Electronic structure of biphenyl on Si(100)

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We report the study of both occupied and unoccupied electronic states of biphenyl adsorbed on Si(100) by using synchrotron radiation ultraviolet photoemission spectroscopy, x-ray photoemission spectroscopy, and near-edge x-ray absorption fine structure spectroscopy. The results are compared with calculations of the occupied densities of states. Evidence is given of two main effects: (i) a down shift in energy of the second highest occupied molecular orbital of the strongly chemisorbed configuration at room temperature compared to the weakly chemisorbed configuration at low temperatures and (ii) an energy splitting of some of the occupied and unoccupied states due to the different interactions of the two phenyl rings of the molecule. The electronic structure of biphenyl on Si(100) appears to be an appropriate test for state of the art experimental and theoretical methods.

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I. INTRODUCTION

Organic molecules adsorbed on silicon surfaces have been of growing interest in the past few years[1–4] for applications in molecular electronics and optoelectronics.

Biphenyl molecules adsorbed on the Si(100) surface under certain conditions act as bistable molecules since their movement can be activated through electronic excitation using the tip of a scanning tunneling microscope (STM).[5] The electronic structure of both the occupied and unoccupied electronic states is needed to properly understand the adsorption configurations of biphenyl on Si(100) as well as the electronic excitation mechanisms for activating its observed bistable movement. Over the past few years, the electronic structure of benzene adsorbed on Si(100) has been studied extensively by using a number of synchrotron radiation based methods, namely, ultraviolet photoemission spectroscopy (UPS),[6] x-ray photoemission spectroscopy (XPS),[7,8] and near-edge x-ray absorption fine structure spectroscopy (NEXAFS).[9–12] The biphenyl molecule is made of two phenyl rings connected by a C-C bond. The torsional angle and the electronic interaction between the phenyl rings depend on the local environment.[13] Studying the adsorption of biphenyl on Si(100) turns out to be a challenge for spectroscopic methods to elucidate the electronic structure and adsorption configurations of organic molecules on semiconductor surfaces. Despite the fact that biphenyl on Si(100) is a simple system, it is much more complicated than benzene on Si(100) (Ref. 14) due to the flexibility of the molecule. Biphenyl adsorbs on Si(100) in two configurations: "weakly chemisorbed" or "strongly chemisorbed" depending on whether the deposition temperature is below or above 300 K, respectively. These configurations will be described in detail in Sec. III. In both adsorption configurations, each of the two phenyl rings of the molecule interacts differently with the substrate surface.[14]

We report here a combined experimental and theoretical study of the electronic structure of biphenyl on Si(100) in the weakly and strongly chemisorbed configurations. Synchrotron radiation has been used for UPS, XPS, and NEXAFS experiments. UPS results have been compared with density of state calculations.

II. EXPERIMENT

Experiments have been carried out at the BESSY II synchrotron radiation facility. The undulator beamline UE56/2-PGM1 has been used as a linearly polarized photon source (horizontal polarization) of variable energy in the 60–1000 eV range. The photon energy resolutions were 25 meV at 65 eV for valence band photoemission, 74 meV at 130 eV for Si $2p$ core level photoemission, and 250 meV at 330 eV for the C $1s$ core level photoemission and for the C $1s$ NEXAFS spectra. The photon energy has been calibrated using neon and nitrogen gas cells. This results in an uncertainty of ±0.12 eV at photon energies around the C $1s$ excitation threshold energy.

The experimental setup has been previously described.[15] The ultrahigh vacuum chamber (base pressure of 2×10^{-10} Torr) was equipped with a hemispherical electron energy analyzer SPECS Phoibos 100. Photoelectrons and Auger electrons were collected in the horizontal plane at an angle of 54.7° from the photon beam with energy resolutions of 150 and 600 meV, respectively.

