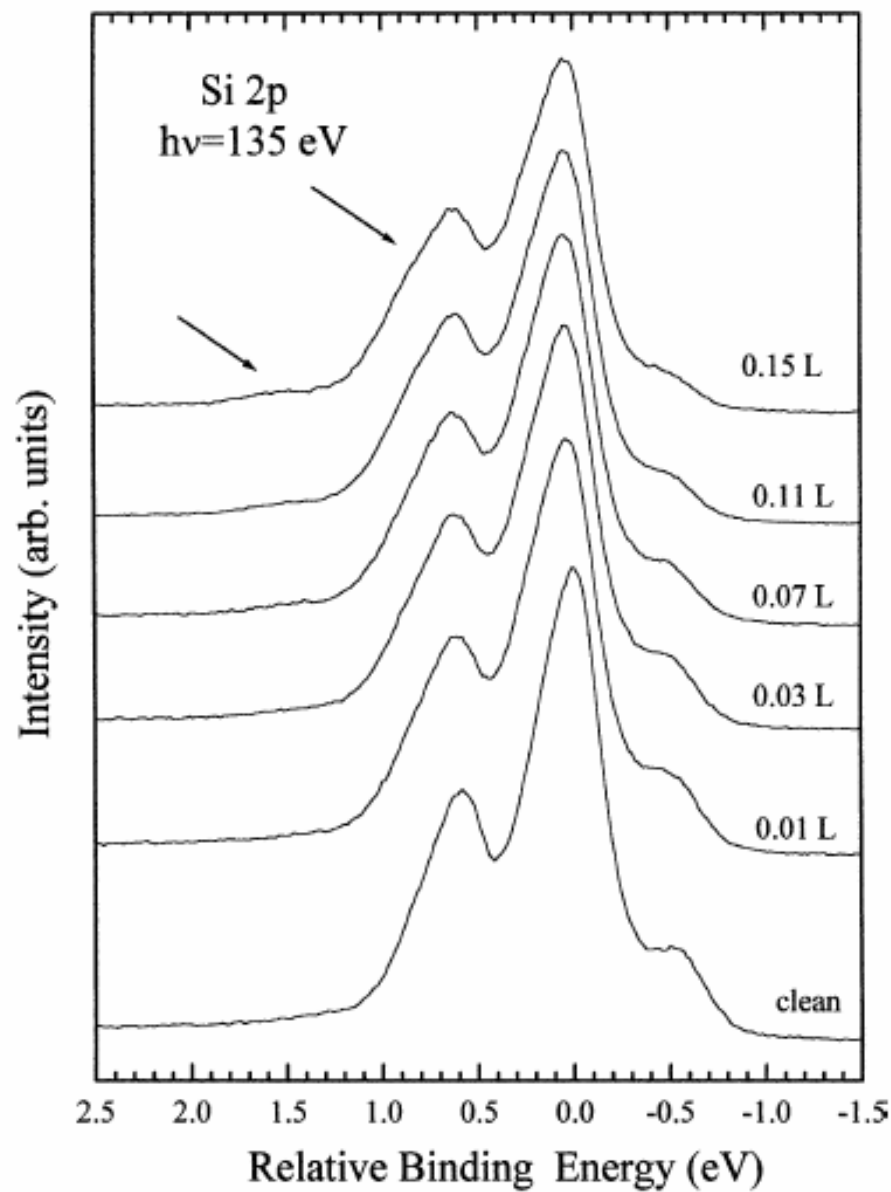


Fig. 1. Si2p spectra as a function of methanol exposure at room temperature. The photon energy is 135 eV. The arrows point to the presence of oxygen-related features.

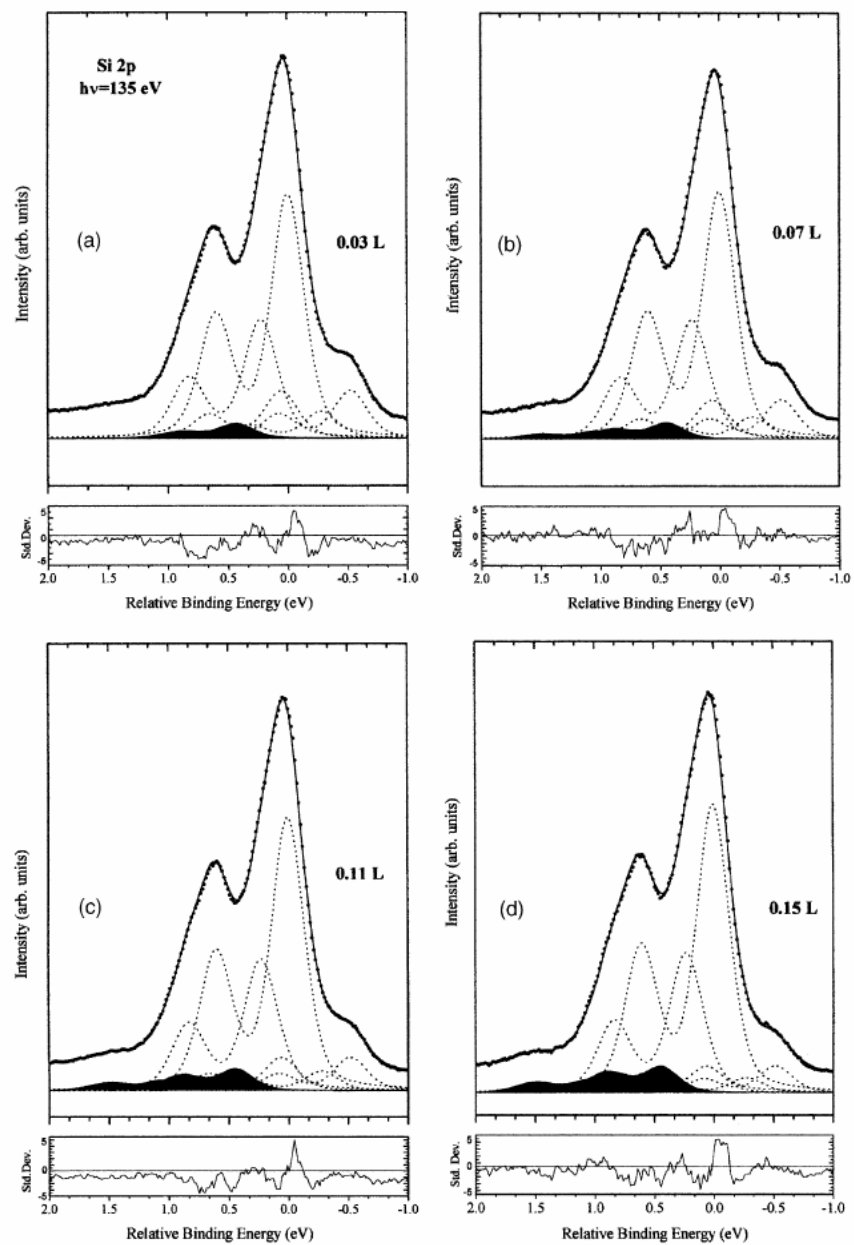


Fig. 4. Line-shape analysis of the Si 2p spectra as a function of methanol exposure at room temperature. In (a), (b), (c) and (d) spectra upon 0.03, 0.07, 0.11 and 0.15 L are shown. The photon energy is 135 eV. The scatter curve refers to the raw data, while the solid line to the fitting results. The single components are plotted as dotted curves and the filled areas show the new Si-H and Si-OCH₃ components. The residual of the line-shape analysis is plotted below each spectrum.

Table 3

Intensity ratio of all the surface components relative to the bulk as a function of methanol exposure

	S ₁	S ₂	S ₃	S ₄	Si-H	Si-OCH ₃
Clean	0.27	0.27	0.48	0.11	–	–
0.01 L	0.23	0.23	0.51	0.12	0.05	0.02
0.03 L	0.20	0.20	0.50	0.11	0.06	0.03
0.07 L	0.16	0.16	0.50	0.09	0.06	0.05
0.11 L	0.13	0.13	0.50	0.07	0.08	0.08
0.15 L	0.10	0.10	0.50	0.05	0.09	0.09

The Si 2p photoemission results provide a strong evidence that methanol is dissociatively adsorbed on the surface through the O–H bond breakage and the Si–O bond formation. The analysis of the photoemission spectral features allows the identification of a Si–O related component in the Si 2p core spectrum after adsorption. The curve-fitting of methanol exposed surfaces requires two new components.

Consequently, they have been assigned to the Si–H and Si–OCH₃ components, resulting from the surface reaction of the H atom and methoxy group of the molecule. The intensity of these new components grows in a 1:1 ratio as a function of exposure and closely parallels the progressive decrease of the buckled up and buckled-down surface dimer components.



