Correlation of electronic and local structure of 4-hydroxy-thiophenol on NaCl(100) and Ag(100)

C. Tegenkamp, and H. Pfnür

Articles you may be interested in

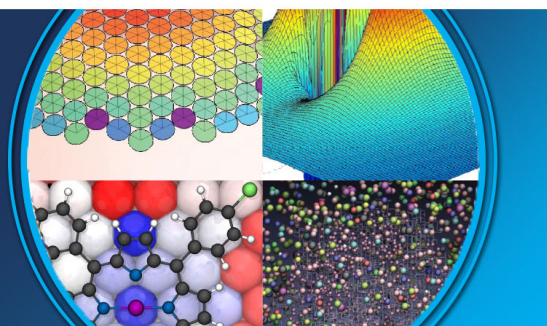Anomalous molecular orbital variation upon adsorption on a wide band gap insulator
The Journal of Chemical Physics **132**, 214706 (2010); 10.1063/1.3431755

Roughness and stability of silicon on insulator surfaces
Applied Physics Letters **84**, 350 (2004); 10.1063/1.1641181

Correlation of electronic and local structure of 4-hydroxy-thiophenol on NaCl(100) and Ag(100)

C. Tegenkamp and H. Pfnür[a)]
Institut für Festkörperphysik, Universität Hannover, Appelstraße 2, D-30167 Hannover, Germany

The electronic structure of 4-hydroxy-thiophenol (HTP) adsorbed on poly-Ag(100) and on NaCl(100) was investigated with photoelectron (UPS) and electron energy loss spectroscopy (EELS), supplemented by DFT/B3LYP and restricted CIS-calculations of isolated molecules in order to identify molecular emissions and characteristic losses. Whereas on NaCl(100) the HTP molecules interact mainly via van der Waals interaction, on Ag(100) a strong level shift of 0.6 eV to lower binding energies of the thiol emission was found, indicating the formation of an Ag–S bond. As concluded from intensity ratios of various emissions both in UPS and in EELS, the HTP molecule on NaCl(100) adsorbs essentially in a planar geometry, whereas on Ag(100) the angle between the HTP molecular plane and the surface is around 70°, in agreement with expectations from orbital symmetry and overlap. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1562193]

I. INTRODUCTION

The properties of small organic molecules at surfaces or between macroscopic electric conductors have attracted much attention recently,[1–3] because their high flexibility allows tailoring of electronic states to specific needs. The potential for molecular electronics has been recognized almost 30 years ago.[4] Nowadays, using specifically synthesized organic molecules, also single electron transistors have been realized.[5] Because the $\pi - \pi^*$-splitting can be in the range of several eV, organic molecules are *per se* a quantum-well structure, which allows us in principle to study Coulomb-blockade and Kondo-resonance effects even at comparably high temperatures.[5,6]

As it is also obvious, the electronic properties of molecules and molecular layers are strongly determined by the bond formation to their environment, electrodes, etc. Therefore, the precise knowledge of the interaction of organic molecules with metal and insulator surfaces is of high importance, because this interaction influences significantly the energetic position of the π-system and thus the resistances of the tunneling barriers.

Whereas thicker layers of organic chain systems and polymers have found already applications in electronics and optoelectronics, such as organic light emitting devices, field effect tranistors and solar cells,[7,8] there are still only a few investigations of monolayers. Within a monolayer, molecule-molecule interactions can lead to laterally ordered organic films, as shown for a variety of planar π-stacking organic molecules like 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) adsorbed on various substrates [e.g., Ag(110), Ag(111), Ni(111)].[8] In these films both the morphology and the electronic structure are determined by weak van der Waals interactions.