Clean Si(100) surfaces from n-doped (As, $\rho=0.004-6\ \Omega\,\mathrm{cm}$) silicon substrates were prepared as described elsewhere.[16] The quality of the Si(100)-2×1 reconstruction was checked through the observation of the surface components in the Si $2p$ core level photoemission spectrum (photon energy of 130 eV)[17] and of the surface states in the

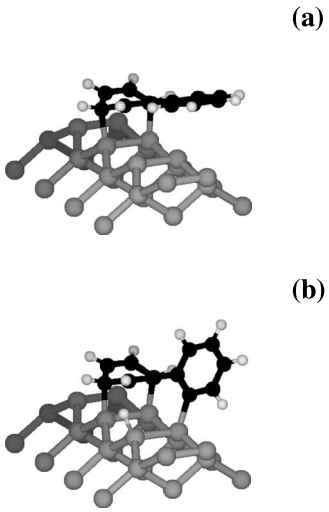

FIG. 1. Atomic structure of biphenyl on a Si(100) surface in (a) the weakly chemisorbed configuration and (b) the strongly chemisorbed configuration. The gray, black, and white balls correspond to silicon, carbon, and hydrogen atoms, respectively.

valence band photoemission spectrum at grazing incidence (photon energy of 65 eV).[18] The silicon sample was attached to the end of a cryostat and could be cooled down to 80 K by liquid helium.

The biphenyl powder (Aldrich, purity of 99.5%) was carefully outgassed through several freeze-thaw cycles. The vapor pressure of biphenyl at room temperature is sufficient to deposit biphenyl through a dosing leak valve. The biphenyl vapor was then directed through a small nozzle right in front of the sample. The amount of biphenyl deposited on the silicon surface was deduced from the intensity of the photoemission bands associated with the silicon surface states (binding energy around 0.8 eV) by assuming that its relative decrease is equal to the molecular coverage (in percent of a full monolayer). Although this is only a rough estimation of the molecular coverage, it provides a good relative calibration from one experiment to another. Relative calibrations of the molecular coverage were also performed from the relative intensity of the C 1*s* core level bands.

III. ADSORPTION CONFIGURATIONS OF BIPHENYL ON Si(100)

Although biphenyl has been much less studied than benzene on Si(100), its adsorption configurations on Si(100) have been recently investigated by STM experiments[5,14,16,19,20] and *ab initio* calculations.[21] When adsorbed on Si(100) at temperatures below or above 300 K, biphenyl is in the so-called weakly chemisorbed configuration[14] [Fig. 1(a)] or strongly chemisorbed configuration [Fig. 1(b)],[5,20] respectively. From STM imaging,[14] the weakly chemisorbed configuration (see Fig. 1(a)) has been assigned to one phenyl ring strongly interacting with the Si(100) surface (fixed phenyl ring) through two Si-C bonds in the butterfly configuration[14,20] and the second phenyl ring having no chemical bond with the surface (mobile phenyl ring). The strongly chemisorbed configuration has been assigned[20] to a dissociative adsorption configuration where the two phenyl rings are chemically bound to the surface [see Fig. 1(b)]. One phenyl ring (fixed phenyl ring) is dissociatively bound through a single Si-C bond with the dissociated hydrogen atom bound to the neighbor silicon atom (Si-H bond). The second phenyl ring (mobile phenyl ring) is chemically bound to the Si(100) surface in the butterfly configuration through two Si-C bonds. The exact temperature transition from the weakly to the strongly chemisorbed configuration is not known with precision. Such a transition temperature is very difficult to measure accurately as it requires varying continuously the sample temperature while recording a signal proportional to the population of either the weakly chemisorbed or the strongly chemisorbed configuration. This has been done in the case of the transition between the physisorbed and the chemisorbed adsorption configuration of benzene on Si(111),[22,23] where the two adsorption configurations could be easily distinguished either by photoemission[22] or by photodesorption.[23] This method would not work in the case of biphenyl since the two weak and strong adsorption configurations cannot be distinguished easily by photoemission and photodesorption. Furthermore, in the case of benzene,[22] the transition temperature could not be determined with a precision better than about 30–50 K due to the difficulty in measuring the temperature of a silicon sample. In the following, we will consider that the dominant adsorption configuration is the weakly chemisorbed configuration at 80 K and the strongly chemisorbed configuration at 300 K. The dissociative strongly chemisorbed configuration has been deduced from the comparison between STM imaging and density of states calculations.[21] This strongly chemisorbed configuration has been shown to be a bistable configuration. Under electronic excitation with the STM tip, the molecule is moved from one position to the other by rotation around the Si-C bond of the fixed phenyl ring[5] [Fig. 1(b)].