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Surface Science 529 (2003)144

**Fully polarization resolved X-ray
absorption spectroscopy
of C₂H₄ on single-domain
Si(001)(2×1)**

We present a polarization resolved near edge X-ray absorption fine structure (NEXAFS) investigation of ethylene (C_2H_4) adsorbed on the oriented single-domain $Si(001)-(2\times 1)$ surface. From the detected resonances and their polarization dependences C_2H_4 is found to be strongly bound to the silicon dimers with the carbon atoms in a sp^3 -hybridized state. The molecular axis is rotated around the surface normal with respect to the dimer axis.



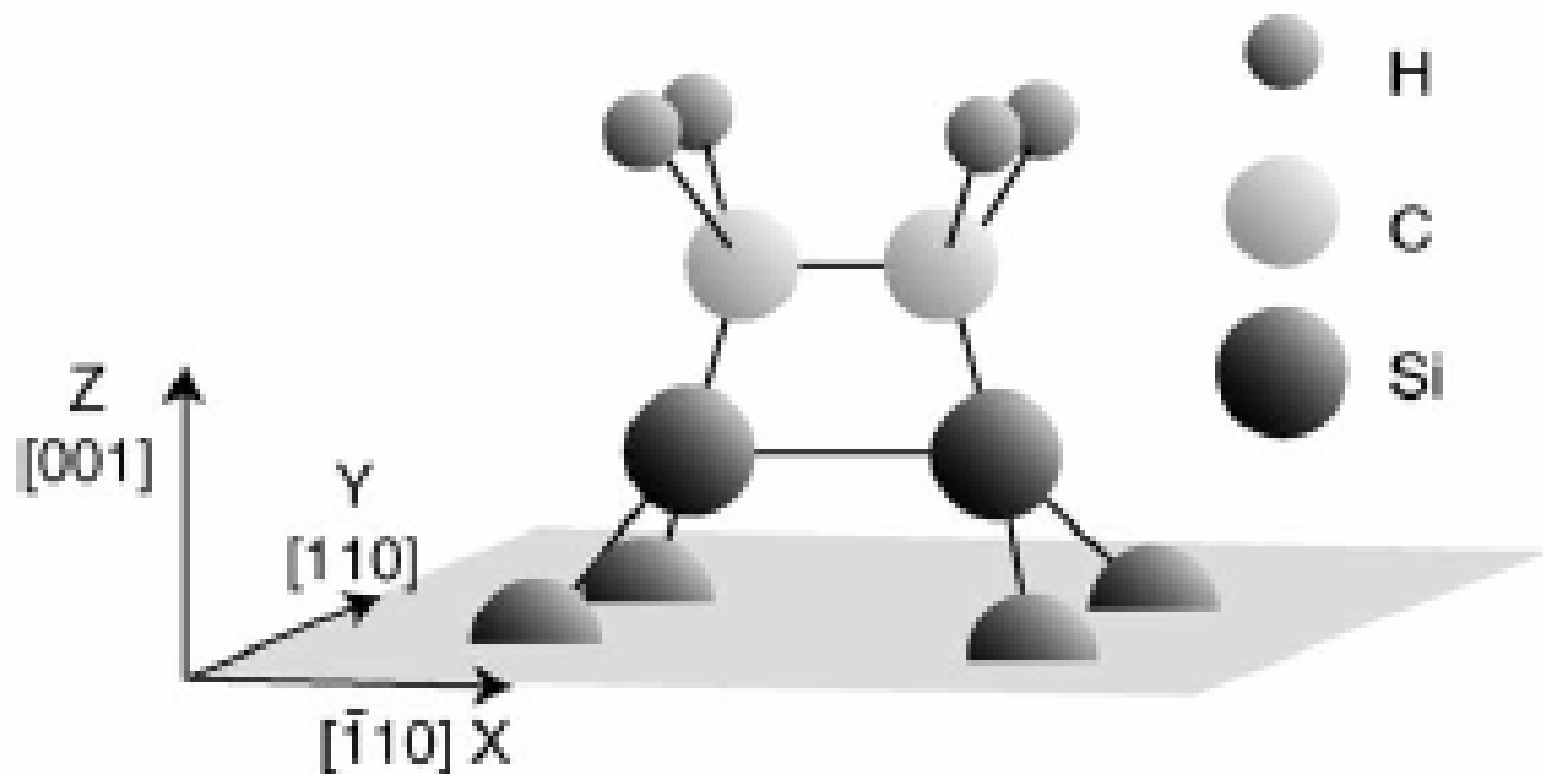


Fig. 1. Adsorption model of ethylene C_2H_4 on $Si(001)-(2 \times 1)$.

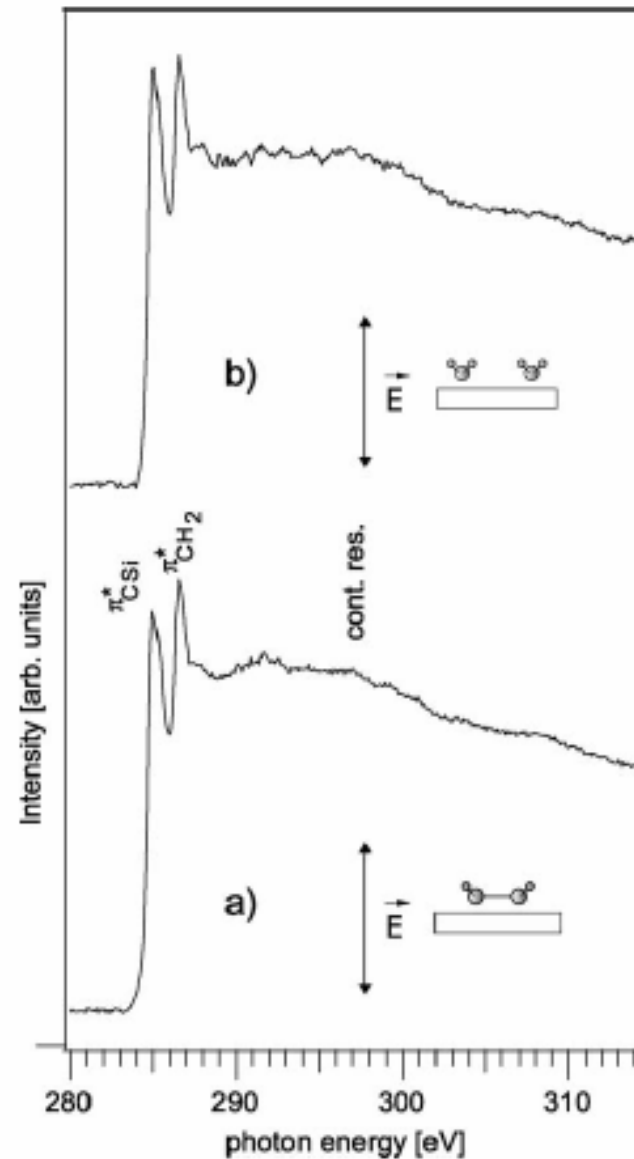


Fig. 2. NEXAFS spectra of C_2H_4 adsorbed on $Si(001)-(2 \times 1)$ at room temperature measured on two samples with their (2×1) domains rotated 90° with respect to each other. The \vec{E} -vector of the incident photon beam is aligned along the Z -axis (compare sketch). Peak assignment see text.