The choice to investigate the adsorption of HTP more closely is motivated by the fact that it is one of the simplest organic molecules that contains an OH and an SH side group opposite to each other. From the literature it is well known, that thiol (SH) as a functional group of alkane chains or of benzene rings interacts strongly with metallic surfaces, e.g., Ag or Au films by forming strong Ag–S or Au–S bonds, respectively.[10] Generally, this influences sensitively the orientation of the organic molecules. Also lateral order in such systems can be found at high densities within the first layer, as shown for decanethiol $[CH_3(CH_2)_9SH]$ on Ag(111).[9] In the recent past, our group concentrated on adsorption properties of pure and OH-substituted benzoic-acids on insulator surfaces. In this context we used epitaxially grown NaCl(100) and KCl(100) surfaces.[11,12]

This motivated us to perform spectroscopic investigations of 4-hydroxy-thiophenol (HTP) on both Ag(100) and NaCl(100) to determine directly differences and similarities in the bonding mechanisms on both substrates. Here we combine the experimental studies with density functional (DFT) and restricted configuration interaction singles (RCIS) calculations of isolated molecules. These turned out to be crucial for the identification and interpretation of the experimental spectra obtained.

II. EXPERIMENT

The experiments have been carried out in an UHV-chamber, equipped with LEED, UPS, EELS and XPS to characterize both the morphology, the cleanliness and the electronic structure of the surface and of the adsorbate. For a detailed description of the experimental setup and the *in situ* cleaning procedure of the Ge(100) substrate see Ref. 12.

8 ML thick NaCl(100) films have been grown on Ge(100) surfaces at substrate temperatures below 200 K followed by annealing to 500 K for at least 2 min. Thereafter, a brilliant (1×1)-structure of NaCl(100) could be observed with LEED.

---

a)Electronic mail: pfnuer@fkp.uni-hannover.de

Ag films have also been grown on Ge(100) at low temperatures followed by subsequent annealing to 600 K. Although there is a lattice misfit of 27% between Ag(100) and Ge(100), a streaky (1×1) structure with the Ag lattice constant and four-fold symmetry was observed with LEED after the deposition of approximately 30 ML of silver, indicating the formation of a polycrystalline, but preferentially (100)-oriented Ag film [poly-Ag(100)]. The sample temperature was measured by a Ni/NiCr-thermocouple attached to the sample holder in close thermal contact with the sample. The sample itself was heated either by direct current or by radiation from a filament right behind the substrate.

The exposure of the sample to HTP was done by a standard gas inlet system, which was evacuated several times for purification. Because the vapor pressure of HTP is very low at room temperature, the reservoir for HTP was heated externally up to approximately 50 °C. At this temperature the dosing time for 1 Langmuir (L) was about 200 seconds. A rough calibration of thickness was done by determing the damping of the Ge2p-emission with XPS, assuming that the electron mean free path of the Ge2p-photoelectrons ($E_{\text{kin}} = 270$ eV) corresponds to a thickness of 3 ML HTP.

In order to identify the experimentally observed peaks in photoemission, we carried out DFT-calculations of a single HTP molecule using the GAUSSIAN 98 package.[14] As already shown previously,[12] a comparison of such calculations with experimental photoemission data of adsorbed molecules turned out to be helpful. Generally, we expect this method to work sufficiently well for larger adsorbed molecules that remain intact during adsorption and interact moderately with the substrate. This means that the electronic structure of the adsorbed molecule has to be mainly unchanged compared with the free molecule. This assumption was found to be valid, e.g., for salicylic acid on NaCl(100).[12] Prior to a final DFT/B3LYP single-point calculation of the molecule using the high-dimensional $6\text{-}311+\text{G}(2d,p)$ basis set, the geometry was optimized by a restricted Hartree–Fock calculation [RHF/6-31G(d)]. Transition energies have been worked out using restricted CIS (RCIS) at the $6\text{-}31+\text{G}(d)$ basis level. Since no reference data for pure HTP was available, we compared in a first step the geometry of the HTP molecule obtained by our theoretical calculation with the ZIDREJ structure of $[\text{C}_{18}\text{H}_{10}\text{Fe}_2\text{O}_8\text{S}_2, 2(\text{C}_6\text{H}_6\text{O}_1\text{S}_1)]$ from the Cambridge Crystallographic Data Center (CCDC).[15] The largest deviation of about 0.9% was observed for the O–C bond. All other distances could be reproduced to within a limit better than 0.2%.

