Photoelectron diffraction of C_6H_8/Si(001): A model case for photoemission study of organic molecules adsorbed on silicon surfaces

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The core-level photoemission of 1,4-cyclohexadiene molecules on the quasi-single-domain 2×1-Si(001) surface below the saturation condition was studied. Taking advantage of core-level-shift photoelectron diffraction of the C $1s$ core level, the details of the surface structure were found. The model was essentially constituted by an unbuckled (planar) molecule chemisorbed on the surface, inclined at an angle of about $18°$ with respect to the surface normal, keeping one double bond unsaturated. An accurate analysis of the line shape parameters of the strongly asymmetric C $1s$ core level was mandatory for the structural study. Conversely, the success of the structural determination represented a confirmation of the correct deconvolution procedure. Such a feedback loop was decisive in reducing the indeterminacy affecting the analysis of core-level photoemission in the case of complex molecules adsorbed on surfaces.

I. INTRODUCTION

Chemical-shift core-level photoemission is a powerful method of investigation of surfaces.[1] Core-level binding energies supply information on the adsorbate-induced charge redistribution in the ground state and screening changes, while the small mean free path of the electron guarantees the short-range order sensitivity. The two properties are at the basis of photoelectron diffraction (PD), i.e., the study of angular and/or photon energy anisotropy of photoemission intensity from core levels, which represented so far one of the leading means of investigation of the atomic structure of surfaces.[2] PD can be used to investigate organic molecule adsorption on semiconductor surfaces in terms of bonding and atomic structure. In such systems the formation of strong bonds with the substrate and the anisotropy induced by the surface[3] hamper the thermodynamic evolution of the adsorption. As a result, the system could be driven by the kinetics toward local minima in the energy landscape.[4]

A class of interesting systems to investigate is represented by the unsaturated organic molecules on Si surfaces. Chemisorption of these molecules is efficient with respect to the coordination-saturated organic molecules for applications related to molecular electronics.[5] During adsorption, unsaturated organic molecules react with Si dimers (C—Si di-σ bonding) through a $[2+2]$-type cycloaddition,[6] in which only one C=C double bond per molecule is saturated. As a consequence, molecules adopt an upright configuration. Two opposite C=C double bonds can be saturated as well by two adjacent Si dimers in the so-called dual $[2+2]$ reaction.[7] In the latter case a molecule lying flat is obtained. Also a flat

final configuration, with possible charge transfer from the substrate, is obtained for the reaction known as $[4+2]$-type, or "Diels-Alder," cycloaddition, with the presence of two C—Si σ bonds and a six-member ring of carbon atoms,[6] as in benzene adsorption on Si(001).[8]

In the present work, attention is dedicated to the case of 1,4-cyclohexadiene (CHD) (C_6H_8) on the Si(001)-2×1 quasi-single-domain surface. Several investigations have been performed on this system;[9–18] nevertheless, the information is still incomplete for several aspects like the structure configuration,[16] the effects due to the kinetics,[13,14] and the possible dependence on the coverage. In previous studies valence-band ultraviolet photoelectron spectroscopy (UPS), low-energy electron diffraction (LEED), and scanning tunneling microscopy (STM) were used to investigate this system. UPS was able to detect the features of the unsaturated C=C double bond.[10,11] Experimental evidence of well-ordered 2×1 reconstructed surfaces were obtained by low-energy electron diffraction. Analogously, scanning tunneling microscopy images, at coverages well below the saturation limit at 300 K, showed elliptic protrusions between Si dimers arranged mostly in a 2×2 configuration (the distance between molecules along the dimer row was 7.6 Å). The above observations suggested that the unsaturated C=C double bond was parallel to the Si dimer, while the molecule was inclined to exhibit states protruding right between two adjacent silicon dimers along the dimer row. The picture obtained resembled an almost unperturbed molecule, sticking out of the Si surface with one unsaturated C=C double bond.

On the other hand *ab initio* total energy methods did not

support the picture described above. Calculations showed that unsaturated organic molecules on silicon experience a facile reaction with a complete saturation of the C≡C double bonds by means of two adjacent silicon dimers. Such a flat-lying molecule configuration, resulting from the dual $[2+2]$ reaction, is known as bridge or pedestal configuration.[16] Much less convenient from the energy point of view but more consistent with the experimental observations are the "boat-type" (a C ring bent to form a dihedral angle) and "plane-type" (with an unperturbed C ring) models.[13] These latter configurations have only one out of two C=C bonds saturated by a Si dimer and about the same probability to occur.