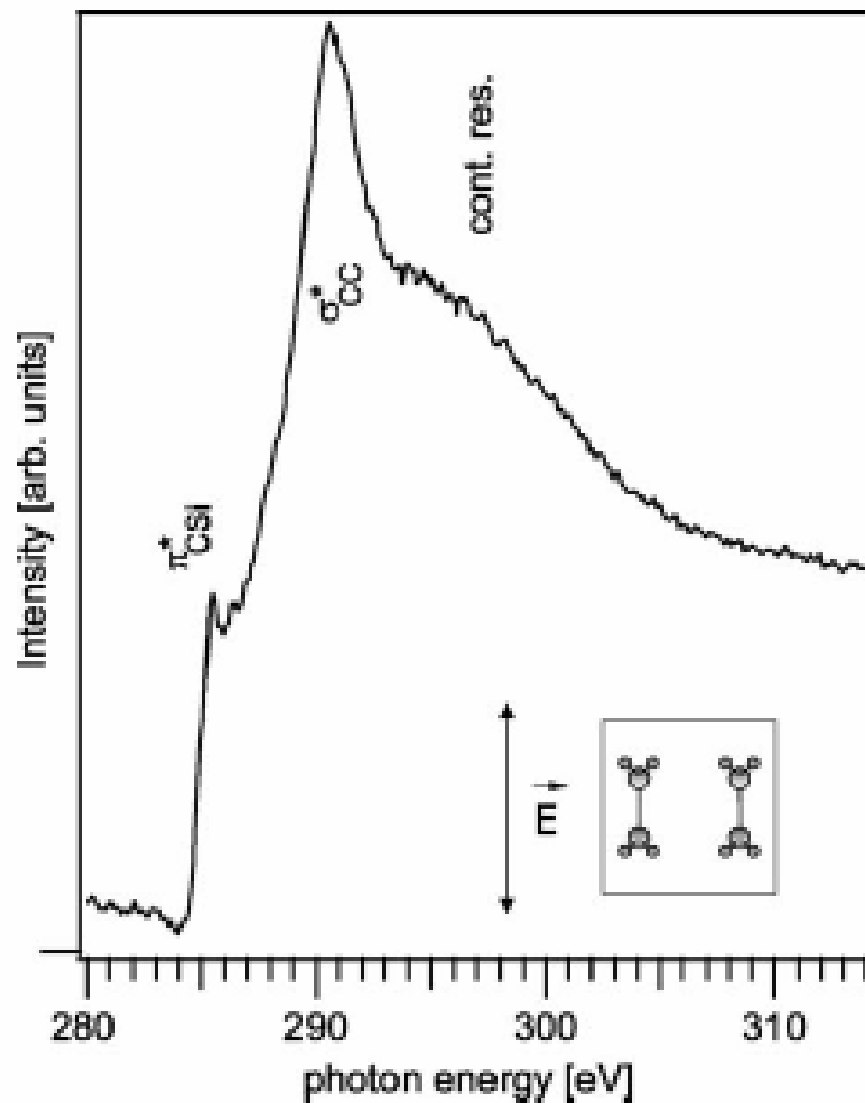


Fig. 3. NEXAFS spectra of C_2H_4 adsorbed on $Si(001)-(2 \times 1)$ at room temperature. The \vec{E} -vector of the incident photon beam is aligned along the X -axis (compare sketch). Peak assignment see text.

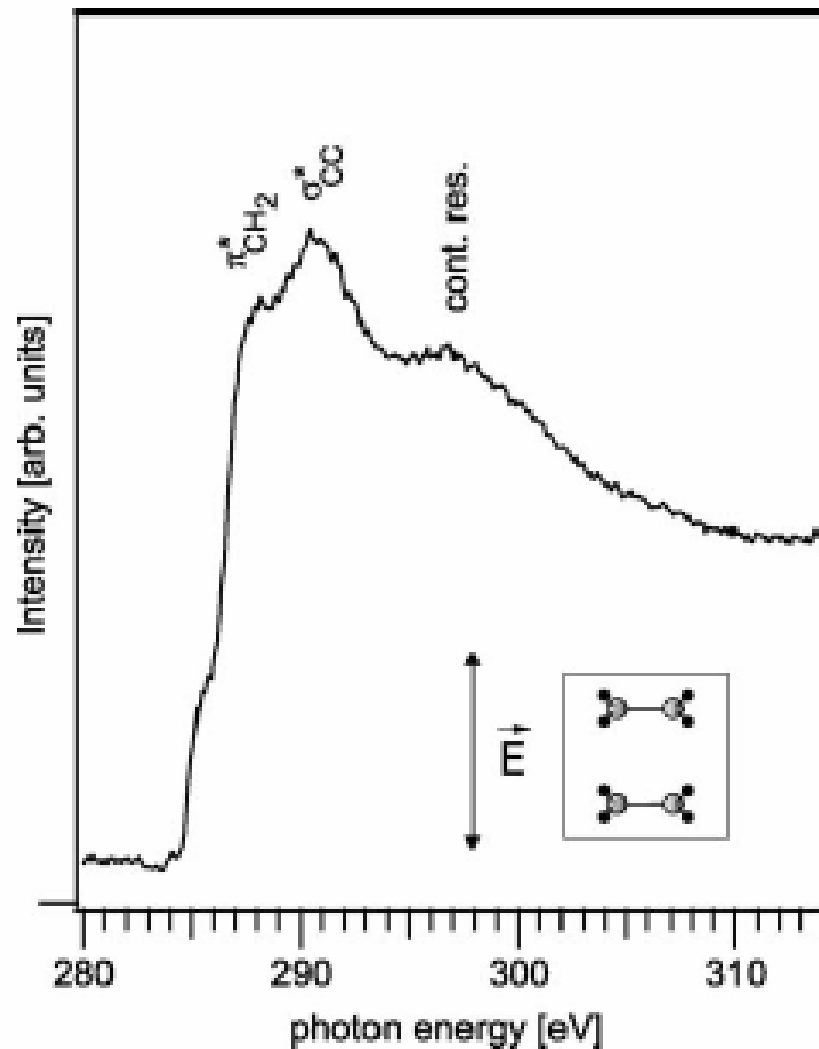


Fig. 4. NEXAFS spectra of C_2H_4 adsorbed on $Si(001)-(2 \times 1)$ at room temperature. The E -vector of the incident photon beam is aligned along the Y -axis (compare sketch). Peak assignment see text.

We start the discussion of our data with the resonance at 291 eV. This feature is dominant with x-polarization and can clearly be observed with y-polarization. Only a very small admixture of this state can be detected with z-polarization. The occurrence of this peak in the spectrum recorded with x-polarization can therefore be explained by assigning the feature to excitation into a σ -resonance. The corresponding bond is therefore parallel to the x-axis. We can interpret this resonance as the antibonding orbital corresponding to the C–C bond.

We now have to understand why this resonance can be clearly seen with y-polarized light as well. If the bond is totally aligned along the x-axis respectively if the C–C bond is parallel to the Si–Si dimer bond axis this transition would not be allowed. This deviation of the C–C axis from the dimer orientation can explain the occurrence of the σ -resonance in spectra recorded with y-polarization. Without any assumptions our NEXAFS measurements therefore give the direct experimental evidence for the rotation of the C–C bond axis against the Si dimer axis around the surface normal in C_2H_4 adsorbed on Si(001).

Next we turn to the discussion of the “ π ”-type resonances at 285.3 and 286.5 eV. From the absorption measurements on free C_2H_4 , one would expect a very strong single π -resonance for orientation of the polarization vector perpendicular to the plane of the molecule. Our spectra instead show two resonances that are much weaker, even weaker than the σ -resonance seen in Fig. 3. Here we can prove that C_2H_4 has lost its π -bond and is rehybridized when adsorbed to Si(001).

In the absorption spectra we can see the antibonding counterparts of the tetrahedrally oriented sp^3 - bonds, i.e. one C–Si bond directed towards the surface and two C–H bonds which are now seen to be lifted upwards. The fourth bond is the C–C σ bond. The C–H bonds are equivalent and we assign one of the split π to the antibonding C–Si state and the other to the C–H₂. Our fully polarization resolved measurements however give a certain way to identify the bonds in the observed resonances.

The first resonance at 285.3 eV is not only strongly enhanced with z-polarization but can also clearly be seen with x-polarization. As a slight shoulder it occurs very weakly in the spectra recorded with y-polarized light. That it is clearly visible with x-polarization but can hardly be seen with y-polarization gives a strong indication to identify this resonance to have predominant C–Si character. If this bond would be aligned with the Si dimer it would only be visible with z- and x polarization. But since the molecule is rotated this explains the observation of this state as a shoulder in the spectrum recorded with y polarization.

We then have to assign the second resonance at 286.5 eV to a state with major C–H₂ admixture. Its strong contribution to the spectra recorded with z polarization gives an experimental evidence that this bond is not lying in the molecular plane any more, but that the H atoms are lifted out of the plane. This again confirms the sp₃-hybridization. As a C–H₂ bond it then should show up with x- as well as with y-polarization. Its part in the spectra measured with x-polarization is difficult to determine because it lies in the strong rise of the r-resonance. Anyhow the flank of the r-resonance seems to include the part of another resonance. With y-polarization this state can clearly be seen.

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Phys.Rev.B 68, (2003) 115408

**Polarization and angle-resolved
NEXAFS of benzene adsorbed
on oriented single-domain Si
(001)-2×1 surfaces**



We have investigated the adsorption of benzene on oriented single-domain Si(001)-(2×1) surfaces at room temperature by means of fully polarization-resolved near-edge x-ray-absorption fine-structure (NEXAFS) experiments.

The present study reveals that benzene chemisorbs in a stable cyclohexadiene-like configuration, labeled as a “butterfly” in the literature, which is di- σ bonded to silicon atoms.