IV. RESULTS AND DISCUSSION

Low temperature (80 K) and room temperature (300 K) valence band photoemission spectra of the Si(100)-2×1 surface have been recorded before and after biphenyl adsorption. At low temperature, the clean Si(100) surface is first cooled down to 80 K and then exposed to biphenyl. The photoemission spectra have been recorded with a photon energy of 65 eV both at normal emission and with the sample rotated by 44.7°. In the normal emission geometry, the angle of incidence of the synchrotron light with respect to the surface normal is 54.7° corresponding to the magic angle.[24] In the other geometry, the angle of incidence is 80° corresponding to grazing incidence. The photoemission spectrum of biphenyl in condensed multilayers on the silicon surface at 80 K has also been recorded to follow the evolution of the biphenyl bands from the condensed phase to the chemisorbed one. In Figs. 2(a) and 2(b), the valence band spectra of the Si(100) surface before and after biphenyl adsorption for grazing incidence at 300 K are shown in the 0–13 eV range. The band associated with the surface states of the silicon dimers of the clean surface [see Fig. 2(a)] has a binding energy of 0.9 eV relative to the Fermi level.[18] After a 6 L

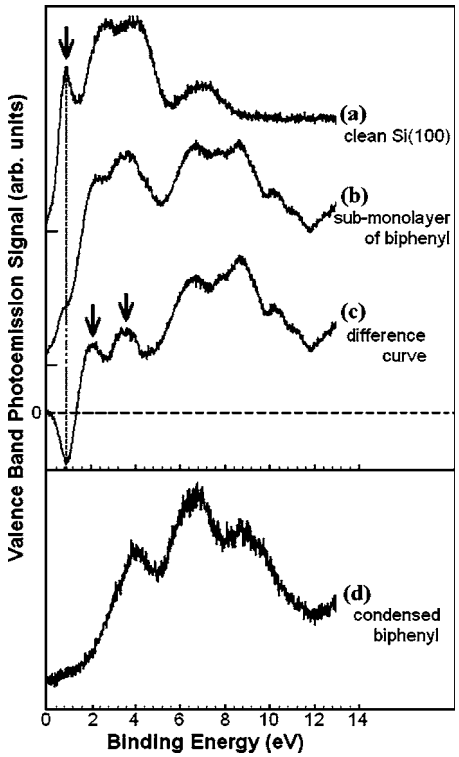

FIG. 2. Valence band photoemission spectra of the Si(100)-2 $\times 1$ surface at room temperature and grazing incidence (10°) (a) before and (b) after submonolayer biphenyl exposure. The biphenyl exposure for curve (b) is 6 L. (c) is obtained by subtracting (a) from (b). (d) is the valence band photoemission spectrum of condensed biphenyl. For all spectra, the photon energy is 65 eV. The arrows indicate the silicon surface state band in (a) and the first and second HOMO bands of adsorbed biphenyl in (c). Binding energies are relative to the Fermi level.

