C 1*s* core-level photoemission spectra of stilbene on Si(100)2×1 surface from first-principles calculations

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Adsorption of the *cis* and *trans* stilbene on the Si(100)2×1 surface was studied using plane waves density functional theory (DFT). Configurations across a silicon dimer, along the dimers and along the channels between dimers were probed for the two isomers. *Trans* and *cis* stilbene both bind preferentially across the dimers. In the former case only the ethylenic carbon atoms are involved and the aromatic character is preserved. In the latter case the adsorption interaction involves also the two phenyl rings with the conversion to two 1,3-cyclohexadiene, yielding a more stable local minimum. The corresponding calculated C 1*s* core level shifts are distributed in an energy range of about 2.5 eV. The overall shape of the spectra of the two adsorbed isomers shows differences consistent with chemical changes observed upon adsorption. There is a good agreement between the simulated and the experimentally observed spectrum of *trans* stilbene on the Si surface.

PACS number(s): 47.55.dr

INTRODUCTION

Metastable molecules on surfaces as well as multiconformation molecules with low transition barriers between conformations are the ideal candidate systems to develop the concept of molecules as nanomachines in themselves.

The first example of a single molecule as a functionalized nanomachine is biphenyl on Si(100)2×1. Tunneling electrons from a low-temperature (5 kelvin) scanning microscope were used to control, through resonant electronic excitation, the molecular dynamics of an individual biphenyl molecule adsorbed on a silicon (100) surface.[1] Density functional theory (DFT) studies suggest 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 scanning tunneling microscope (STM) tip, the interaction of the molecule with the surface is modified such that it becomes a multistable device.[2]

Stilbene is another candidate for developing such devices, since it exists as *cis* and *trans* isomers with an energy difference between them of 0.15 eV in the isolated molecule. Isomerization of *trans-cis*[3,4] stilbene can start from either *cis* or *trans* stilbene geometry with a transition barrier of no more than 0.05 eV.[5,6] It is a prototype molecule for investigating photoisomerization[7–11] a model for understanding both the behavior of more complicated systems, such as retinal (the choromofore of rhodopsin) and the effects of different environments on photoisomerization. After electronic excitation the molecule undergoes rotation about its ethylene bond.[12] A hula-twist pathway was proposed for the photochemical *cis*-to-*trans* isomerization of free stilbene.[13] This kind of mechanism can be assumed to work as well in constraint systems as on surfaces, thus assessing a "molecular switch." Recently, an investigation was performed on *cis* and *trans* stilbene on Si(100)2×1 surface by synchrotron radiation photoemission and NEXAFS.[14] The authors measured the photoemission spectra and hypothesized an ordered adsorption of the molecules on the surface. However, the interpretation of the spectra is not straightforward, especially since stilbene, though symmetric as isolated molecule, can yield complex adsorption patterns, due to the presence of three functional groups of two different types.

As a consequence, we performed a DFT study of the adsorption of *cis* and *trans* Si(100)2×1, in order to establish the most stable adsorption configurations and calculated the corresponding photoemission spectra of the C 1*s* level. We also calculated the difference density maps and related them to the spectral chemical shifts.

COMPUTATIONAL METHODOLOGY

We performed *ab initio* DFT based calculations using the CPMD code.[15] Since the accuracy in the description of the chemical processes on silicon surface has been shown to improve with respect to the pure local density approximation (LDA) when gradient correction is taken into account, we adopted the corrected gradient approximation (GGA) to the BLYP[16] functional for exchange energy.

The calculations were carried out using norm-conserving Trouiller-Martins pseudopotentials.[17] The wave functions were expanded in plane waves with an energy cutoff of 60 Ry, a value for which the structural and binding properties of the systems are all well converged. The calculations were performed under periodic boundary conditions with the periodically repeated unit cells referred to as supercell. A surface model is built with SiH corresponding to 6 layers of Si atoms and 15 (5×3) surface dimers.

This surface size is large enough to allow the optimization of the stilbene position on all possible surface sites.

The silicon layers were included in this supercell with vacuum regions of about 14 Ångstrom in the [001] direction (twice as much as the slab dimension in the [001] direction, i.e., 12 interlayers). For such a supercell the Brillouin zone was sampled by Γ-point approximation. A monolayer of hydrogen was used to saturate the dangling bonds on the lower side of the slab.
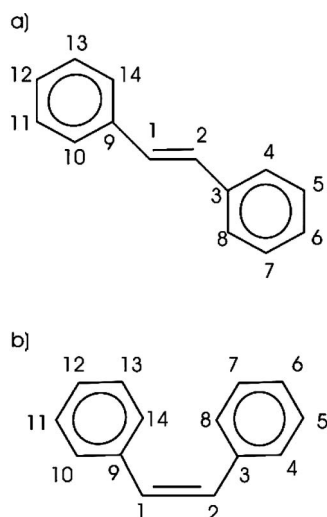
FIG. 1. Numbering of the stilbene carbon atoms: (a) *trans* isomer, (b) *cis* isomer.