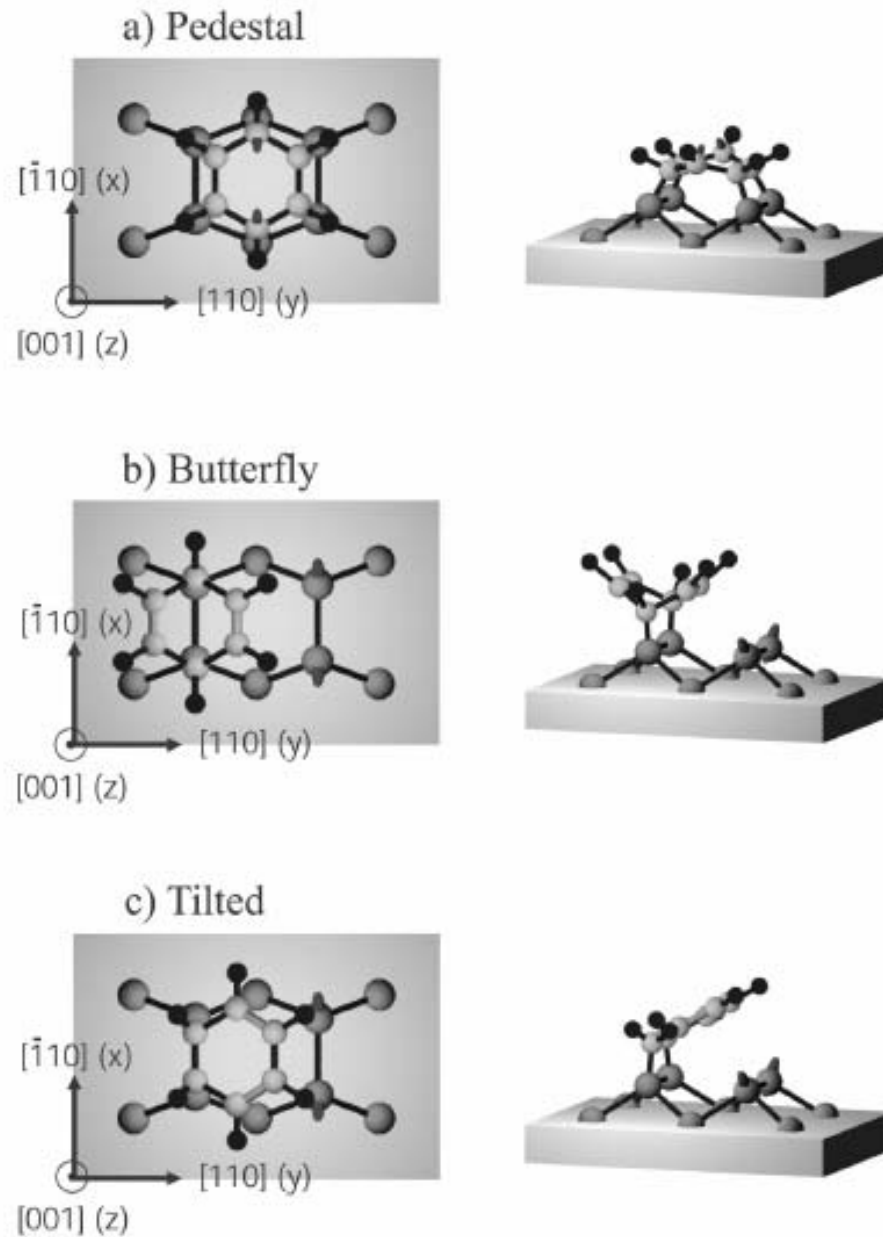


FIG. 1. Schematic representation of the different structural models for the adsorption of benzene on Si(001)-(2×1): (a) pedestal, (b) butterfly, and (c) tilted (the gray bonds represent C=C double bonds) from Ref. 5.

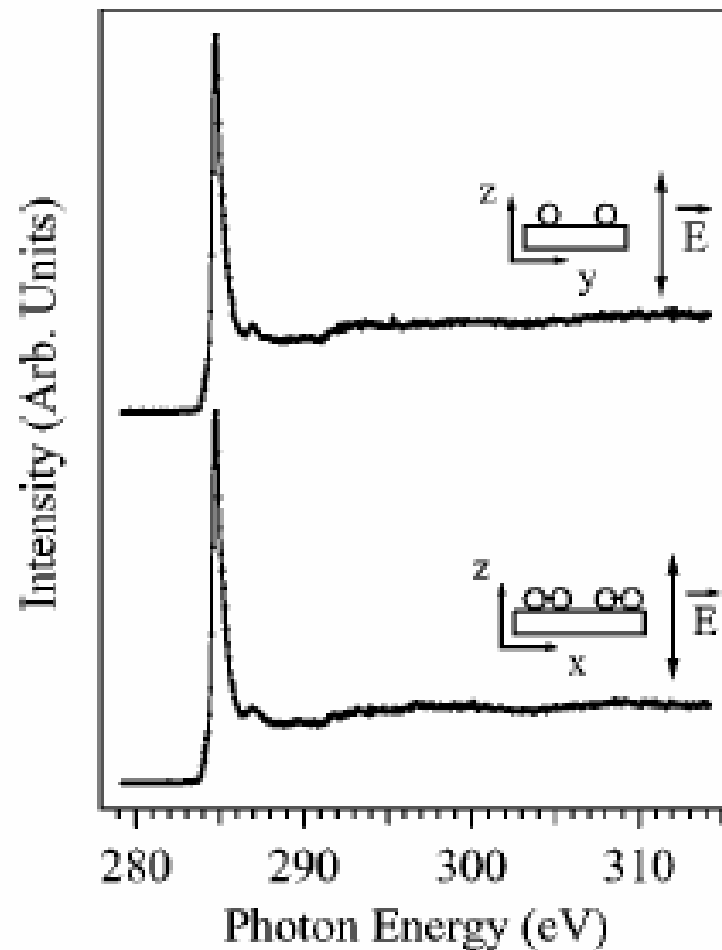


FIG. 2. NEXAFS spectra of benzene adsorbed on Si(001)-(2 \times 1) at room temperature measured on two samples with their (2 \times 1) domains rotated 90° with respect to each other. The \vec{E} vector of the grazing incident photon beam is aligned along the [001] direction.

In Fig. 2, we present the NEXAFS spectra obtained for room-temperature benzene saturation coverage (10 L) taken with the electric field vector E normal to the surface or along the z direction, using the definition of x , y , and z relative to the crystallographic axis as given in Fig. 1, where the (2×1) domains on the two samples are rotated by 90° in plane, respectively. In this excitation geometry, we are probing in the carbon K -edge absorption the unoccupied states of carbon $2p$ character, which are oriented normal to the surface. We observe that these spectra on the two samples are very similar. The peak at 284.8 eV is dominating next to a small feature at 286.9 eV.

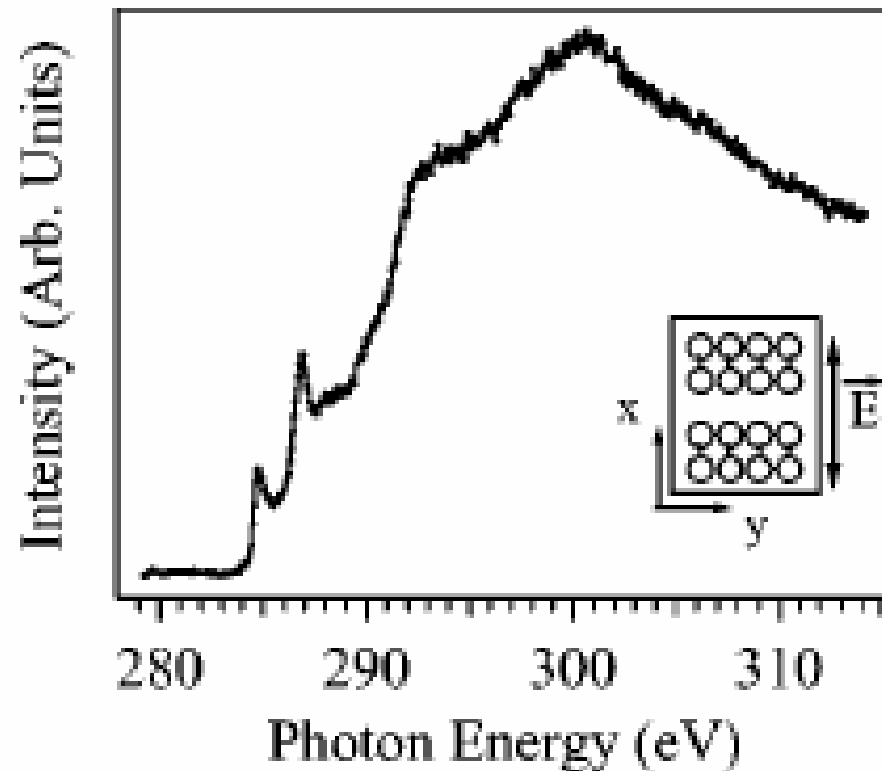


FIG. 3. NEXAFS spectra of benzene adsorbed on Si(001)-(2 \times 1) at room temperature. The \vec{E} vector of the grazing incident photon beam is aligned along the x axis (i.e., parallel to the Si dimers).