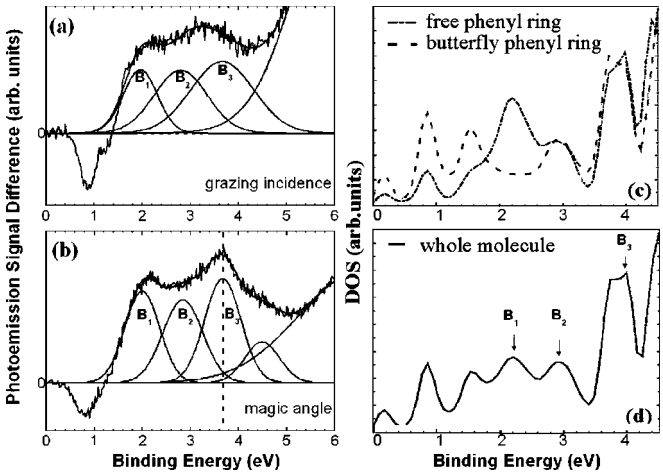

FIG. 3. Left part: Details of the valence band photoemission spectra at low temperature (80 K) after subtraction of the corresponding spectra of the clean Si(100) surface. The biphenyl exposure is 2.7 L and the photon energy is 65 eV: (a) grazing incidence (10°) and (b) magic angle incidence (54°). The spectra have been decomposed into three bands (B_1, B_2, and B_3). The extra band in (b) is due to some oxygen pollution. Right part: Calculated occupied densities of states of biphenyl on Si(100). (c) Density of states of the weakly chemisorbed biphenyl projected on the free phenyl ring (dashed-dotted line) and the butterfly phenyl ring (dashed line). (d) Density of states of the weakly chemisorbed biphenyl integrated over the whole molecule. Binding energies are relative to the Fermi level.

(1 L=10^{-6} Torr s) biphenyl adsorption [Fig. 2(b)], the intensity of this band decreases, but it is still visible, which shows that the biphenyl coverage is less than one monolayer. Features, superimposed on the bulk structure of silicon, which characterize the adsorbed species appear. These features are best distinguished after subtracting the silicon bulk signal normalized to the same photon beam intensity. In the resulting curve [Fig. 2(c)], the band attributed to the attenuated surface states of silicon appears as a negative feature. The photoemission spectrum of biphenyl condensed multilayers at 80 K is shown in Fig. 2(d). Comparison of Figs. 2(c) and 2(d) clearly shows that bands appear at low binding energy (around 2 eV) when biphenyl is chemisorbed on Si(100). In the left part of Figs. 3 and 4, the photoemission spectra of biphenyl adsorbed at low temperature (biphenyl exposure of 2.7 L) and room temperature (biphenyl exposure of 6 L), respectively, are shown after subtraction of the corresponding photoemission spectra of the clean Si(100) surface. In each case, the photoemission spectra for grazing incidence (E vector nearly perpendicular to the surface) and magic angle incidence are compared. All photoemission spectra have been deconvoluted into the minimum number of bands whose intensity, energy, and width were adjusted to obtain the best fit with the experimental curve. Only in the case of room temperature data (Fig. 4) it was possible to decompose the experimental curves into two main bands (B_1 and B_3). At low temperature (Fig. 3), it was necessary to introduce a third band (B_2).

As discussed in Sec. III, the low temperature spectra correspond to weakly chemisorbed biphenyl molecules [see Fig. 1(a)]. At room temperature, we expect more than 80% of biphenyl molecules to be in the strongly chemisorbed configuration as deduced from STM observation.[5] To understand the photoemission spectra, we have calculated the density of states of the weakly and strongly chemisorbed biphenyl molecules (see the right part of Figs. 3 and 4, respectively). Calculations have been performed using the Vienna *Ab initio* simulation package[25–27] (VASP) which allows periodic density-functional theory calculations with pseudopotentials and a plane wave basis set. The approach implemented in the program is based on a generalized gradient approximation with the Perdew-Wang 91 functional.[28,29] The interactions between the ions and the electrons are described by ultrasoft pseudopotentials introduced by Vanderbilt[30] and provided by Kresse and Hafner.[31] The k-point sampling was generated following the Monkhorst-Pack procedure[32] with $6\times6\times1$ mesh. The cutoff energy for the plane wave basis set is 350 eV. Further information on these calculations and the bonding of the molecule with the surface can be found in our previous study.[21] Here, we have calculated, for both adsorption configurations, the density of states localized on each phenyl ring (right part of Figs. 3 and 4). Indeed, each phenyl ring of the weakly and strongly chemisorbed configurations interacts differently with the Si(100) surface. Therefore, den-