III. RESULTS AND DISCUSSION

A. Photoemission

Photoemission data of adsorbed HTP already at first sight show significant differences when saturation coverages are adsorbed at a surface temperature of 180 K. Figure 1 shows the spectra obtained with HeI radiation of HTP on NaCl(100) grown epitaxially on Ge(100) and on the polycrystalline Ag film on the same substrate. As obvious from this figure, part of these differences must be due to differences in substrate emissions of NaCl and Ag, respectively.
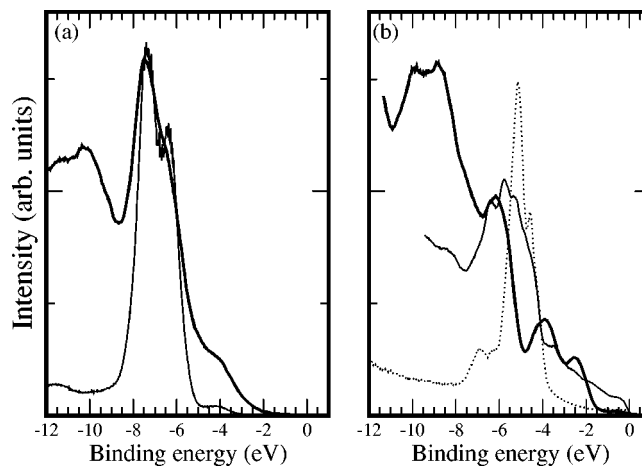
FIG. 1. UP-HeI-spectra of monolayers of HTP on (a) NaCl(100) and (b) poly-Ag(100) (fat lines). The substrate temperature was 180 K in both cases. For reference, the spectra of the uncovered substrates are also shown (thin lines), as well as the spectrum of an Ag(100) single crystal surface (dotted). The energy scale is given with respect to the Fermi-level of Ag. A 10 point averaging method was used to smooth the data. Pass energy 10 eV.

This means that the HTP films are very thin. In fact, as we will show below, they essentially correspond to saturation of the first monolayers, respectively. Despite the apparent differences of the spectra, we demonstrate that the adsorption leaves the molecule intact on both surfaces.

In a first step, we concentrate on the adsorption of HTP on the NaCl(100) surface. Since these NaCl films are almost free of defects,[13] they are chemically inert, and we can safely assume that only molecular adsorption takes place.

As seen from Fig. 1(a), the bare NaCl(100) surface shows the characteristic double peak structure of its valence band representing the high symmetry points X'_4 and X'_5, respectively. After an exposure of 9 L HTP at a substrate temperature of 180 K, the UP-spectrum shows additional intensity on both sides of the NaCl valence band structure [see the fat curve in Fig. 1(a)]. Since no further changes in the spectrum are observed at higher exposures, the curve corresponds to the saturation coverage at this surface temperature. Although the intensity at the position of the bare NaCl(100) surface remains unchanged, the characteristic spot splitting has disappeared. This behavior is a typical indication of weak interaction on NaCl(100) by adsorption, but it is also seen when small concentrations of point defects like color centers are introduced.[16]

The coverage of HTP on NaCl(100) was estimated to be around 1 monolayer (ML) from the damping of the Na1s-emission in XPS. This is qualitatively in agreement with the observed intensity between 8 and 6 eV [see Fig. 1(a)], which is still dominated by the NaCl(100) substrate, taking into account the small escape depth of photoelectrons in this energy range. We will come back to this point below, when presenting our EELS results.