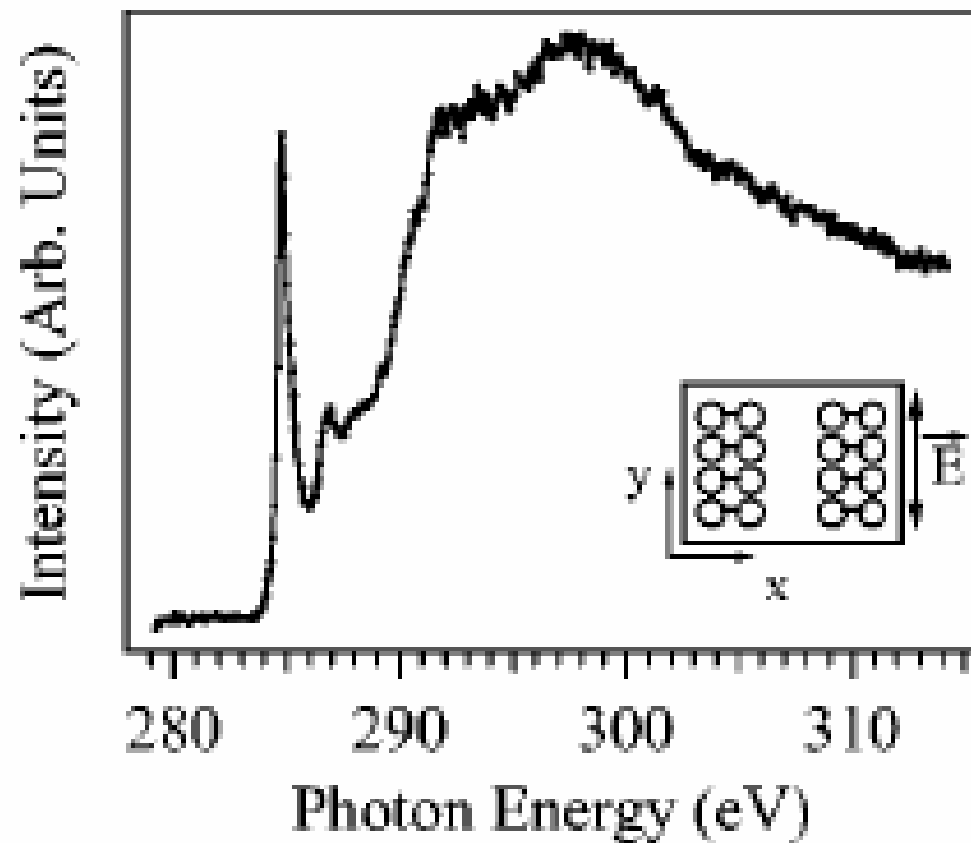


FIG. 4. NEXAFS spectra of benzene adsorbed on Si(001)-(2 \times 1) at room temperature. The \vec{E} vector of the grazing incident photon beam is aligned along the y axis (i.e., perpendicular to the Si dimers).

In Figs. 3 and 4, we present the NEXAFS spectra taken for the E vector lying in the surface plane, along the Si dimers (the x axis) or normal to the Si dimers (the y axis), respectively. Here we observe very different spectral distributions and intensities. The peak at 284.8 eV, which we have observed strongly for out-of-plane polarization in Fig. 2, is also present in Figs. 3 and 4. However, for in-plane polarization the intensities are weak. This clearly indicates a strong out-of-plane amplitude of this unoccupied state, which is in correspondence with the π^* orbital of a lying benzene molecule.

A completely flat lying benzene would only show this π state for out-of-plane polarization and no intensity for in-plane polarization as has been reported for benzene adsorbed on metals. We thus directly see that the benzene molecule either does not lie flat or is geometrically distorted upon adsorption. In particular for the in-plane polarization, the stronger appearance of the E vector normal rather than parallel to the Si dimers indicates that the π^* resonance has an in-plane component normal to the Si dimers.

Therefore the adsorption configuration has to be either the benzene molecule “tilted” normal to the Si dimers or the benzene molecule in the “butterfly” configuration.

To investigate the adsorbed species further, we now turn to the peak appearing at 286.9 eV, which is almost equally strong for all three polarizations in comparison to the continuum step height. This state has been previously assigned as due to the C-H* resonance. As the C-H bonds are distorted from the planar geometry of the free benzene molecule upon adsorption, where the hydrogen atoms—independent of the adsorption model “pedestal,” “tilted” or “butterfly”—are pointing away from the surface, we observe this state for both in-plane and out-of-plane polarization.

Let us now turn to the spectral features towards higher photon energies. Here both spectra in Figs. 3 and 4 exhibit a broad structure around 292.5 eV and quite pronounced in Fig. 3, a feature around 300.7 eV, mainly seen for the E vector parallel to the Si dimers. In the framework of a localized bond description, the feature at 292.5 eV could be assigned to a σ^*_{C-C} resonance with an energy lower than in the gas phase, as the C-C bond in chemisorbed benzene has been elongated in comparison to the benzene gas phase, as is the case for the “butterfly” adsorption model.

The state at 300.7 eV would then be assigned to a $\sigma^*_{C=C}$ resonance of the carbon double bond. In particular the reduced intensity of the latter structure for the polarization normal to the Si dimers (Fig. 4) favors the “butterfly” model, where the carbon double bonds are parallel to the dimers, and speaks against the “tilted” and “pedestal” configurations. In the case of a “tilted” configuration we would expect contributions of C-C double bonds for both in-plane polarizations, and for the “pedestal” configuration, we would expect a strong σ^*_{C-C} resonance and no structures for C-C double bonds around 300 eV.

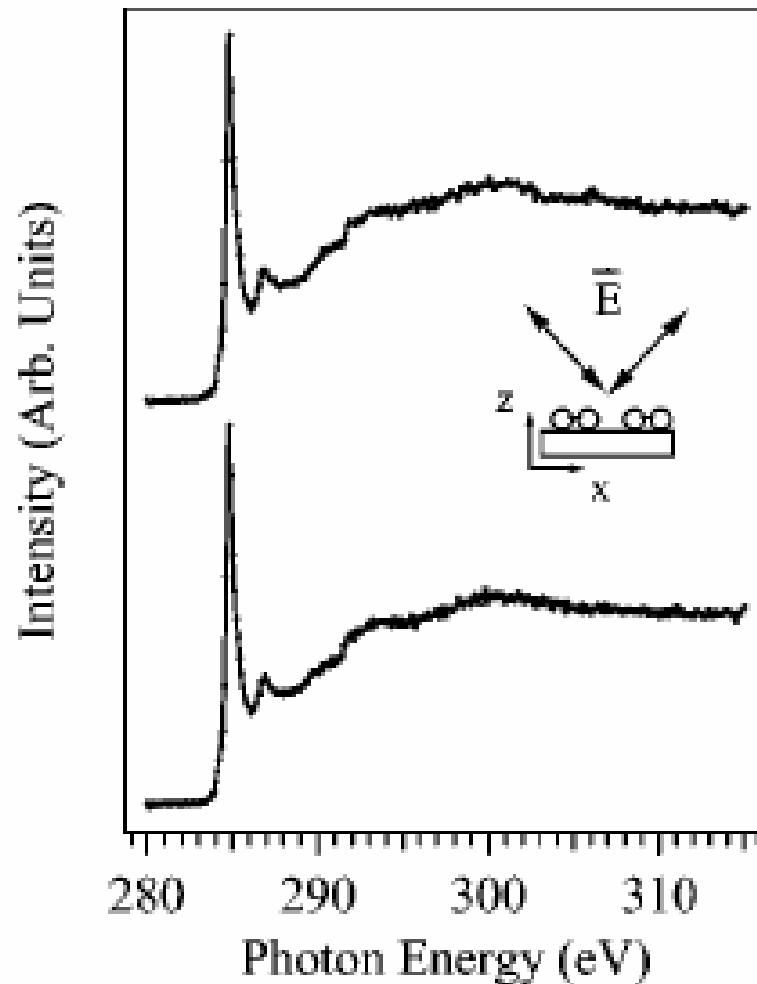


FIG. 5. NEXAFS spectra of benzene adsorbed on Si(001)-(2 \times 1) at room temperature. The \vec{E} vector of the grazing incident photon beam is oriented $\pm 45^\circ$ from the z axis along the Si dimers as indicated in the sketch.