The supercell parameters were kept fixed during the optimization and geometry structures were relaxed until forces dropped below 10^{-4} a.u.

The reliability of this approach has been probed by calculations of the gas-phase *trans* and *cis* stilbene, in identical conditions as the adsorbate models, i.e., with a supercell of identical size, same cutoff, and pseudopotentials. The numbering of the carbon atoms of *trans* and *cis* isomers is reported in Fig. 1 and it is used throughout the paper. The hydrogen atoms, not included in the figure are identified with the same number of the carbon atom they are bonded to.

The resulting geometrical parameters were compared to those obtained using DFT B3LYP/cc-p[18] and summarized in Table I. The agreement of the internal coordinates obtained with the two methods is very good.

For the silicon surface, symmetric dimers were used as a starting model, and the top two layers were allowed to fully relax. The output geometry was the well-known model with asymmetric dimers. We obtained Si dimer bond length of 2.25 Å and a buckling angle of 19°, in agreement with the reconstruction calculated by Krüger and Pollmann[19] at the LDA level.

Adsorption energies are calculated as difference between the energy associated to an adsorption model upon geometry optimization and the energy of separate stilbene and silicon moieties calculated using the same computational parameters as the adsorbate-silicon system. Adsorption energies are, then, reported with inverted signs, in Table II.

Furthermore, difference-density maps were calculated for the most representative adsorption sites in order to correlate this information to calculated core level shift (CLS) of carbon (1s).

The simulation of the C 1s photoemission spectra of *cis* and *trans* stilbene on Si(100)2×1 requires, first of all, the identification of the most stable structures (local minima) on the surface.

We used here a methodology to calculate the relative CLS based on the DFT total energy differences within a pseudopotential-plane-wave technique.[20] This approach has

TABLE I. Geometrical parameters of the optimized free and adsorbed *cis* and *trans* stilbene. The distances are given in ångstroms. The values of free stilbene are compared to those calculated in Ref. 18.

TRANS	Free	B3LYP/cc-p VDZ (Ref. 18)	Adsorbed
C1-C2	1.351	1.3508	1.558
C2-C3	1.464	1.4677	1.485
C3-C4	1.410	1.4096	1.415
C4-C5	1.394	1.3957	1.390
C5-C6	1.395	1.3970	1.394
C6-C7	1.399	1.4007	1.404
C7-C8	1.390	1.3930	1.413
C3-C8	1.410	1.4114	1.394
C1-C9	1.465		1.483
C9-C10	1.411		1.412
C10-C11	1.390		1.387
C11-C12	1.399		1.394
C12-C13	1.395		1.401
C13-C14	1.393		1.414
C14-C9	1.409		1.398
Si-C1			1.971
Si-C2			1.976
Si-C7			2.321
Si-C13			2.382
C1-C2-C3	127.51°	127.2°	119.46°
C2-C3-C4	118.36°	118.7°	119.39°
C3-C4-C5	121.17°	121.4°	121.69°
C4-C5-C6	120.49°	120.1°	120.65°
C5-C6-C7	119.31°	119.4°	118.81°
C6-C7-C8	121.17°	120.5°	120.09°
C7-C8-C3	121.29°	120.9°	121.35°
C4-C3-C8	117.16°	117.7°	117.31°
C2-C1-C9	126.99°		119.82°
C1-C9-C10	118.68°		121.45°
C9-C10-C11	121.10°		119.46°
C10-C11-C12	120.58°		121.45°
C11-C12-C13	119.24°		121.17°
C12-C13-C14	120.18°		120.06°
C13-C14-C9	121.50°		121.41°
C14-C9-C10	117.4°		117.26°
C3-C4-H4	119.07°	119.0°	118.90°
C4-C5-H5	119.74°	119.8°	119.58°
C5-C6-H6	120.44°	120.4°	121.32°
C6-C7-H7	119.91°	119.9°	120.28°
C7-C8-H8	118.89°	119.1°	117.77°
C3-C2-H2	118.79°	118.7°	111.18°
C9-C10-H10	119.73°		119.81°
C10-C11-H11	119.60°		119.63°
C11-C12-H12	120.29°		120.54°

TABLE I.   (*Continued.*)

TRANS	Free	B3LYP/cc-p VDZ (Ref. 18)	Adsorbed
C12-C13-H13	119.93°		120.80°
C13-C14-H14	119.42°		117.82°
C9-C1-H1	118.41°		110.60°
Si-C1-C9			111.12
Si-C2-C3			112.47
C1-H1	1.095		1.095
C2-H2	1.095	1.0949	1.096
C4-H4	1.093	1.0934	1.093
C5-H5	1.092	1.0925	1.088
C6-H6	1.092	1.0922	1.089
C7-H7	1.092	1.0926	1.091
C8-H8	1.091	1.0915	1.086
C10-H10	1.091		1.093
C11-H11	1.092		1.088
C12-H12	1.092		1.089
C13-H13	1.092		1.091
C14-H14	1.093		1.087
Dihedral angle 1	0°		0°
Dihedral angle 2	0°		4°