Since the molecular interaction with the substrate is expected to be weak, it seems to be allowed to take a difference spectra even in UPS in order to identify the molecular contribution to the UP spectra. Because of the broad structures induced by the molecule this alone turned out not be a viable
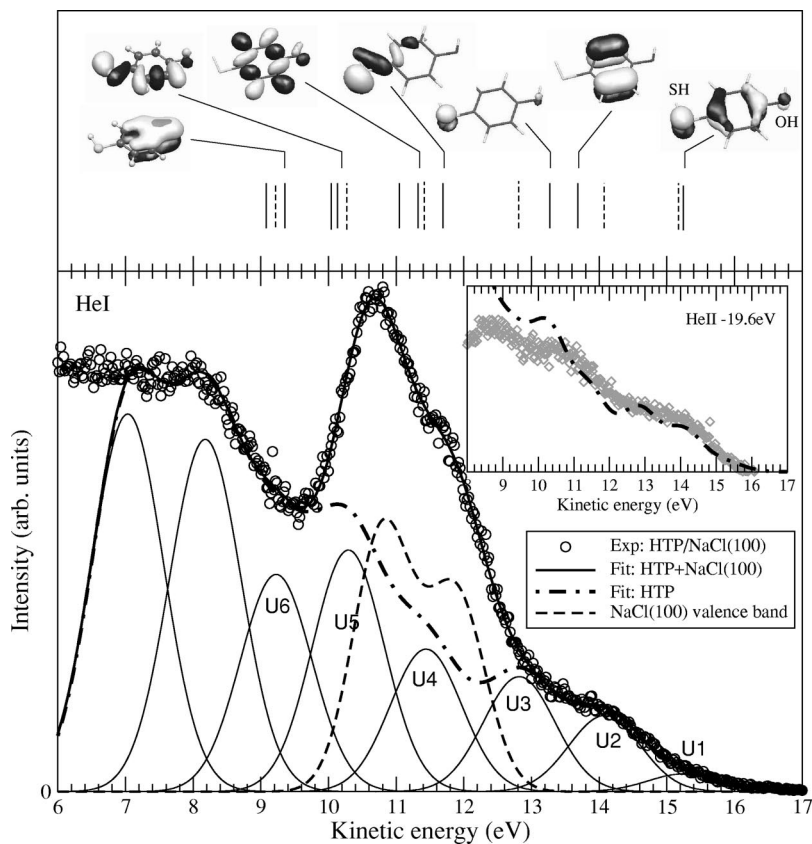
FIG. 2. Top: Energetic positions of occupied molecular states of the HTP molecule (vertical lines) together with some of the corresponding molecular occupation probabilities. The HOMO has been adjusted energetically to the photoemission peak with the highest kinetic energy. The dashed lines represent the experimentally determined peak positions. Bottom: UP-spectrum of 1 ML HTP on NaCl(100) (circles). The fat solid line represents a fit taking into account both the underlying NaCl(100) substrate (dashed curve) and six Gaussians (solid curves, U1–U6) representing emissions from different groups of molecular orbitals. Adding only U1 to U6, the dashed–dotted curve results. For further details see the text. Inset: Section of the UP spectrum taken with HeII radiation, which originates almost completely from the HTP molecule.

procedure to identify the molecular contributions, but a more detailed knowledge of individual contributions from different molecular orbitals was needed.

Therefore, we performed DFT-calculations of single HTP-molecules, because to the best of our knowledge no reference data about the electronic structure of HPT was available. The energetic positions for the ten uppermost occupied states are shown by vertical lines in the top part of Fig. 2 together with plots of envelopes of the molecular orbital occupation probabilities. The energy scale has been adjusted so that the HOMO coincides with the experimentally observed photoemission feature with the highest kinetic energy. When comparing these results with the experimental photoemission curve, it is obvious that most of these molecular orbitals cannot be resolved, and only a fit, based on these calculations, can be attempted. For this purpose, groups of calculated peaks separated by less than 0.5 eV have been combined into one peak in the fit.

With these restrictions, the HTP/NaCl(100) spectrum could be fitted perfectly (see Fig. 2) assuming six Gaussian functions (denoted by U1 to U6), representing the HTP molecular orbitals, taking also into account a damped intensity signal of the NaCl(100) valence band structure, as shown in the lower part of Fig. 2. The dashed-dotted curve shows the sum of only the molecular contributions. In this fit, the FWHMs of the Gaussians were set equal. The two Gaussians at 7 and 8.2 eV kinetic energy, respectively, are mainly used to stabilize the fit, but have not been analyzed in detail.

A test of consistency of the fit has been carried out by comparing it with an experimental spectrum obtained with HeII radiation. This is shown in the inset of Fig. 2 after

shifting it by 19.6 eV in order to align it energetically with the results obtained with HeI. The shorter elastic mean free path of the electrons emitted by HeII results in a much higher surface sensitivity so that the contribution of the HTP layer is dominant. It corresponds now reasonably well to the spectrum calculated from the fit of the molecular orbitals alone (dashed–dotted line).