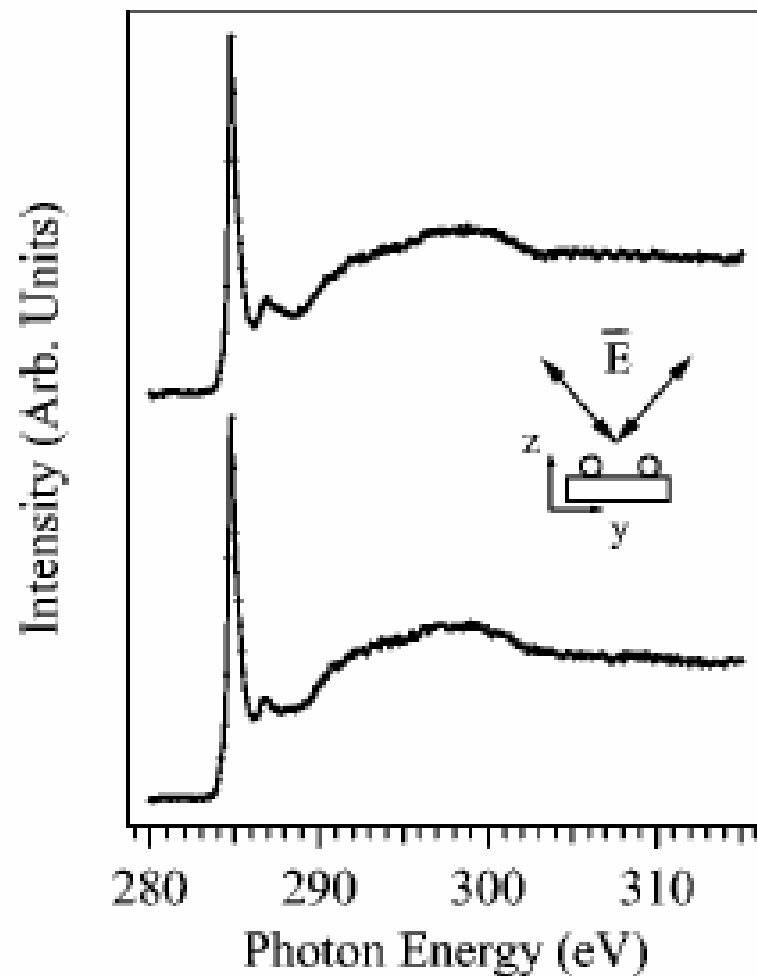


FIG. 6. NEXAFS spectra of benzene adsorbed on Si(001)-(2 \times 1) at room temperature. The \vec{E} vector of the grazing incident photon beam is oriented $\pm 45^\circ$ from the z axis perpendicular to the Si dimers as indicated in the sketch.

To gain further information to distinguish between the “tilted” and “butterfly” adsorption models, we also took NEXAFS data with the E vector oriented at $\pm 45^\circ$ from the (001) direction in order to distinguish an overall preferential orientation of the benzene molecules. In Fig. 5, the two NEXAFS spectra presented for the two orientations of the E vector are totally superimposable which indicates that the molecules are symmetric with respect to the plane which is perpendicular to the dimers.

This would agree with both models, as the adsorption geometry has local mirror symmetry normal to the Si-Si dimers.

The spectra in Fig. 6 are taken with the E vector $\pm 45^\circ$ around the Si-Si dimer, thus probing the orientation perpendicular to the dimers. For the two angles of polarization, we can see that the two spectra are very similar. Assuming that the benzene molecules in the “tilted” configuration are all to be found at the same tilt angle, we would expect a strong difference in the NEXAFS spectra for the different polarizations $+45^\circ$ and -45° with respect to the (001) direction.

The small variations observed in Fig. 6 prove that the molecules are symmetric with respect to the dimer axis. This is the case for the “butterfly” configuration.

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**Mastering the Molecular Dynamics
of a Bistable Molecule by Single
Atom Manipulation**



At low temperature (5 K), a single biphenyl molecule adsorbed on a Si(100) surface behaves as a bistable device which can be reversibly switched by electronic excitation with the scanning tunneling microscope tip. Density functional theory suggests that the biphenyl molecule is adsorbed with one dissociated hydrogen atom bonded to a neighbor surface silicon atom. By desorbing this hydrogen atom with the STM tip, the interaction of the molecule with the surface is modified such that it becomes transformed into a multistable device.

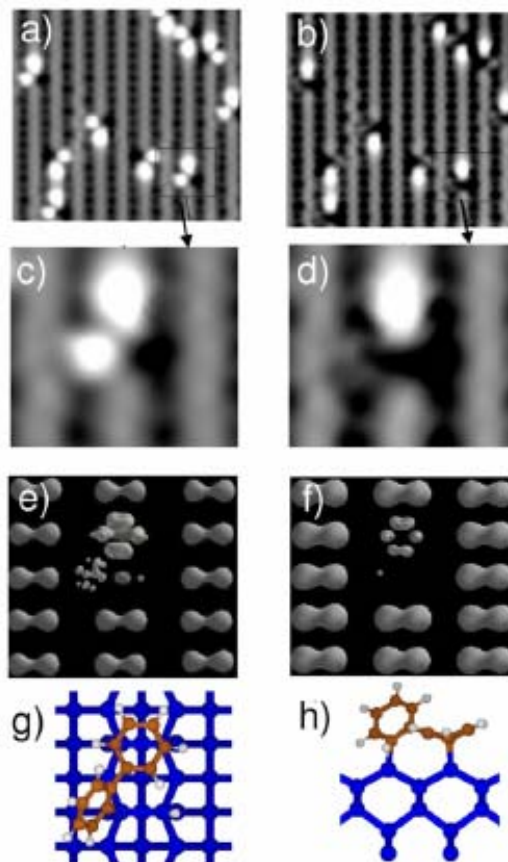


FIG. 1 (color online). (a),(b) ($81 \text{ \AA} \times 75 \text{ \AA}$) STM topographies showing several biphenyl molecules on Si(100)-(2 \times 1) at 5 K recorded at -2 and -1 V surface voltage, respectively. (c),(d) $19 \text{ \AA} \times 19 \text{ \AA}$ enlarged STM topographies of a biphenyl molecule on Si(100)-(2 \times 1) at $V_S = -2$ V and $V_S = -1$ V, respectively. (e),(f) Calculated local density of states (VASP) of a biphenyl molecule adsorbed on Si(100)-(2 \times 1) within an energy windows of -2 and -1 eV to the Fermi levels, respectively. (g) Schematic top view and (h) right-side view of the biphenyl conformation on the Si(100)-(2 \times 1) surface where the dark gray balls are silicon, the light gray balls are carbon atoms, and the white balls are the hydrogen atoms.

STM topographies of biphenyl molecules adsorbed on the Si(100) surface are shown in Figs. 1(a) and 1(b) for a surface voltage of 2 and 1 V, respectively. STM topographies of a single biphenyl molecule are shown in Figs. 1(c) and 1(d). For a surface voltage of 2 V [Figs. 1(a) and 1(c)], each biphenyl molecule is seen as a pair of bright features representing the two phenyl rings of the molecule. The vertical gray lines in Figs. 1(a)–1(d) indicate the silicon dimer rows of the Si(100) surface.

Only one of the two phenyl rings is visible as a bright spot for a surface voltage of 1 V [Figs. 1(b) and 1(d)]. The resulting most stable configuration is shown in Figs. 1(g) and 1(h).

Local density of states calculations were then performed and compared to the experimental STM topographies. The corresponding images are displayed in Figs. 1(e) and 1(f). The model consists of one phenyl ring lying parallel to the surface and attached to a silicon dimer in the so-called “butterfly” configuration through two C-Si chemical bonds. This phenyl ring is centered over the silicon dimer row.

The second phenyl ring, perpendicular to the surface, is attached to a silicon atom through a single C-Si chemical bond. This is a result of the dissociation of the second phenyl ring and one hydrogen atom: The H atom of the phenyl ring is bonded to the Si atom of the dimer as shown in Figs. 1(g) and 1(h). In the hypothesis of a nondissociated biphenyl molecule, less energetically favorable configurations were obtained and the simulations could not reproduce the observed STM topographies. This Si-H bond is seen as a dark spot in the STM topographies [Figs. 1(c) and 1(d)].