CIS	Free	B3LYP/cc-p VDZ (Ref. 18)	Adsorbed
C1-C2	1.354	1.3511	1.551
C2-C3	1.476	1.4786	1.478
C3-C4	1.406	1.4085	1.371
C4-C5	1.396	1.3962	1.453
C5-C6	1.394	1.3977	1.353
C6-C7	1.399	1.3993	1.494
C7-C8	1.390	1.3954	1.558
C3-C8	1.408	1.4088	1.531
C1-C9	1.477		1.470
C9-C10	1.406		1.364
C10-C11	1.396		1.438
C11-C12	1.394		1.350
C12-C13	1.399		1.483
C13-C14	1.390		1.562
C14-C9	1.408		1.533
Si-C1			1.964
Si-C2			1.982
Si-C13			1.943
Si-C7			1.899
C1-C2-C3	127.98°	131.3°	120.54°
C2-C3-C4	122.26°	123.3°	120.11°
C3-C4-C5	121.19°	121.2°	122.42°
C4-C5-C6	120.21°	120.1°	120.14°

TABLE I.   (*Continued.*)

CIS	Free	B3LYP/cc-p VDZ (Ref. 18)	Adsorbed
C5-C6-C7	119.28°	119.4°	120.70°
C6-C7-C8	120.33°	120.5°	114.57°
C7-C8-C3	121.91°	120.8°	110.18°
C3-C4-C8	117.71°	118.0°	117.91°
C2-C1-C9	127.98°		119-73°
C1-C9-C10	120.12°		123.79°
C9-C10-C11	120.82°		121.95°
C10-C11-C12	120.21°		121.91°
C11-C12-C13	119.37°		121.42°
C12-C13-C14	120.21°		117.01°
C13-C14-C9	121.04°		115.73°
C14-C9-C10	117.80°		117.89°
C1-H1	1.905		1.094
C2-H2	1.905	1.0964	1.097
C4-H4	1.903	1.0933	1.094
C5-H5	1.902	1.0926	1.086
C6-H6	1.902	1.0924	1.091
C7-H7	1.902	1.0927	1.097
C8-H8	1.089	1.0906	1.108
C10-H10	1.903		1.093
C11-H11	1.902		1.088
C12-H12	1.902		1.093
C13-H13	1.902		1.098
C14-H14	1.089		1.124
C3-C4-H4	119.33°	119.5°	118.79°
C4-C5-H5	119.58°	119.5°	120.69°
C5-C6-H6	120.39°	120.3°	118.09°
C6-C7-H7	120.18°	120.1°	110.02°
C7-C8-H8	119.72°	119.7°	109.30°
C3-C2-H2	115.30°	115.3°	114.01°
C9-C10-H10	119.34°		119.96°
C10-C11-H11	119.68°		118.62°
C11-C12-H12	120.26°		120.84°
C12-C13-H13	120.10°		112.04°
C13-C14-H14	119.45°		109.93°
C9-C1-H1	115.56°		114.70°
Si-C1-C9			94.8°
Si-C2-C3			96.9°
Dihedral angle 1	37.5°	37.5°	−10°
Dihedral angle 2	40.5°		+24°

been successfully applied both to inorganic[21] and organic systems.[22,23] The core-hole binding energies (BE's) were evaluated as a difference between the energies of the ionized ($E+$) and neutral ($E0$) states in the same geometry. The relative C 1s BE's are, then, given by the energy difference with respect to a reference configuration. This way we fully took

TABLE II. Adsorption energies of *trans* and *cis* stilbene in the various configurations. The values are reported with an inverted sign.

	TRANS	*CIS*
AC	1.00 eV	1.13 eV
AL	−0.52 eV	0.53 eV
CH	−0.62 eV	−0.43 eV

into account electronic relaxation effect in the final state. The C 1s spectra were obtained by convolution the binding energies with a Gaussian broadening function having a standard deviation of 0.35 eV.

RESULTS AND DISCUSSION

The simulations of the *cis* and *trans* stilbene (C 1s) spectra and their analysis in terms of electron density plots require an approach in three steps. The first step is the assessment of possible stable stilbene geometries on the surface (local minima). This was achieved by testing a few sites where the stilbene molecule would maximize the interaction with the surface, taking into account that both the phenyl rings and the ethylenic bond may be involved in an interaction with the surface. We considered three candidates as most convenient sites for adsorption, i.e., with the stilbene molecule in the channel between dimers raws, across the dimers or along the dimers. We probed only the geometries where the molecule lies flat on the surface, since the former offers more possibility of interaction.