As a matter of fact *ab initio* theory is not able to provide a clear-cut picture of the system, while experiments in the low-coverage regime point to a well-defined adsorption state with a high degree of order of the surface. Such a well-defined state is lost at coverages close to saturation where the presence of hindrance effects leads to a much more complicated system and mixing of configurations.[14]

From this overview it emerges that a more quantitative experimental determination of the adsorption geometry and of the chemical bonding is necessary to complete the very rich scenario of this interesting prototypical system.

The core-level photoemission contribution to the understanding of the 1,4-CHD/Si(001) surface could be decisive. Core-level analysis of chemical-shifted components can give insights about the chemical bond population of carbon with other C atoms (with single or double bond) or with Si atoms. Furthermore, the signature of the structural provenance of each C 1s core-level component can be retrieved by a multiple scattering analysis of the PD angular anisotropy. As a result the local geometrical structure around each different photoemitter can be obtained with a precision of the order of 0.02 Å. Last but not least, the two studies, the chemical and the structural one, having origin in the same data, the core-level components should describe a coherent picture with increased accuracy in virtue of the imposed constraint.

The plan of the present work is the following. In Sec. II the description of the apparatus used to collect C 1s core-level-shift (CLS) PD data of 1,4-CHD on Si(001) surface, at single photon energy (330 eV) is reported. In Sec. III A the details of the deconvolution procedure and the analysis of the asymmetric chemical shift components are described. The framework of the multiple scattering calculations used to reproduce the experimental anisotropy is introduced in Sec. III B. Discussion is reported in Sec. IV while conclusions follow in Sec. V.

II. EXPERIMENT

The present experiment was performed in ultrahigh vacuum chambers at the beamline BC-13C at KEK-PF facility in Japan and at the VUV beamline at Elettra, Italy. A well-oriented ($\mp 0.1°$) preoxidized *n*-type Si(001) wafer was used for creating a quasi-single-domain (2×1) surface. After the sample was flashed at 1250 °C and annealed at 1000 °C, we observed 2×1 LEED spots with 80% of majority domains. Afterward the sample was cooled down to room tem-

perature and the surface exposed to the 1,4-CHD gas (purity better than 99%) purified by freeze-pump-thaw cycles. The dosing of the gas was performed through a pulse valve that can precisely control the gas amount. A tube for guiding the gas to the vicinity of the sample surface was attached at the end of the valve to make comparatively high pressure near the sample. The vacuum during the gas dosing was held in the 1×10^{-10} Torr range to minimize the decomposition of the gas by pumps or gauges. The 2×1 LEED spots were observed even after saturation of 1,4-CHD adsorption, suggesting that the dimers on the silicon surface and the domain ratio were preserved.

In order to exclude possible radiation damage effects, caused by the long exposure time necessary to a PD experiment, we measured the line shape of C 1s as a function of the irradiation time at fixed sample position. Even after long-time irradiation (>2 h) the line shape did not show any hint of modification of the molecular structure. Conversely, clear disruption and/or dehydrogenation of the molecule was observed after several minutes heating of the sample above 200 °C.

PD data showed a minor dependence on the coverage from the first stages up to about 0.5 monolayer (ML) (0.5 CHD molecules per Si dimer) corresponding to a dose of 0.05 L as measured by the ion gauge[19] (1 L=10^{-6} Torr s). In order to minimize the occupation of adjacent dimers we performed the present study at 0.4 ML.

III. RESULTS

A. Core-level data analysis

In the analysis of the C 1 s core-level line shape (at the photon energy of 330 eV, commonly used for surface-sensitive studies) two issues should be taken into consideration properly: (1) the presence of inelastic tails on the high-binding-energy (BE) side of the core levels due to vibrations; (2) the unknown number of components effectively contributing to the core-level intensity. Both issues were carefully considered to avoid unjustified additional core-level components in the present fitting procedure.