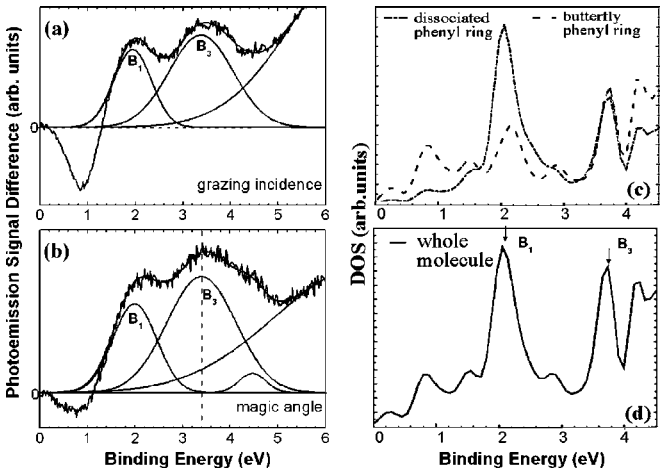

FIG. 4. Left part: Details of the valence band photoemission spectra at room temperature (300 K) after subtraction of the corresponding spectra of the clean Si(100) surface. The biphenyl exposure is 6 L [as for Fig. 2(b)] and the photon energy is 65 eV: (a) grazing incidence (10°) and (b) magic angle incidence (54.7°). Each spectrum has been decomposed into two bands (B_1 and B_3). The extra band in (b) is due to some oxygen pollution. Right part: Calculated occupied densities of states of biphenyl on Si(100). (c) Density of states of the strongly chemisorbed biphenyl projected on the butterfly phenyl ring (dashed line) and the dissociated phenyl ring (dashed-dotted line). (d) Density of states of the strongly chemisorbed biphenyl integrated over the whole molecule. Binding energies are relative to the Fermi level.

sities of states can be considered localized around each phenyl ring as has been demonstrated by scanning tunneling spectroscopy in the case of the strongly chemisorbed biphenyl.[5] As for the adsorption of benzene on Si(100),[6] each phenyl ring of biphenyl is associated with two bands in the 2.0–2.8 and 3.5–4.2 eV binding energy ranges, respectively. According to the analysis of Ref. 6 the 2.0–2.8 eV band is derived from the lowest unoccupied molecular orbital ($1e_{2u}$) of gas phase benzene interacting with the Si(100) surface, whereas the 3.5–4.2 eV band is derived from the highest occupied molecular orbital ($1e_{1g}$) of gas phase benzene interacting with the Si(100) surface.

The comparison between the experimental photoemission spectra (left part of Figs. 3 and 4) and the calculated densities of states (right part of Figs. 3 and 4) exhibits two main features. Firstly, at low temperature and grazing incidence angle [Fig. 3(a)], in the 2.0–2.8 eV binding energy range, the photoemission spectrum can be decomposed into two bands (B_1 and B_2) at about 2.0 and 2.8 eV, respectively, whereas only one band at 2.0 eV is observed at room temperature and grazing incidence angle [Fig. 4(a)]. This low temperature splitting of the 2.0–2.8 eV band into B_1 and B_2 bands is also observed in the calculated densities of states of the weakly chemisorbed biphenyl due to the very different binding configurations of the free and butterfly phenyl rings. We note that this low temperature splitting is also observed at magic angle incidence [Fig. 3(b)]. The B_1 and B_2 bands are assigned to the π highest occupied molecular orbital (HOMO) bands of the two phenyl rings. The splitting is not observed at room temperature, most probably because, as observed in Ref. 5 the B_1 and B_2 band energies are closer to each other (2.1 and 2.5 eV from Ref. 5) in the strongly chemisorbed configuration than in the weakly chemisorbed configuration (2.0 and 2.8 eV from this work). Secondly, at low temperature and magic angle incidence angle [Fig. 3(b)], the B_3 band at 3.7 eV is higher in energy than the corresponding band at room temperature (3.4 eV). This energy shift is also observed in the calculated densities of states [Figs. 3(d) and 4(d)] and is due to stronger interactions of the phenyl rings with the surface at room temperature as compared to low temperature.