The most stable adsorption geometries for *trans* and *cis* stilbene on Si(100)2×1 were, then, used to calculate the corresponding density maps and the C 1s binding energies for each carbon atom of the molecule. The outcome of the three steps of calculation is given separately in the following sections.

Geometry optimizations

Both for the *trans* and the *cis* isomer three adsorption geometries were probed: across the dimers (AC), along the dimers (AL), and along the channels (CH). The geometrical models upon optimizations are sketched in Fig. 2. The corresponding adsorption energies are reported in Table II. The configuration across the dimers appears to be the most stable with respect to the adsorption for both isomers. The other geometries along the dimer and along the channel are only slightly or not at all bound, hinting at some possible weak physisorption of stilbene in these geometries.

The geometrical parameters of *trans* and *cis* stilbene upon adsorption across the silicon dimers are reported in Table I.

It is important to notice that, in spite the favorable configuration for both isomers is across the dimers, the adsorption geometries are significantly different.

In the case of *trans* stilbene, the adsorption process occurs trough the binding of the ethylenic carbon atoms to silicon dimer. This results in an elongation of the C=C bond from 1.351 Å to 1.558 Å, i.e., from the value of a double to single
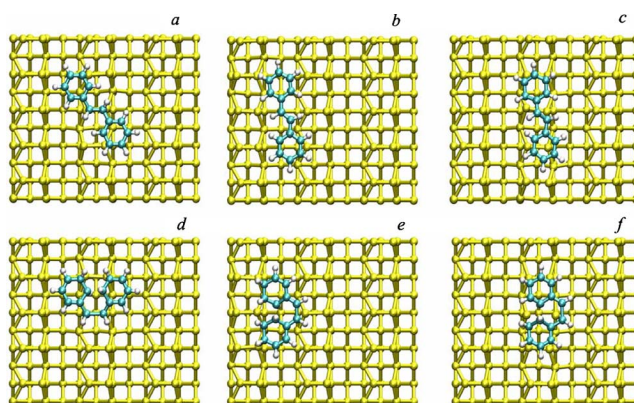

FIG. 2. (Color online) Optimized geometries of *trans* (top) and *cis* (bottom) stilbene different Si(100)2×1 surface sites. a,b,c: *trans* stilbene across the dimers (AC), in the channel (CH), and along the dimers (AL). d,e,f: *cis* stilbene across the dimers (AC), in the channel (CH), and along the dimers (AL).

bond. The distance between the ethylenic carbon atoms and the phenyl rings (C2-C3 and C1-C9) is also slightly larger. The silicon-carbon bond distances are 1.971 Å (Si-C1) and 1.976 Å (Si-C2), comparable to the values obtained for ethylene adsorbed on the same surface.[24] The silicon dimer bonded to C1 and C2 becomes symmetric upon adsorption. The overall picture suggests a rehybridization of the ethylenic carbon atoms from sp^2 to sp^3, with loss of the double bond and covalent Si-C bond formation. The density plots presented in the next section uphold the ethylenic carbon rehybridization.

The geometrical parameters of the free and adsorbed *trans* stilbene are quite similar. The only difference in the overall geometry is the dihedral angle of one of the rings that increases to 4°, hence with a loss of coplanarity of the 2 rings. In the adsorption process the atoms C7 and C13, come relatively close to the surface (2.321 and 2.382 Å respectively). However, the geometry of the corresponding silicon dimers underneath is not affected, i.e., the dimers remain asymmetric. The adsorption geometry of *trans* stilbene in Si(100)2×1 is shown in Fig. 3(a).

At variance with *trans* stilbene, the adsorption of *cis* stilbene on Si(00)2×1 occurs with significant modifications in the geometry. As it can be seen in Fig. 3(b), the phenyl rings loose their planarity, hence the aromatic character, and four carbon atoms are at bond distance with the silicon. C8 and C14 move alternatively upward and downward towards the surface, to yield two 1,3-cyclohexadiene rings. The C-C ethylenic bond is elongated from 1.354 Å to 1.551 Å, hence from double to single bond, similarly to what happened in
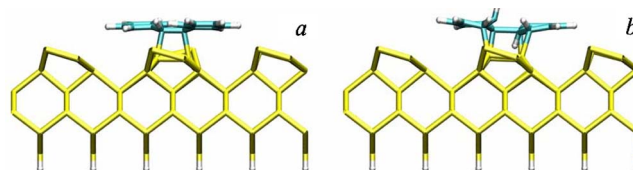

FIG. 3. (Color online) Optimized geometries of (a) *trans* and (b) *cis* stilbene across the dimers.

adsorbed *trans* stilbene. The phenyl bonds C7-C8, and C3-C8 (upward deviated ring) and C13-C14 and C14-C9 (downward deviated ring) are stretched to 1.558 Å, 1.531 Å, 1.562 Å, 1.533 Å, respectively. The C8-H8 and C14-H14 distances also become longer. Furthermore, the bonds C3-C4 and C5-C6 are shorter than in the free counterpart, and the bond C4-C5 is longer. The bond distances between the carbon and the silicon atoms are 1.964 Å (C1), 1.899 (C7) Å for the upward and 1.982 (C2) Å, 1.943 (C13) Å for the downward ring. Both silicon dimers involved in the binding process with *cis* stilbene become symmetric upon adsorption.