About the first point, we followed the work of Yamashita *et al.*[20] In the linear coupling approximation they considered an asymmetric component as a linear composition of three Voigt functions (Gaussian line shape convoluted with a Lorentzian function) equally spaced in energy ($\hbar\omega$) and with intensity $I_n = e^{-S} S^n / n!$, for $n=0$, 1, and 2. The S factor was defined as $\delta^2 \mu\omega/2\hbar$, where δ, μ, and ω were, respectively, the normal coordinate of the core excitation, the reduced mass, and the vibrational frequency.[20]

Regarding the second point, the findings of both a partial conservation of the carbon double bonds and the nondissociative adsorption on silicon,[10,11] were clear evidences that the present system was highly symmetric and only slightly perturbed by the chemisorption. As a consequence, a reduced number of independent C atoms and of chemical-shifted core levels were expected. Two cases could be reasonably considered: (1) two C components with one C bonded to Si and one bonded to other C atoms; (2) three C components with two components as in the case (1) and an additional component

TABLE I. Line shape parameters for the deconvolution of the C 1s core level of 1,4-CHD adsorption on a quasi-single-domain 2×1-Si(001) surface. C1, C2, and C3 are the components at the given relative binding energies (RBEs). W_G and W_L are the Gaussian and Lorentzian full width at half maximum broadening. S and $\hbar\omega$ are parameters of the asymmetric line shapes as discussed in the text and in Ref. 20.

Component	RBE (eV)	W_G (eV)	W_L (eV)	S	$\hbar\omega$ (eV)
C1	0.0	0.25	0.05	0.42	0.37
C2	0.42	0.25	0.05	0.48	0.37
C3	−0.27	0.25	0.05	0.40	0.40

in order to distinguish between double-bond carbon and single-bond carbon. For the two cases above a total of four different configurations were examined: (a) three core-level components with asymmetric line shapes; (b) three components with symmetric Voigt functions; (c) two components with asymmetric line shapes; (d) two components with symmetric Voigt functions. A possible mixing of asymmetric and symmetric core-level components was not considered but cannot be excluded in principle.

The choice of the suitable core-level composition followed a "trial and error" procedure in which line shape parameters were optimized on the whole PD data set of about 400 core levels collected at various angles. One parameter set included core-level shift energies and the shape and Gaussian width of Voigt functions. For asymmetric curves, the S and $\hbar\omega$ values of each component were also considered. In order to establish that the introduction of one or more additional parameters in the fitting analysis had statistical relevance we evaluated the confidence levels. The confidence levels, i.e., the probability related to the range of validity of the parameters, were evaluated by means of the normalized χ^2 function defined as the sum of squared differences between experimental and theoretical line shapes divided by the squared experimental errors (less than 2% of the photoemission peak intensity).

From cases (a) to (d) the confidence levels were, respectively, 74%, 68%, 36%, and 1%. Even not including physical considerations about the relative intensities of the components, the sign and size of the core-level shifts and the structural models pointed by the various decomposition procedures, a pure statistical analysis in terms of the χ^2 function clearly indicated the higher probability of case (a), i.e., the presence of three components of the C 1s with strong asymmetric line shape.

The results of the core-level line shape analysis reported in Table I were in agreement with those found in other similar studies[20] and consistent with the C—H stretching mode of 0.385 eV in a wide class of organic molecules. The core-level components had an average Gaussian full width at half maximum of 0.25 eV, and a shape coefficient of 0.12 corresponding to an average Lorentzian width of about 50 meV. To summarize, the characteristics of the components were (C1) the central component at 284.0 eV BE, having 29% integrated intensity and parameters $S=0.42$ and $\hbar\omega=0.37$ eV; (C2) the component with 0.42 eV higher BE
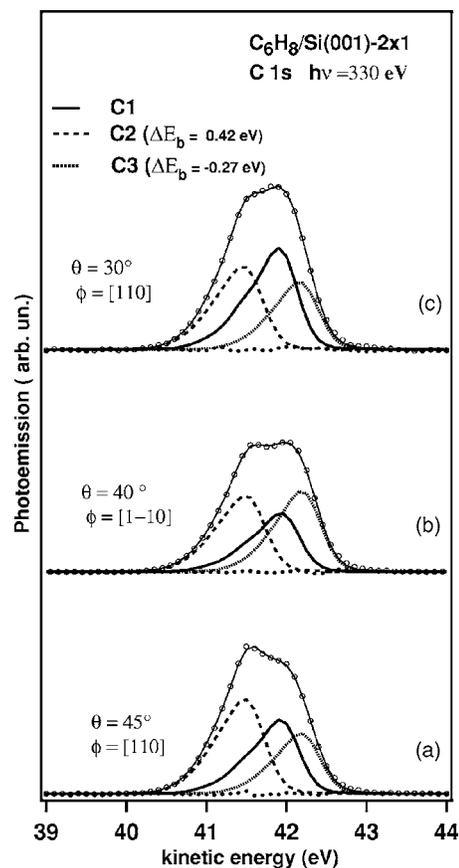