The good agreement between experiment and calculations yields a consistent picture of molecular adsorption, as expected. It should be pointed out that the width of the peaks is not limited by experiment.(The instrumental resolution is at least one order of magnitude better than the fitted peak widths). Apart from intrinsic lifetime effects, it is partly caused by multiplets of closely spaced emissions, as shown by our DFT-calculations. The FWHMs might also be affected by structural disorder within the HTP layer. With LEED only diffusely scattered intensity was observed besides the (1×1)-pattern from the NaCl(100) surface. This indicates that no long range order between HTP molecules exists. Only for the U2 and U3 emissions some deviations (by 0.5 eV) between experimental positions and those calculated have been found. This may indicate that additional substrate-adsorbate interactions beyond pure van der Waals interaction play some role.

Summarizing this first part, the HTP molecule on NaCl(100) remains intact and the specific orbital energies are mainly given by intramolecular forces. This is in agreement with previous investigations of benzoic-acids on insulating surfaces like NaCl(100) and KCl(100).[11,12] We found that the interaction of these organic molecules is also weak, i.e., mainly a van der Waals interaction takes place.

J. Chem. Phys., Vol. 118, No. 16, 22 April 2003

4-hydroxy-thiophenol on NaCl(100) and on Ag(100)   7581

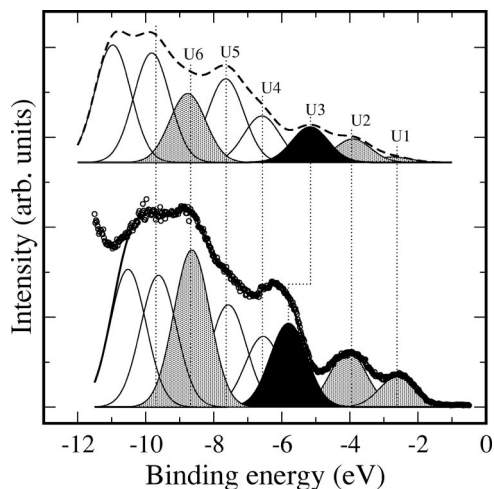FIG. 3. A comparison of UP-spectra of HTP without contributions from the NaCl valence band (top) with HTP on poly-Ag(100) (bottom). Both data sets were fitted by the same model (see the text). Apart from the energetic shift of U3 towards lower binding energies also the integral intensities of U1, U2, and U6 are higher on poly-Ag(100) than on NaCl(100).

FIG. 4. Dependence of the photoelectron intensity of σ- and π-like orbitals, $g_\sigma(\vartheta)$ and $g_\pi(\vartheta)$, respectively, on the polar angle for random azimuthal orientation and for the geometry used in our experiments. f is explained in the text.

The photoemission spectrum of HTP adsorbed on poly-Ag(100) is shown in Fig. 1(b). This spectrum also represents the saturation coverage of HTP/poly-Ag(100) adsorbed at 180 K. Compared to the insulating surface, the substrate induced features seem to be more strongly modified compared with the insulating NaCl surface. For example, a significant minimum in intensity around -5 eV BE evolves, although this is the energetic position, where the silver d-band sets in [compare with the dashed curve in Fig. 1(b)]. This indicates either a higher density of HTP molecules on poly-Ag(100) or other possible modifications of the molecules and its adsorption geometry. As it turns out from the EELS experiments described below, these molecules are still located in only one monolayer.

Despite the differences seen in Fig. 1 for HTP adsorption on NaCl and on Ag, the photoemission spectrum of HTP on poly-Ag(100) can be described by the same model of molecular adsorption as on NaCl, i.e., with the same number of peaks at almost the same peak positions in the fits on both surfaces. This is demonstrated in Fig. 3, where we compare spectra of HTP on poly-Ag(100) (bottom) and HTP/NaCl(100) (top). For the latter case, the contributions of the substrate valence bands have been subtracted. There are, however, a few important differences. The emission denoted by U3 shifts significantly by 0.6 eV to lower BE. The shifts of the other emissions are less than 0.2 eV. Furthermore, the ratios of integral intensities of group U1, U2, U3, U6 relative to the group U4, U5 are reversed on the two substrates.