Electronic density plots

The electronic density was calculated for the optimized models across the dimers (AC) in their local minimum structure and for the separate moieties (silicon surface and stilbene molecule) in the same configuration. The difference of the electronic densities was, then, plotted in Fig. 4(a) and 4(b) for the *trans* and *cis* stilbene, respectively. The blue areas in the plots represent the electronic density depletion, the red ones are areas of density enrichment. The value of electronic density in the figure is 0.0032 el/Å. Top and side views are reported for each isomer and contour density.

The difference density plot for the *trans* isomer shows a substantial density transfer from the surface to the region between the Si dimer and the ethylenic carbon atoms and a depletion of electron density between the ethylenic carbon bonds. This is in line with the geometrical parameters (Si-C at bond lengths, lengthening of the double bond to a single one), confirming the Si-C covalent bond formation and a change of hybridization from sp^2 to sp^3.

Density enrichment also occurs between C7 (and C13) and the Si atoms underneath, though to a lesser extent than the ethylenic atoms, at expenses of the silicon area right below. The difference density distribution is mostly symmetric for the two rings, but some differences must be noticed. The phenyl ring on the left in the top view projection (C9 through C14), i.e., the one slightly tilted with respect to the surface, has larger areas of density redistribution. Small density depletions are localized on C11 and H11 with a simultaneous enrichment localized on the bond between C11 and H11. At variance with this behavior, the corresponding carbon and hydrogen atom of the bottom ring (C5, H5) are completely unaffected.

The difference density plot of the *cis* isomer shows four areas of enrichment between the Si atoms and the corresponding carbon atoms at bond distance (C1, C2, C7 and C13). Hence, there are two types of bond of silicon with the stilbene molecule, i.e., two occur with ethylenic bonds and two with two carbon atoms of the phenyl rings. In both cases there is a contribution to the electron density from the surface and an enrichment between the surface and the carbon atoms. However, in the former case a simultaneous depletion of the area between C1 and C2 occurs, similarly to *trans* stilbene. C7 and C13 belong to two phenyl rings with opposite behavior, i.e., one pointing downwards towards the surface, the other one upwards far from the surface. The formation of the Si-C bonds in this case occurs at expenses of the
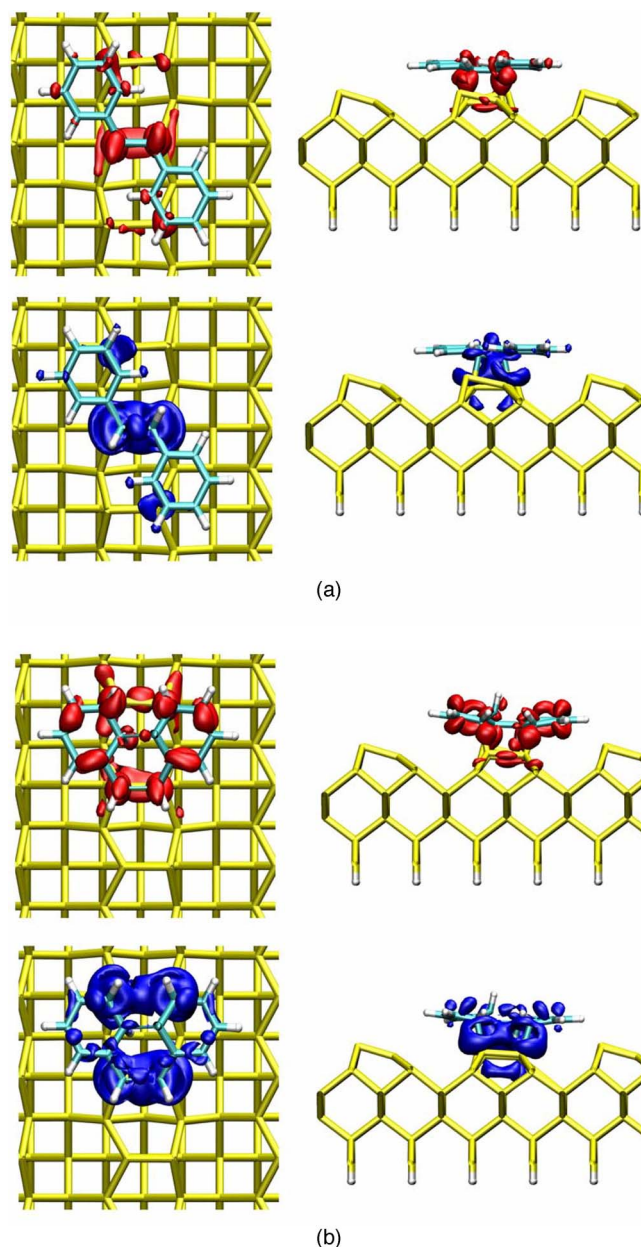