Figure 5 shows the normalized NEXAFS spectra around the C(1*s*) ionization energy in the 284–290 eV photon energy range. The C 1*s* Auger electron yield has been recorded at both grazing incident angle and magic angle for biphenyl condensed multilayers and for chemisorbed biphenyl at low temperature (80 K) and room temperature (300 K). Chemisorbed biphenyl exposures are similar to those of the valence band photoemission spectra.

Interestingly, these NEXAFS spectra of biphenyl on Si(100) can be compared to the well studied NEXAFS spectra of benzene on Si(100).[9,11,12] NEXAFS spectra of biphenyl on Si(100) have been previously reported,[16] although with a larger photon energy bandwidth than in the present work.

The NEXAFS spectrum of the biphenyl condensed multilayers [Fig. 5(a)] is very similar to that of benzene condensed multilayers.[9] The two peaks at 285.0 and 288.8 eV correspond to an excitation of a C(1*s*) electron into the unoccupied degenerate π_1^* and the nondegenerate π_2^* orbitals of the aromatic rings, respectively. The peak at 287.0 eV corresponds to an excitation of a C(1*s*) electron into the $\sigma_{(C\text{-}H)}^*$ orbital. The similarity between the biphenyl and benzene NEXAFS spectra has been previously observed in the gas phase[10,12,15] and ascribed to the localization of the unoccupied molecular orbitals after C(1*s*) excitation.

The NEXAFS spectra of the low temperature [Figs. 5(b) and 5(c)] and room temperature [Figs. 5(d) and 5(e)] biphenyl submonolayers show a much less intense (or even absent) π_2^* resonance. As in the case of benzene, the absence of the π_2^* resonance is indicative of a chemisorbed interaction with the surface.[9,16]

An interesting feature of the NEXAFS spectra in Fig. 5 is the occurrence of two separate π_1^* resonances (285.0 and 285.9 eV) in the room temperature spectra, whereas a single π_1^* resonance (285.0 eV) is observed at low temperature. This room temperature separation of the π_1^* resonances is not expected to originate from different C(1*s*) ionization energies. Indeed the C(1*s*) ionization energies of a number of gas phase aromatic hydrocarbon molecules[10] have been observed to broaden the NEXAFS peaks by much less than 0.9 eV. Also, high resolution core level photoelectron spectroscopy of benzene adsorbed on Si(100) (Ref. 7) has evidenced C(1*s*) core level shifts of 0.3 eV at most for different adsorption configurations of benzene. This is further supported by our recorded high resolution C(1*s*) core level photoemission spectra which show no difference between low temperature and room temperature (see Fig. 6). Therefore, we assign the two π_1^* resonances separated by 0.9 eV in the NEXAFS spectra at room temperature to the lowest unoccupied mo-