From our DFT-calculations, it is known that the peak denoted by U3 is related to the molecular orbital located at the sulphur (see Fig. 2). This state is shifted to a position at the top of the d-band of Ag(100), i.e., it is now in resonance with the Ag d-band. This shift is a clear indication that the HTP molecule is bound with its thiol-group to the Ag-substrate. On NaCl(100) nothing similiar is found.

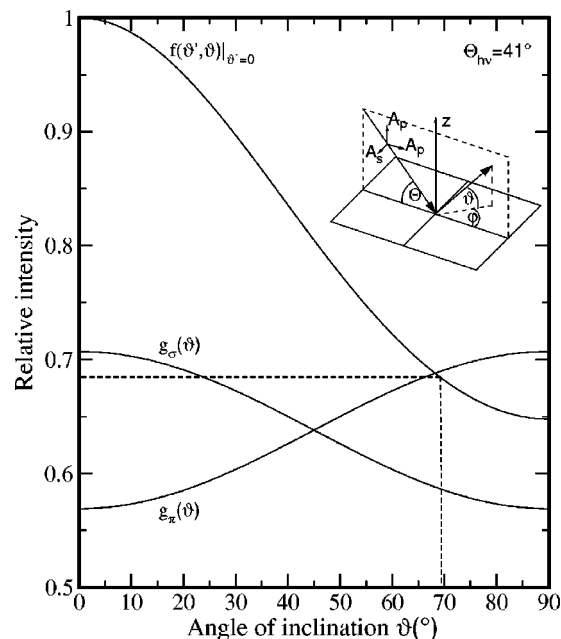The alignment of molecular emissions from the HOMOs with those of the upper edge of the valence band on insula-

tors for HTP, but also for benzoic-acids,[12] indicates that additonal contributions beyond pure van der Waals interactions must be present. From symmetry considerations we concluded in Ref. 12 that the mixing of $p_{x,y}$-type orbitals from the carboxylic OH-group with the valence band of NaCl(100) and of KCl(100) is most likely responsible for this energetic pinning. A similiar argumentation can be applied also to HTP/NaCl(100), because the U4-emission from HTP contains the emission from the $p_{x,y}$-type orbital of the phenolic OH-group [see Fig. 1(a) and Fig. 2], which is energetically in resonance with the valence band of NaCl(100).

Our DFT-calculations (see Fig. 2) also allow us to correlate relative changes in the photoelectron intensity with the determined orbital symmetries of the emissions U1-U6. The peaks denoted by U1, U2, U3 and U6 show π-like orbital symmetry, whereas U4 and U5 consists of orbitals located in the plane of the HTP molecule. The relative change in intensity between adsorption on NaCl and on Ag can be easily explained as an effect of different local orientation of the molecule with respect to the surface normal. Although for the UPS experiments unpolarized radiation was used, a dependency of the integral intensity is still expected. This is demonstrated in Fig. 4, where we calculated the expected relative photoemission intensity for π-like and σ-like orbitals assuming unpolarized HeI radiation. A schematic of the geometry of the UPS experiment is shown in the inset of Fig. 4. The angle of incidence of the photons in our case was 41° with respect to the surface. Photoelectrons have been detected in the direction normal to the surface.