(a)

(b)

FIG. 4. (Color online) (a) *Trans* stilbene on Si(100)2×1 across the dimers (AC). Three-dimensional difference electron density plots at the isovalue of 0.0032 el/Å^3, evaluated in the local minimum structure. Upper part: top and side view of the of the positive density difference. Bottom part: top and side view of the of the negative density difference. (b) *Cis* stilbene on Si(100)2×1 across the dimers (AC). Same as (a).

bonds with the neighboring carbon atoms in the ring i.e., C6 and C12, respectively, as it can be seen in the top view of the difference density maps which shows an electronic depletion above the bond between C6 and C7. The loss of aromatic character that comes along with the loss of planarity is supported by the overall density redistribution in a 1,3 cyclohexadiene fashion, i.e., by an electronic localization above and below some of the C-C bonds. As it can be expected for a density rearrangement that converts an aromatic system into adjacent π bonds, electronic enrichments and depletions

alternate, moving along the ring. The bond between C3 (C9) and C4(C10) shows an electronic enrichment localized above and below the bond, C4(C10)-C5(C11) a depletion C5(C11)-C6(C12) again an enrichment. The overall density balance makes the single carbon atoms electronically non-equivalent.

Furthermore, the two rings are not symmetric with respect to their density distribution, with the left ring in the top view showing slightly larger electron depletion.

C 1*s* spectra simulations

Core-level photoemission spectroscopy is a powerful tool to investigate the changes induced by chemical reactions in the local environment around the ionized atom, yielding useful fingerprints of any interaction.

We calculated the C 1*s* CLS in the lowest local minimum structures found for both *trans* and *cis* stilbene on the silicon surface using the procedure described above. One ethylenic carbon of each isomer (labelled C1 in Fig. 1) was chosen as a reference state of our BE's calculations for all the carbon atoms of the corresponding adsorbed isomer. This is an arbitrary choice suggested by the similar configuration of the ethylenic C atoms in the adsorbed state, hence with a similar chemical shift, in both conformers. Moreover the C 1*s* calculated BE's is located at the center of the energy range of the spectrum, since the carbon atoms of the rings, after adsorption, have higher or lower BE's with respect to our reference states. The BE's difference between the two reference states for *cis* and *trans* stilbene is less than 0.093 eV.

Numerical results for all the 14 carbon atoms in both isomers are given in Table III. The spectra, obtained by Gaussian convolution of the C 1*s* calculated BE's as previously mentioned, are presented in Figs. 5(a) and 5(b).

Our model consists of one stilbene molecule on the Si(100)2×1 surface subject to periodic boundary conditions: we have then one molecule per supercell. This situation represents, in a realistic way, the first adsorbed monolayer assuming that no supramolecular interaction occurs during the adsorption process. We report the experimental spectrum of adsorbed *trans* stilbene,[14] the only one available to our knowledge, superposed to the calculated one in Fig. 5(a). The simulated spectra have been rigidly shifted in order to match the experimental one, being our energy scale arbitrary. The agreement between experimental and calculated spectra is quite good. The shape and the signal broadening are well reproduced. Our results suggest anyway a different interpretation, because not all the carbon atoms belonging to the pristine aromatic ring have the same behavior. Moreover, their interaction with silicon surface is quite different for the two conformers.

Trans stilbene isomer is bound to the silicon surface through the ethylenic carbon atoms (labeled C1 and C2) and, in spite of a small charge rearrangement, the aromatic rings preserve their planarity when adsorbed. In such a local minimum structure we have higher and lower C 1*s* BE's with respect to our reference state due to the interaction with the surface. Some carbon atoms, interacting with the silicon surface have lower BE's (C7, C8, C13 and C14) and the other carbon atoms, being at larger distances, interact to a lesser

TABLE III. Relative binding energies of the stilbene carbon atoms as numbered in Fig. 1.

Carbon atom	Relative binding energy
Trans stilbene	
C1	0
C2	−0.077
C3	0.373
C4	0.365
C5	0.227
C6	0.202
C7	−0.381
C8	−0.305
C9	0.182
C10	0.421
C11	0.563
C12	0.312
C13	−0.454
C14	−0.389
Cis stilbene	
Carbon atom	Relative binding energy
C1	0
C2	−0.028
C3	0.404
C4	−0.175
C5	0.123
C6	0.376
C7	−0.049
C8	0.596
C9	0.684
C10	−0.098
C11	0.474
C12	0.670
C13	−0.342
C14	0.681

extent with the silicon surface. This interpretation is supported by density plot where the formation of C1 and C2 bonds with surface is visible, and some charge flows towards the aforementioned carbon atoms which have lower BE's as a consequence of their local electronic charge enrichment. The large CLS energy distribution is partially related to the small differences in the configurations of the two rings that cause a slightly different chemical shift for equivalent positions. This is the case, for instance, of C11 and C5. Though they have equivalent positions they belong to phenyl ring with different dihedral angles with respect to the surface. The consequent localization of a small electron depletion area on C11 pushes the chemical shift to 0.563 eV to be compares to the 0.227 of C5.