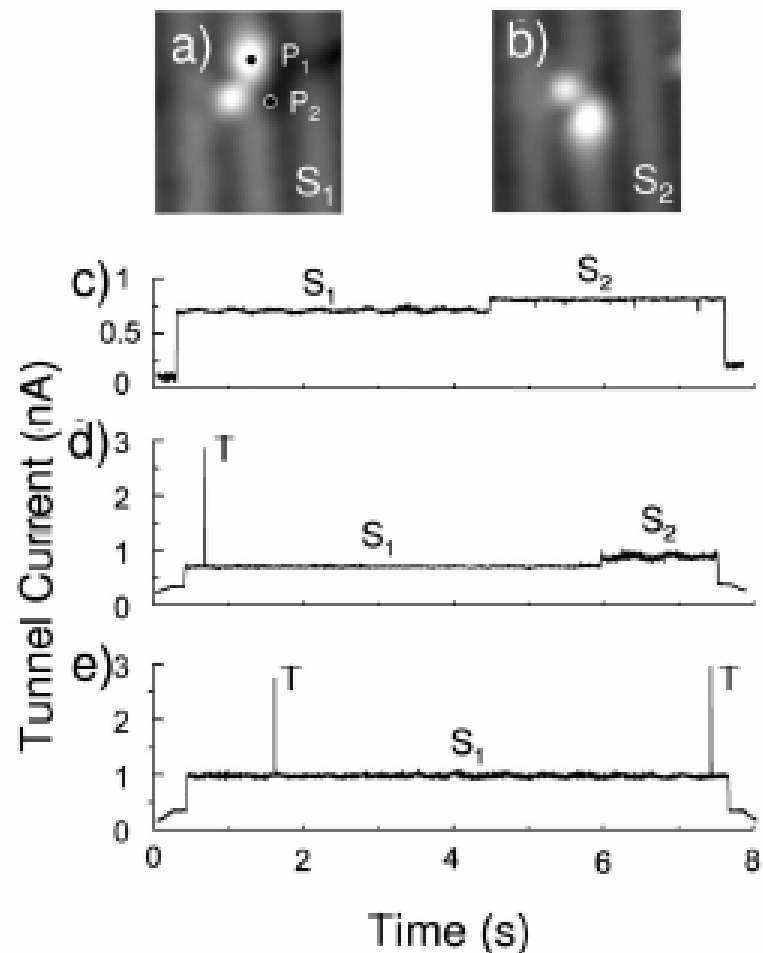
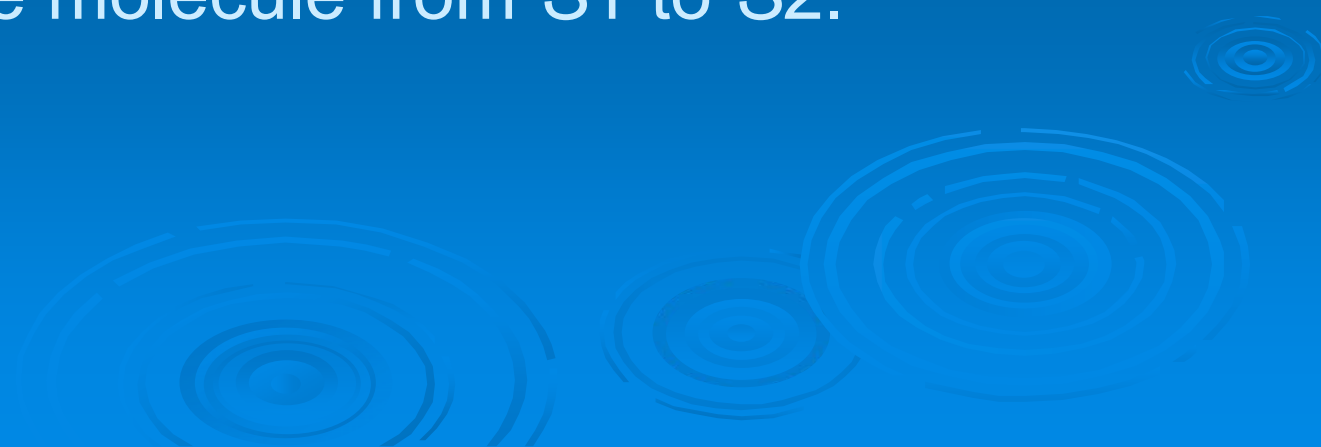


FIG. 2. (a) ($23 \text{ \AA} \times 23 \text{ \AA}$) topography ($V_s = -2 \text{ V}$, $I = 220 \text{ pA}$) of a single biphenyl molecule in the stable configuration S_1 . The dots indicate the STM tip position (P_1 and P_2) where the negative bias pulse is applied. (b) Same as (a) after the surface pulse. The molecule has switched to its second stable configuration S_2 . (c)–(e) Three typical tunnel current curves recorded during negative bias pulses at P_2 ($V_s = -3 \text{ V}$).

The biphenyl molecule adsorbed at room temperature on the Si(100) surface has two equivalent stable positions $S1$ and $S2$, shown in Figs. 2(a) and 2(b), respectively. The reversible switching of the molecule from $S1$ to $S2$ can be activated through resonant electronic excitation by positioning the STM tip at different positions inside the molecule [for example, positions $P1$ and $P2$ in Fig. 2(a)] and applying a pulse voltage on the surface.

Recording the tunnel current during the pulse voltage enables a detailed investigation of the dynamics of the molecule for the duration of the time of excitation. The tunnel current curves in Figs. 2(c)–2(e), recorded with the STM tip in position $P2$, illustrate some of the molecular movements that can occur. The small steps in curves 2(c) and 2(d) correspond to the switching of the molecule from $S1$ to $S2$.



The tunnel current curves show additional features consisting of very narrow peaks (T) that are related to the brief passage through a transient molecular state, i.e., the $S1 \rightarrow T$ movement rapidly followed by the reverse $T \rightarrow S1$ movement.

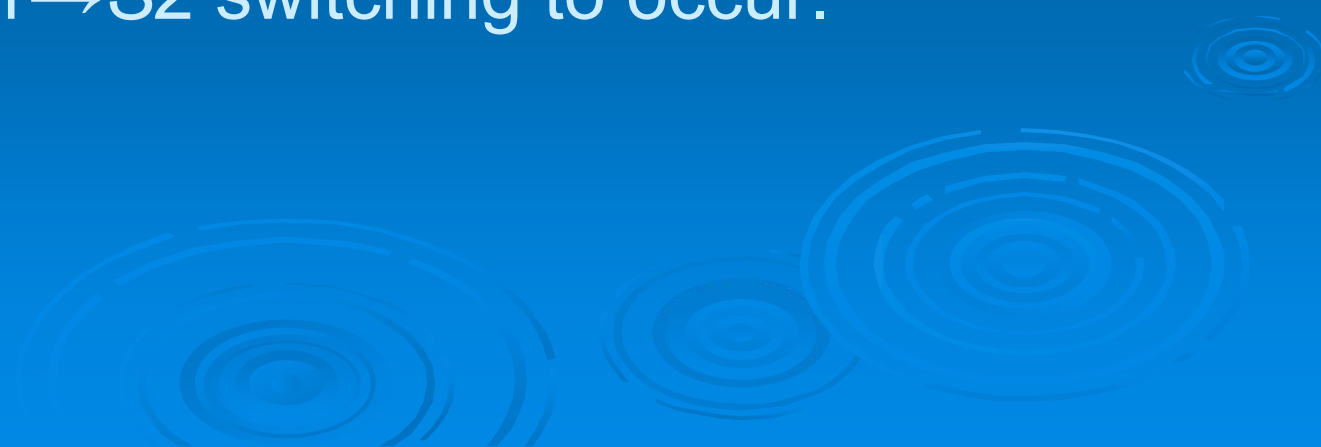
Both the $S1 \rightarrow T$ and the $T \rightarrow S1$ movements are induced by electronic excitation with the STM tip.

From previous experiments and the high tunnel current of the T peaks, one can anticipate that the T state molecular configuration involves one phenyl ring of the molecule being close to the $P2$ position in Fig. 2(a).

The $S1 \rightarrow S2$ switching requires one of the molecular phenyl rings (called the mobile phenyl ring) to break two Si-C bonds in its butterfly position, to move over the Si-H bond, and to make two new Si-C bonds to recover its butterfly position at the second silicon dimer site



In the
meantime, the other molecular phenyl ring (called
the fixed phenyl ring) is expected to rotate around
its single Si-C bond. It follows that the Si-H bond
acts as an obstacle to
the movement of the bistable molecule since the
mobile ring has to pass over the hydrogen atom for
 $S1 \rightarrow S2$ switching to occur.



Therefore, we decided to desorb this hydrogen atom with the STM tip in order to explore the resulting dynamics of the molecule.

The desorption of hydrogen atoms from the hydrogenated Si(100) surface with the STM tip has been extensively studied with both positive and negative surface voltages. Here we have used a negative surface voltage $V_S = -4$ V with the STM tip on top of the hydrogen atom [position *P2* in Fig. 2(a)].