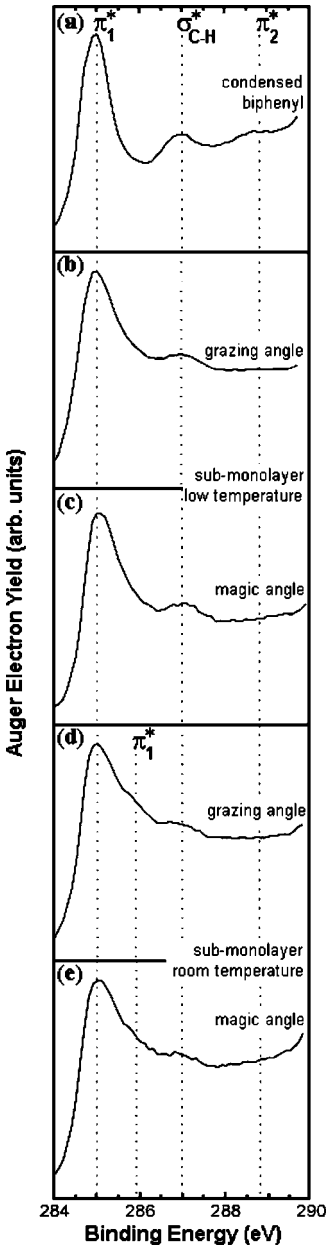

FIG. 5. NEXAFS spectra of biphenyl: (a) condensed on Si(100) and [(b)–(e)] adsorbed on Si(100). (b) Grazing incidence (10°) and low temperature (80 K). (c) Magic angle (54.7°) incidence and low temperature (80 K). (d) Grazing incidence (10°) and room temperature. (e) Magic angle incidence (54.7°) and room temperature. The uncertainty on the photon energy is ±0.12 eV, while the photon energy resolution is 0.25 eV. The NEXAFS spectra have been corrected for the transmission of the beamline by dividing the NEXAFS signal by the signal of a golden mesh set at the input of the experimental chamber.

lecular orbitals of the two phenyl rings of the biphenyl molecule in the strongly chemisorbed configuration. This corroborates the splitting of the highest occupied molecular orbitals of these two phenyl rings (0.4 eV) as observed by local scanning tunneling spectroscopy.[5] However, this splitting cannot be seen in the valence band photoemission spectra [see Figs. 4(a) and 4(b)] due to an insufficient separation of the corresponding broad bands.

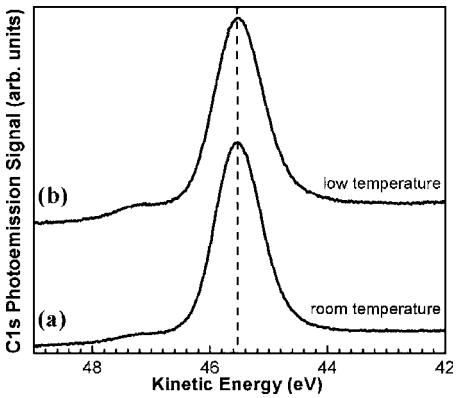

FIG. 6. C 1*s* photoemission spectra after biphenyl adsorbed on Si(100)-2×1 at (a) 80 K and (b) 300 K. The photon energy is 330 eV.

V. CONCLUSION

We have demonstrated the feasibility and the interest of studying occupied and unoccupied valence bands of biphenyl adsorbed on the Si(100) surface at low temperature and room temperature. This turns out to be much more challenging than the previous corresponding studies of benzene on Si(100) due to the presence of two phenyl rings interacting differently with the surface and the different adsorption configurations at low temperature and room temperature.

The comparison between the experimental valence band photoemission spectra and the calculated densities of states has allowed us to understand the main observed features. In the UPS spectrum at low temperature and grazing incidence angle, the first HOMO band is split into two components due to the different interactions with the surface of the two phenyl rings of the weakly chemisorbed biphenyl. Furthermore, a shift in energy of the second HOMO band from 3.7 to 3.4 eV has been observed when comparing biphenyl interaction with the Si(100) surface at low temperature (weakly chemisorbed configuration) and room temperature (strongly chemisorbed configuration). In the case of NEXAFS, the energy splitting of the lowest unoccupied molecular orbital has been observed only at room temperature and assigned again to the different interactions with the surface of the two phenyl rings of biphenyl. One puzzling problem is that the energy splitting of the bands associated with the two phenyl rings has been observed at room temperature (strongly chemisorbed configuration) only in the unoccupied states (NEXAFS) and not in the occupied states (UPS), whereas an energy splitting has been clearly observed in the occupied states by scanning tunneling spectroscopy.[5] Further UPS experiments involving angle resolved photoemission spectroscopy are needed to explore possible band dispersion effects. Another further development of this study would be to precisely measure the temperature for transition from the weakly chemisorbed configuration to the strongly chemisorbed one in order to be able to perform experiments on

molecules adsorbed in only one of the configurations.

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