In the *cis* stilbene, we have a different interaction with the Si surface producing a spectrum with a different orientation,
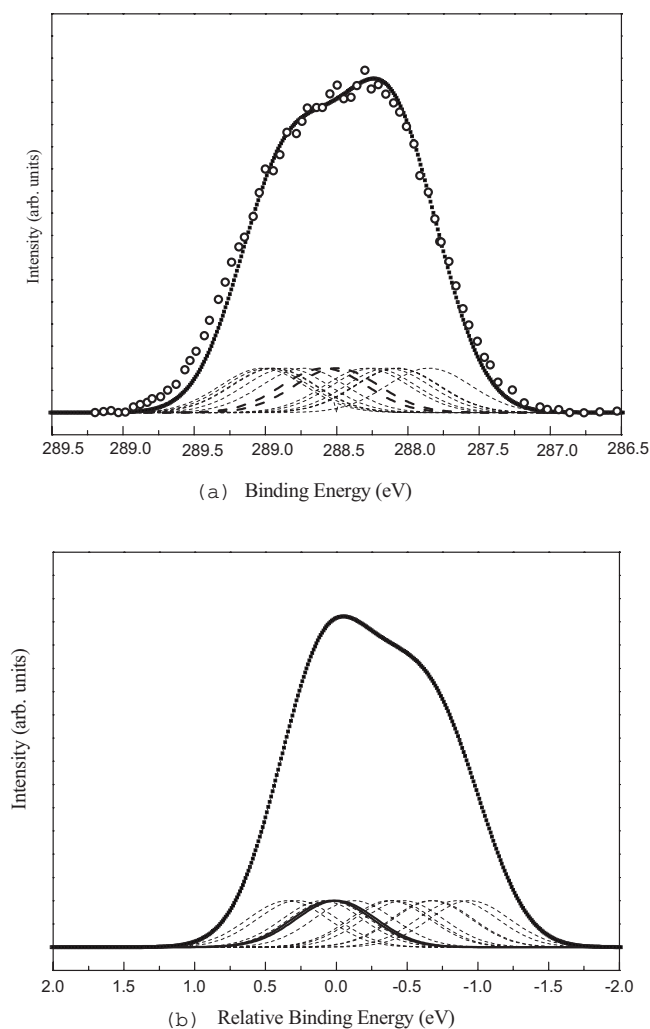
FIG. 5. (a) C 1s simulated spectrum of *trans* stilbene (filled squares) as well as all the single components (dashed lines). C1 and C2 spectra are marked with dashed bold lines. Open circles: Experimental data, taken from Ref. 14. The calculated spectrum was rigidly shifted to match the experimental values. (b) Same as (a) but for *cis* stilbene on Si(100)2×1. The corresponding experimental spectrum is not available. The scale is referred to the C1 taken as zero. Experimental data, taken from Ref. 14. The calculated spectrum was rigidly shifted to match the experimental values.

where more carbon atoms have higher BE's with respect to *trans* isomer. *Cis* conformer is bound to Si not only through the ethylenic C1 and C2, but through C7 and C13 as well (see also the related distances in Table I).

As a result, the distorted *cis* stilbene molecule has a configuration in which the rings are much more similar to cyclohexadiene rather than phenyl molecules. This picture is also upheld (besides the bond distances and angles) by the difference electron density plots where the covalent bond formation between carbon atoms (C1, C2, C7 and C13) with the surface is observed and some depletion of charge is present around the other carbon atoms. We have, then, a spectrum which has a mirror shape with respect to the one

obtained for *trans* stilbene because here more C 1s BE's are shifted towards higher energies region due essentially to the loss of aromatic character and consequent charge localization. This behavior finds a correspondence in the CLS which are, on average, higher for the left ring due to the slightly more pronounced depletion.

CONCLUSIONS

Several adsorption conformations of *trans* and *cis* stilbene on the Si(100)2×1 surface were studied by plane wave density functional theory. For both *trans* and *cis* isomers, the adsorption across dimers (AC) is the most favorable, though the adsorption geometries are rather different in the two cases. *Trans* stilbene is bound essentially through the ethylenic C atoms, while *cis* stilbene binds through the ethylenic atoms as well as through C7 and C13 atoms, with a consequent loss of the aromatic character and conversion of the phenylic rings into 1,3 cyclohexadienes. The difference density maps support the description of these adsorption processes, with an electronic enrichment of the areas between silicon dimers and the ethylenic carbon atoms. Extra interactions occur, for *trans* stilbene where the phenyl rings come closer to the surface. In the adsorbed *cis* isomer, due to the bonds between C7 and C13 with the silicon surface atoms, a rearrangement of the aromatic electron occurs, with a consequent electronic redistribution to form more localized double bonds.