The functions $g_\sigma(\vartheta)$ and $g_\pi(\vartheta)$ represent the expected change of intensity for σ- (parallel to molecular plane) and π-like orbitals (perpendicular to the molecular plane) for the given geometry. That is, $g_\sigma(\vartheta)$ is used for U4, U5, and
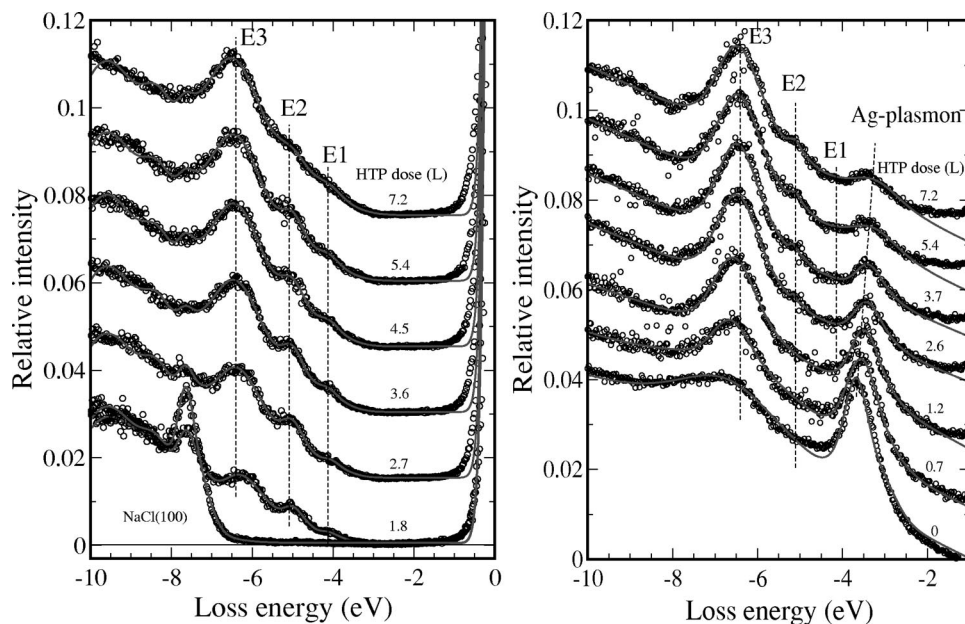
FIG. 5. EEL–Spectra of HTP/NaCl(100) (left) and HTP/poly-Ag(100) (right) as a function of HTP exposure. The final curve in each graph represents the saturation coverage of HTP. On both substrates new loss-features denoted by E1 (4.1 eV), E2 (5.1 eV) and E3 (6.4 eV) appear. Electron energy 52 eV (30° off-specular). The substrate temperature was 180 K. The spectra are shifted against each other for better visibility.

$g_\pi(\vartheta)$ for U1, U2, U3, and U6 (see Fig. 2). $g_\sigma(\vartheta)$ and $g_\pi(\vartheta)$ were obtained by purely geometrical considerations, whereby the expected intensity was averaged with respect to the azimuthal orientation, φ, of the molecule, as motivated by the LEED results.

In a simple picture, the total photoemission intensity I from a molecular orbital is determined by the coverage, the power of the radiation source, the cross-section for excitation and the above mentioned geometry of the molecule. However, the former dependencies are divided out by forming ratios of σ- and π-orbitals on both substrates at fixed geometries of photoemission, e.g., $(U6/U4)_{NaCl}/(U6/U4)_{Ag}$. This ratio, $f(\vartheta', \vartheta)$, is also shown also in Fig. 4 for the case that $\vartheta' = 0$, i.e., the HTP molecule is assumed to adsorb on NaCl(100) with its molecular plane parallel to the surface. With this assumption, and using the experimentally determined ratios, the angle of adsorption for HTP/poly-Ag(100) is 70° with respect to the surface plane (the dashed lines in Fig. 4). Considering the rather large uncertainty (estimated to be around ±15°), because of the indirect determination of integral intensities by fitting, this result would also be compatible with an HTP molecule standing upright on the Ag(100) surface.

These results show that also for HTP on poly-Ag(100) the electronic states of the HTP molecule are mainly determined by intramolecular forces, i.e., there is little distortion in the adsorbed molecule compared with the molecule in the gas phase. We found evidence for the formation of an Ag–S bond. This bond formation seems to be the reason for the difference in adsorption geometry, which can be easily rationalized. From the energetic position of the U3 emission relative to the Ag valence bands we conclude that the π orbital associated with the thiol group mainly interacts with the silver d-band. As seen from Fig. 3, overlap of this orbital with orbitals located in the surface plane can only be maximized for a nonplanar orientation of the HTP molecule. A smaller contribution to binding of HTP might also be due to the

sp-hybrid states because these states are also in resonace with the U1 state of the molecule.