FIG. 1. Adsorption of 0.4 ML 1,4-CHD on the quasi-single domain 2×1-Si(001) surface. Core-level decomposition and diffraction effects in the asymmetric C 1s core-level components along three different electron detection directions (θ and ϕ) are shown from (a) to (c). ϕ=[110] is the majority dimer bond direction.

contributing 34% with $S=0.48$ and $\hbar\omega=0.37$ eV; (C3) the component with 0.27 eV lower BE contributing for the 37% with $S=0.40$ and $\hbar\omega=0.40$ eV. In Figs. 1(a)–1(c), we reported the decomposition of the C 1s core levels into C1, C2, and C3 components along three different emission angles, for the set of optimized parameters summarized in Table I. Relative errors on these parameters were less than 10%. Strong diffraction effects were clearly observed in Fig. 1 as large modulations ($\geqslant 25\%$) of the relative intensity of each core-level component, indicating a high degree of order of the adsorbed surface.

The above core-level analysis showed, within 10% of error, that the three core-level components contributed with the same weight to the C 1s core level. The resulting scheme was consistent with the structural model reported in Fig. 2, showing a molecule with a (110) mirror plane and three independent C atoms labeled C1, C2, and C3, respectively.

B. PD anisotropy and multiple scattering calculations

In the final stage of the core-level fitting, during the determination of the experimental PD anisotropies, all the line
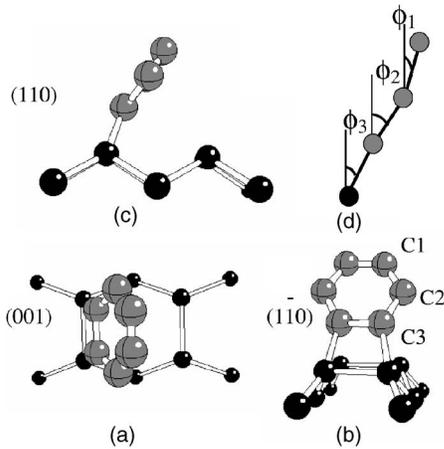
FIG. 2. Plan view along (001) crystal plane (a), (1$\bar{1}$0) plane (b), and (110) plane (c) of the stick and ball sketch of 1,4-CHD on Si(001)-2×1. Silicon is depicted by black spheres and carbon by gray spheres. Hydrogen atoms are not included. Angles with respect to the (1$\bar{1}$0) plane describing the molecule inclination are defined in (d).

shape parameters were kept fixed at the values of Table I. Such PD anisotropies for all the related CLS components were studied to provide the local geometric structure around each atomic emitter by means of the comparison with multiple scattering calculations.

The PD anisotropy was defined normalizing the photoemission intensity for each ϕ scan at the θ polar angle of collection as $[I(\phi)-I_{min}(\phi)]/[I_{max}(\phi)-I_{min}(\phi)]$. A wide angular range from 30° to 80° in polar angle with respect to the normal to the surface and along 120° in the azimuth direction, including both the majority ([1$\bar{1}$0]) and minority ([110]) dimer row directions, was explored. In order to improve the PD anisotropy and consequently reduce the error in the PD structural analysis a quasi-single-domain surface was used for the experiment, with a resulting twofold symmetry of the PD anisotropy. The low kinetic energy of the photoelectron (about 40 eV), obtained by the synchrotron radiation photon energy of 330 eV, was chosen in order to have high electron energy resolution and to maximize the backscattering to probe the surface geometry.