C 1s ionization energies were calculated for all the 14 carbon atoms of the two adsorbed isomers in the lowest local minimum configuration found (AC). The chemical shifts of carbon atoms of adsorbed stilbene isomers cover an energy range of 2.5 eV. The ethylenic carbon atoms (1s) binding energies have a rather central position and the carbon labeled C1 is chosen as a reference for the relative CLS evaluation. C 1s chemical shifts of the phenyl ring atoms are either higher or lower than this value, for both isomers. As a consequence of the different charge redistribution on the phenyl rings in the two adsorption structures considered, the overall spectral shape for the two isomers is slightly different: it is interesting to note that one isomer spectrum shape is a mirror image of the other. In *cis* stilbene, due to rings deformation and lost of aromaticity, a C 1s shifts distribution is more pronounced at higher BE's. The opposite happens in adsorbed *trans* isomer where the pronounced distribution is found at lower BE values.

The only experimental photoelectron spectrum available, at least to our knowledge, was measured for *trans* stilbene on Si(100)2×1 surface at different coverages.[14] The agreement between calculated and experimental spectrum is good, but the computational analysis provides an accurate interpretation of the data.

[1] M. Lastapis, M. Martin, D. Riedel, L. Hellner, G. Comtet, and G. Dujardin, Science **308**, 1000 (2005).

[2] M. Martin, M. Lastapis, D. Riedel, G. Dujardin, M. Mamatkulov, L. Stauffer, and Ph. Sonnet, Phys. Rev. Lett. **97**, 216103 (2006).

[3] J. A. Syage, P. M. Felker, and A. H. Zewail, J. Chem. Phys. **81**, 4706 (1984).

[4] T. S. Zwier, E. Carrasquillo, and D. H. Levy, J. Chem. Phys. **78**, 5493 (1983).

[5] S. Abrash, S. Repinec, and R. M. Hochstrasser, J. Chem. Phys. **93**, 1041 (1990).

[6] D. C. Todd, J. M. Jean, S. J. Rosenthal, A. J. Ruggerio, D. Yang, and G. R. Fleming, J. Chem. Phys. **93**, 8658 (1990).

[7] D. H. Waldeck, Chem. Rev. (Washington, D.C.) **91**, 415 (1991).

[8] A. B. Myers and R. A. Mathies, J. Chem. Phys. **81**, 1552 (1984).

[9] H. Görner and H. J. Kuhn, Adv. Photochem. **19**, 1 (1995).

[10] H. Meier, Angew. Chem. **104**, 1425 (1992).

[11] R. J. Sension, S. T. Repinec, A. Z. Szarka, and R. M. Hochstrasser, J. Chem. Phys. **98**, 6291 (1993).

[12] Y. Doua and R. E. Allen, J. Chem. Phys. **119**, 10658 (2003).

[13] W. Fuß, C. Kosmidis, W. E. Schmid, and S. A. Trushin, Angew. Chem., Int. Ed. **43**, 4178 (2004).

[14] P. M. Schmidt, Th. U. Kampen, J. Hugo Dil, and K. Horn, BESSY Annual Report 224 (2005).

[15] CPMD, Copyright IBM Corp. 1990–2006, Copyright MPI für Festkörperforschung Stuttgart 1997–2001.

[16] A. D. Becke, Phys. Rev. A **38**, 3098 (1988); C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[17] N. Trouiller and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[18] P. C. Chen and Y. C. Chieh, J. Mol. Struct.: THEOCHEM **624**, 191 (2002).

[19] P. Krüger and J. Pollmann, Phys. Rev. Lett. **74**, 1155 (1995).

[20] E. Pehlke and M. Scheffler, Phys. Rev. Lett. **71**, 2338 (1993).

[21] A. Pasquarello, M. S. Hybersten, and R. Car, Phys. Scr. **T66**, 118 (1996).

[22] S. Meloni, A. Palma, A. Kahn, J. Schwartz, and R. Car, J. Am. Chem. Soc. **125**, 7808 (2003).

[23] Y. Travaly, D. Vanderbilt, and X. Gonze, Phys. Rev. B **61**, 7716 (2001).

[24] P. Baumgärtel, R. Lindsay, O. Schaff, T. Giessel, R. Terborg, J. T. Hoeft, M. Polcik, A. M. Bradshaw, M. Carbone, M. N. Piancastelli, R. Zanoni, R. Toomes, and D. P. Woodruff, New J. Phys. **1** 20.1 (1999).