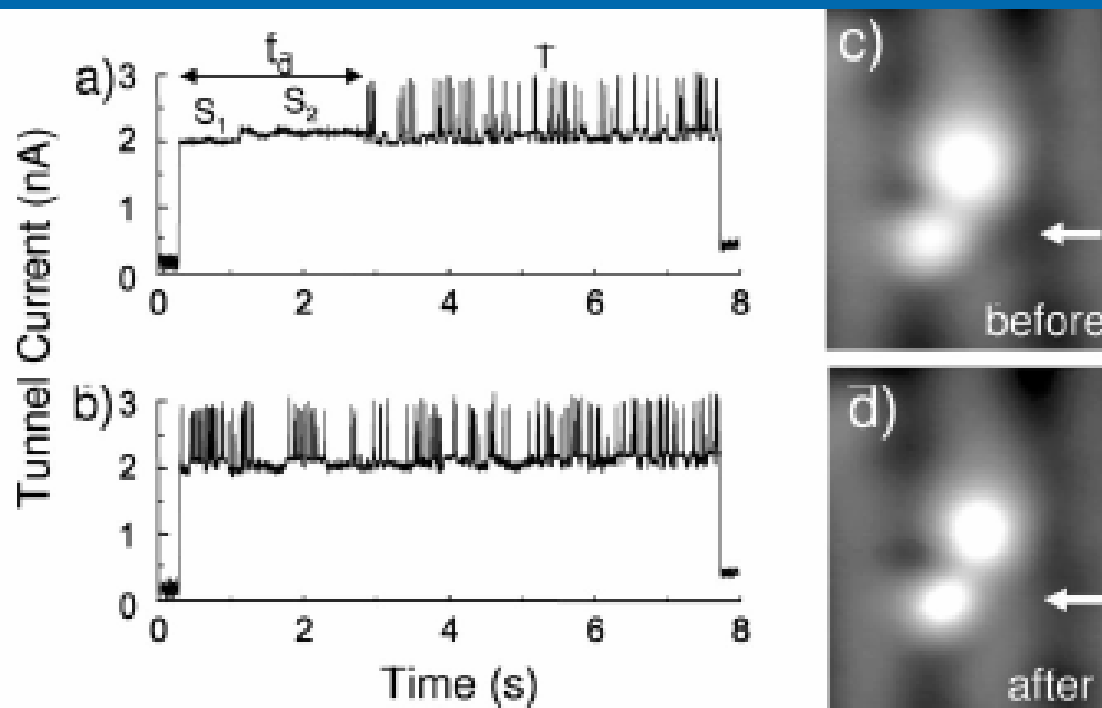
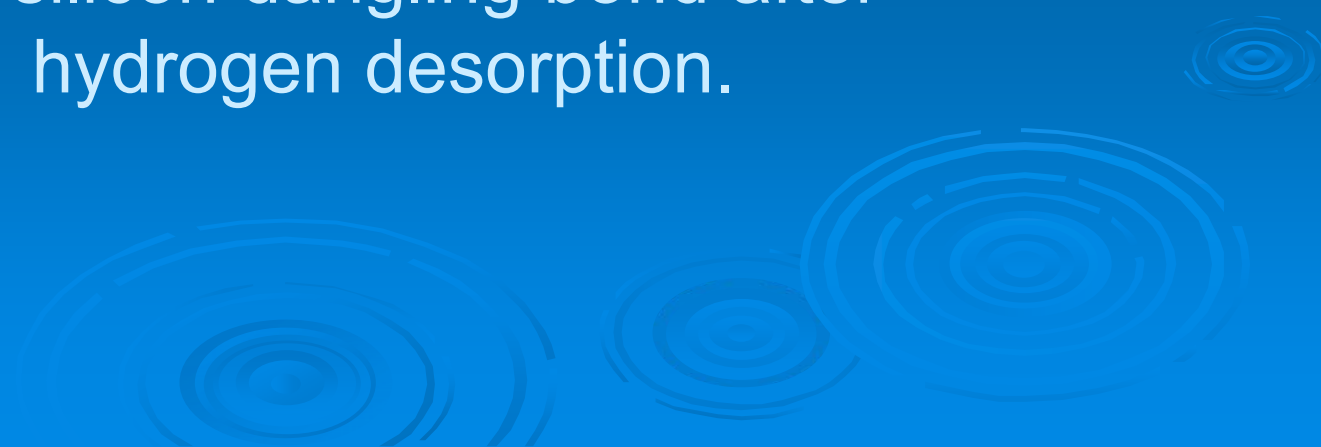


FIG. 3. (a) Tunnel current during a negative bias pulse at P_2 ($V_s = -4$ V). Desorption of the hydrogen atom occurs at time t_d . (b) Tunnel current during a negative bias pulse ($V_s = -4$ V) after hydrogen desorption. (c),(d) $20 \text{ \AA} \times 20 \text{ \AA}$ STM topographies ($V_s = -2$ V, $I = 220$ pA) of the biphenyl molecule before and after the hydrogen desorption. The arrow indicates the area where the hydrogen atom has been removed leading to a slightly higher local density of states. See Fig. 2 for the description of positions P_1 and P_2 .

The actual desorption of the hydrogen atom can be verified by comparing STM topographies of the biphenyl molecule before [Fig. 3(c)] and after [Fig. 3(d)] applying the first surface voltage pulse. The hydrogen site which appears dark in Fig. 3(c) becomes brighter in Fig. 3(d) as expected from the appearance of the silicon dangling bond after hydrogen desorption.



The consequence of the hydrogen atom desorption can be understood as a lowering of the energy barrier for the switching dynamics. Indeed, it is known from the desorption induced by electronic transition mechanism that lowering the energy barrier of the ground state can dramatically increase the yield of the electronic excitation process.



Another interesting result of the hydrogen desorption is that the molecule can now be switched (by applying a pulse voltage at $V_S = -3.5$ V) into any of the four molecular configurations imaged in Fig. 4. Once the hydrogen atom has been removed, every molecule studied shows the same multistable sites. From the STM images in Figs. 4(b) and 4(d), the molecule in the S3 and S4 states appears to lie between the S1 and S2 states.

Furthermore, these two molecular configurations overlap partially with the silicon dangling bond resulting from the hydrogen desorption. One can expect some interaction between this silicon dangling bond and the molecule, thus explaining the stability of the *S3* and *S4* states after hydrogen desorption under these imaging conditions ($V_S = -2$ V). The most stable configuration of the *S3* (*S4*) state deduced from DFT calculations is shown in Fig. 4(h) [Fig. 4(i)].

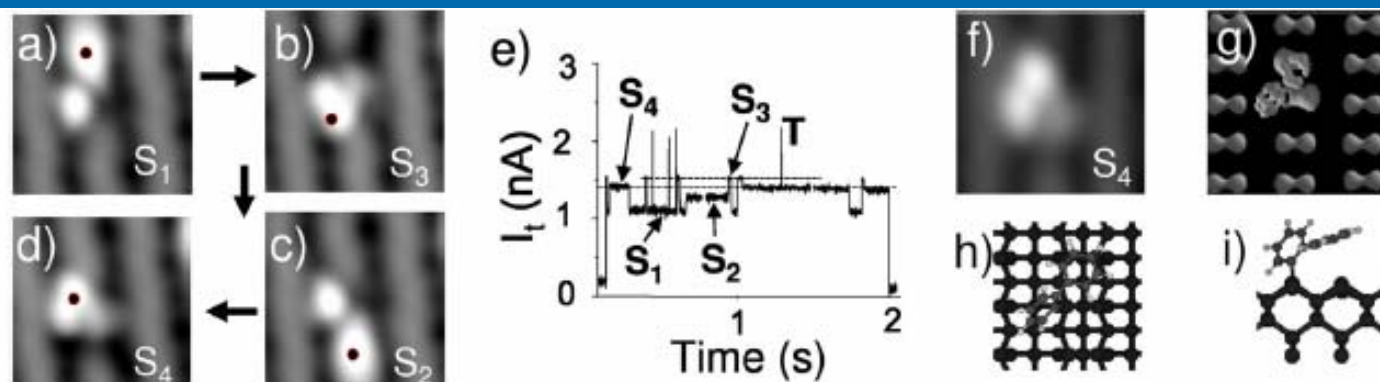


FIG. 4 (color online). ($23 \text{ \AA} \times 23 \text{ \AA}$) STM topographies of the four stable configurations of the biphenyl molecule after H atom desorption. (a),(c) ($V_S = -2 \text{ V}, I = 220 \text{ pA}$) depict the S_1 and S_2 configurations, respectively. (b),(d) show the two new stable S_3 and S_4 configurations. The series (a)–(d) (following the arrows) is a succession of molecular manipulations of the multistable molecule using negative surface pulses ($V_S = -3.0 \text{ V}$) applied at the indicated black dots. (e) Tunneling current during a negative bias pulse at P_2 ($V_S = -3.0 \text{ V}$) after hydrogen desorption indicating the coexistence of the four stable states with the transient states (T). In addition to the peaks (T states), plateaus with four different current levels can be observed and are assigned to the four stable states S_1 to S_4 . See Fig. 2 for the description of positions P_1 and P_2 . (f) ($21 \text{ \AA} \times 21 \text{ \AA}$) STM topography of the S_4 state ($V_S = -2 \text{ V}, I = 300 \text{ pA}$). (g) Calculated local density of states (VASP) of the S_4 state configuration adsorbed on Si(100)-(2 \times 1) within an energy window of -2 eV to the Fermi level. (h) Schematic top view and (i) right-side view of S_4 conformation on the Si(100)-(2 \times 1) surface (see Fig. 1 for color definition).