In such a kinetic energy regime a correct use of multiple scattering to accurately calculate the angular photoelectron cross section was needed. In particular, to avoid the slow convergence in the number of scattering paths, a solution of the problem to all orders was chosen by a suitable inversion of the scattering matrix.[21,22] Furthermore, special attention to the details of the potential was dedicated because of the high sensitivity to the valence charge density.[21,22] The package MSPHD,[23] recently used in the chemical-shift analysis of Si(001) native oxide,[24] represented a suitable tool to investigate this system. In the case of the 1,4-CHD/2×1-Si(001) surface a $p(2\times2)$ periodicity with 50% saturated Si symmetric dimers and 50% unsaturated symmetric dimers was used.

The angular-dependent photoemission intensity of the three core-level components C1, C2, and C3 was compared with theoretical calculations. For each inequivalent C photo-
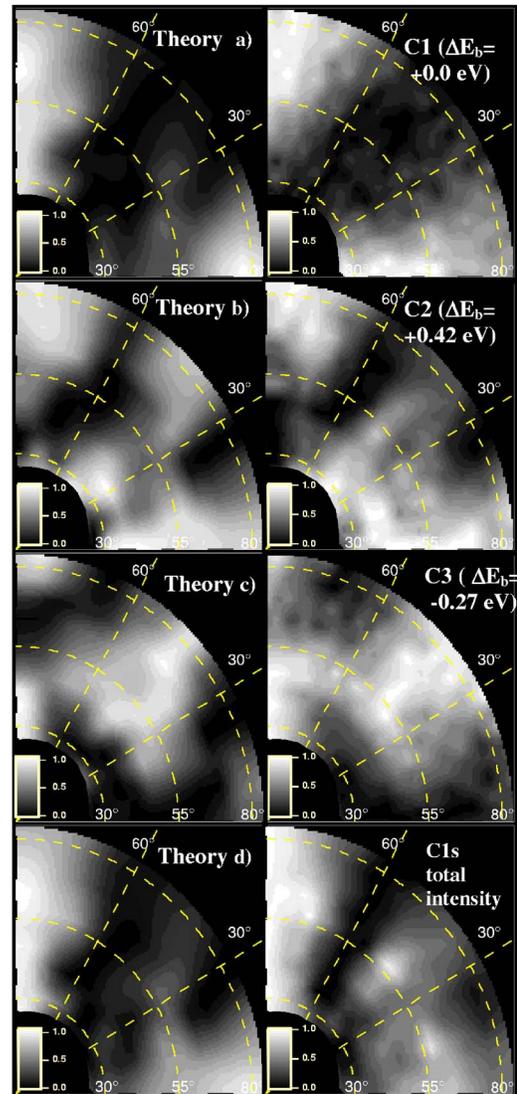

FIG. 3. (Color online) Comparison of theoretical (left panel) vs experimental (right panel) PD anisotropy of the C 1*s* core level of 0.4 ML 1,4-CHD on quasi-single-domain 2×1-Si(001) surface. From top to bottom the three C 1*s* PD patterns corresponding, respectively, to components C1 and C2 at +0.42 eV BE and C3 at −0.27 eV BE are reported together with the total C 1*s* core-level pattern. *x* axis is the majority dimer bond direction.

absorber a centered spherical cluster was constructed with a radius of 9 Å (twice the estimated mean free path) and a complex potential to mimic inelastic extrinsic losses of the photoelectrons was used.[22]

In Figs. 3(a)–3(d) we report the comparison between the experimental PD anisotropies (right panel) and the theoretical ones (left panel) that obtained the best agreement for the three components C1, C2, and C3 and the total C 1*s* peak. During the best fitting comparison between theoretical and experimental PD anisotropy the structural parameters of the surface were retrieved using an automatic simulated annealing "simplex" routine for the minimization of the *R* factor.[25] In this way the optimized parameters were less affected by local minima problems. The model for which the best comparison with the experiment was found is model (c) of

TABLE II. Structure parameters obtained in total energy calculations for the pedestal saturated surface (a) (Ref. 16) and the upright buckled (b) (Ref. 13) adsorption of 1,4-CHD on Si(001) -2×1. In (c) are reported the parameters optimized in the present experiment. Distances and angles (ϕ) are defined according to Fig. 2.

Atomic model	(a) Pedestal	(b) Upright	(c) This work
d_{SiC} (Å)	1.97	1.96	1.95(0.15)
d_{C3} (Å)	1.58	1.58	1.62(0.12)
d_{C2-C3} (Å)	1.55	1.54	1.64(0.06)
d_{C2-C1} (Å)	1.55	1.51	1.44(0.10)
d_{C1} (Å)	1.58	1.35	1.48(0.15)
ϕ_3 (deg)	14.9	9.7	18(6)
ϕ_2 (deg)	67.6	−39.7	37(4)
ϕ_1 (deg)	111.3	11.4	32(10)

Table II, closely resembling the atomic sketch of Fig. 2. Parameters in Table II, like the three angles ϕ_1, ϕ_2, and ϕ_3 formed by the molecular plane with the $(1\bar{1}0)$ plane, were defined in Fig. 2 as well. In Table II models (a) and (b) report, for reference, two adsorption geometries obtained by total energy calculations for the pedestal and upright configurations.[16]

IV. DISCUSSION

Assignment of core-level shifts of hydrocarbons is not straightforward due to complicated competition and correlation of initial and final state effects. In the present study we started the analysis taking advantage of the intrinsic higher-energy resolution of gas-phase core-level photoemission from the 1,4-CHD molecules. For the purposes of the present study we referred to the work of Oltedal and co-workers[26] about the C 1s core-level spectrum of the gas phase 1,4-CHD. In that work the spectrum was quite evidently composed by a cyclohexanelike (C$_6$H$_{12}$) component due to single-bond C—C carbon atoms, and one C component, characteristics of the benzene photoelectron C 1s core level, with lower BE (0.48 eV) due to four C═C double-bond carbon atoms.

The study is more puzzling in the case of adsorption on surfaces, where atomic attributions of core levels are not univocally determined; for instance in literature it is possible to find a C═C unsaturated double bond with higher BE than the C—C single bond.[27] More established is that the Si—C component is observed at lower BE's because Si acts as an electron donor to carbon. The insights provided by the CLS PD technique are expected to complement *ab initio* calculations of core-level shifts, often entangled by the localization of the core hole and by the relaxation effects. In fact, response from the comparison of PD anisotropy with multiple scattering model is extremely clear-cut in assigning the structural origin of core-level components.

In this study the analysis allowed the assignment of the components C1, C2, and C3, respectively, to a C═C double
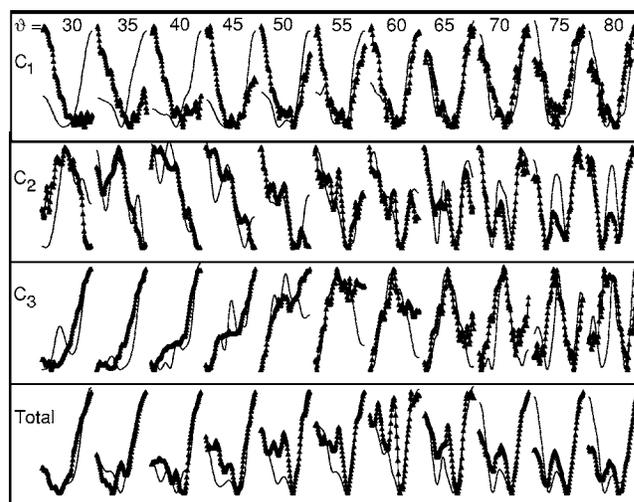

FIG. 4. Azimuthal cuts of theoretical (continuous line) vs experimental (triangles) PD anisotropy of the C 1s core level of 0.4 ML 1,4-CHD on quasi-single-domain 2×1-Si(001) surface. From top to bottom the three C 1s PD patterns corresponding, respectively, to C1 and C2 at +0.42 eV BE and C3 at −0.27 eV BE are reported together with the total diffraction intensity. From left to right each cut at θ values in the range 30°–80° reports the normalized anisotropy for the values ϕ in the range 0°–90°, with $\phi = 0°$ the majority Si dimer bond direction.

bond, C—C single bond, and Si—C bond, respectively. Any attempt to assign the atomic origin of the three components in a way different from the one outlined above led to higher values of the R factor, and to unrealistic models of surface structures. Structural results obtained here were in agreement with a planar configuration with the $\pi_{C═C}$ bond oriented parallel to the Si dimer and located between two Si dimers along a dimer row (see top view of Fig. 2). The molecular plane was inclined by about 18° with respect to the normal to the surface. The structure obtained was fully compatible with the STM measurements at coverages below the surface saturation limit.[10]

The overall agreement of the theoretical and experimental gray scale patterns in Fig. 3 is evident. A closer inspection of the patterns might put in evidence some disagreement between theory and experiment in some particular angular directions, for instance around $\theta = 35°$ for the C1 component and $\theta = 55°$ for the C3 component. In order to better understand the level of success of the present investigation we reported in Fig. 4 the azimuthal cuts through the data at the different polar angles of the experiment. We found such a comparison particularly gratifying if we consider the number of constraints put on the data [about 44 theoretical diffraction curves reproduced with the same atomic model (c) of Table II]. The disagreement affected mainly the absolute value of the anisotropy but not its general character, like peak positions and the signs of the convexity of the curves. Furthermore, it is worth underlining that azimuthal cuts in Figs. 3 and 4 were all normalized to unity.

Also the accuracy was very satisfying: errors reported in Table II were evaluated for each parameter by means of a
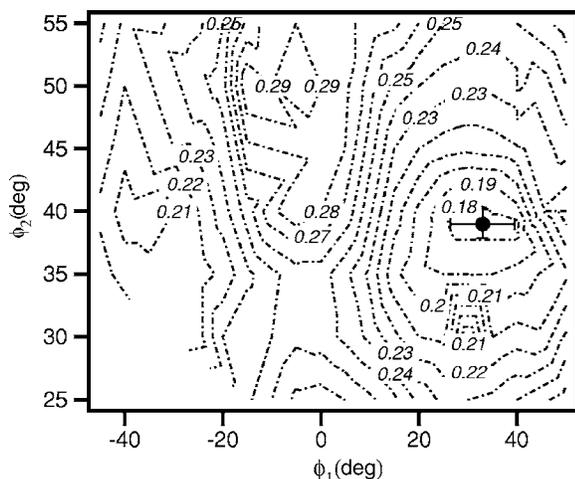
FIG. 5. *R*-factor values in the (ϕ_1, ϕ_2) parameter space at the ϕ_3 value of model (c) of Table II. The errors affecting the two parameters are indicated by bars according to the criterion of the 10% *R*-factor variation from the best fit.

10% criterion in the *R*-factor variation from the minimum value. For the best fit, the value of 0.16 of the *R* factor was obtained. In the plot of Fig. 5 is shown the degree of sensitivity of the technique to the two ϕ_1 and ϕ_2 structural parameters at the ϕ_3 value of model (c) of Table II. A larger indeterminacy in the value of ϕ_1 with respect to ϕ_2 was probably due to the larger wagging mode of the molecule C atoms more distant from the surface.

A preliminary analysis of the present data[17] was performed using two symmetric components (a small third one at higher BE was filtered out and considered hydrocarbon

contamination). This approach gave rise to a less satisfactory agreement with the PD experiment. In fact the theory was able to fit only the total intensity (because of a minor constraint) leading to multiple shallow minima in the parameter space. But, more important, to show the largest lack of agreement, was the one-by-one comparison between the experimental and theoretical PD anisotropy singled out for each C 1*s* component. Such a mismatch on the fine details of the CLS PD anisotropy represented the real driving force for the present approach to peak deconvolution in terms of three asymmetric C 1*s* components.

V. CONCLUSION

In conclusion, the problem of 1,4-CHD on a quasi-single-domain Si(001)-2×1 surface was successfully studied by a CLS PD experiment. The adsorption geometry was a planar molecule inclined at an angle of 18° with respect to the normal to the silicon surface but different from the buckled geometry suggested by the total energy calculations. Such a discrepancy could be due to underlying surface kinetics effects. The CLS PD analysis proved to be effective if based self-consistently on the determination of the core-level shifts, asymmetric line shape parameters, and molecular structure using an extended data set. The present methodology will open the way toward more specific investigations of related systems formed by organic molecules on Si interfaces, where complexity hampers a suitable application of core-level photoemission, for instance, in the study of selective modifications of functionalized surfaces and in the investigation of kinetics effects in adsorption.

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