B. EELS results

In addition to UP spectra, also electron energy loss spectra (EELS) have been recorded for both HTP/NaCl(100) and HTP/poly-Ag(100). This is shown in Fig. 5 as a function of HTP exposure. The intensities are normalized with respect to the elastic peak. Starting with the insulating surface (left graph), the lowermost spectrum shows the characteristic loss features of clean NaCl(100), i.e., a band gap of approximately 8 eV and an excitonic state at 7.6 eV. Already at the lowest exposure of HTP three new losses can be observed within the original band gap of NaCl(100) at loss energies of 4.1, 5.1 and 6.4 eV. (An identification of these peaks will be given below, when presenting our RCIS-results.) These peaks shift very little as a function of increasing coverage. The saturation coverage is reached after dosing approximately 4 L of HTP. Taking into account a damped signal contribution from the clean NaCl(100) surface, the new loss spectrum can be fitted perfectly using three Gaussians representing the adsorbate induced loss peaks. Interestingly, the full width at half maximum (FWHM) for the E3-loss was found to be approximately two times larger than for E1 and E2 (1.8 eV for E3 and 0.8 eV for E2), an indication that this peak may consist of a nonresolvable multiplet of characteristic losses.

The corresponding loss spectra of HTP on poly-Ag(100) are shown in the right graph of Fig. 5 as a function of increasing HTP coverage. A fit for the metallic system was more difficult compared to NaCl(100), because of large background contributions that increased monotonously towards higher loss energies. But again, taking into account the surface plasmon loss of Ag around 4 eV loss energy, there are no indications from the fits that more than three adsorbate induced loss peaks are present in these spectra. The fit
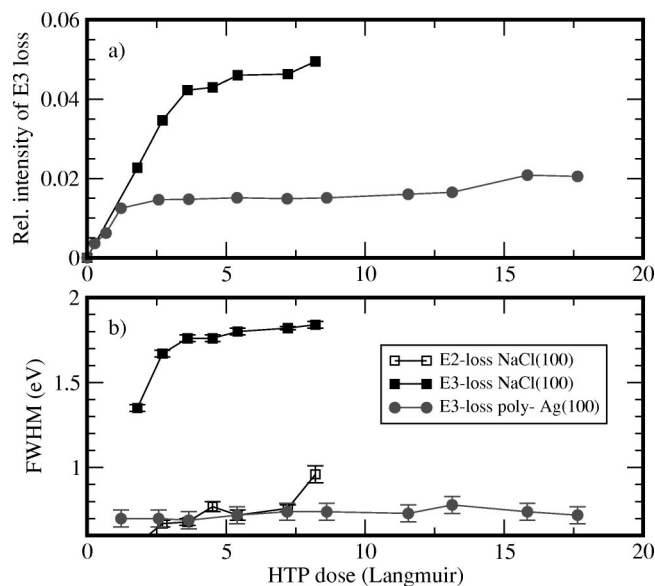
FIG. 6. Results of the relative intensity of the E3-loss (a) and of FWHM (b) for HTP/NaCl(100) (squares) and HTP/poly-Ag(100) (circles) obtained from fitting the spectra of Fig. 5.

FIG. 7. A comparison between theoretical results obtained by CIS-calculations and experiment for HTP/NaCl(100).

gives the same loss energies for E1, E2, and E3 as on NaCl(100). On Ag the peak position of E1 is quite uncertain, because its position is almost in resonance with the Ag interface plasmon. Here the FWHM for the E3-peak is around 0.7 eV and thus significantly smaller than for HTP/NaCl(100).

In the following we will discuss the E3-loss in more detail, since the E3-peak is the most dominant feature within the loss spectra. In addition to the FWHM of E3 also the integral intensity has been evaluated in detail. The relative intensity of the E3-peak of HTP on both substrates as a function of HTP exposure is shown in Fig. 6(a). After a linear increase, the intensity starts to saturate at 3.8 L for HTP/NaCl(100). In contrast, on poly-Ag(100) the saturation of intensity is reached already around 2 L. Because of the high background on Ag, the actual loss intensities at saturation, normalized to the elastic peaks, respectively, differ by a factor of 3 on both surfaces.

This difference, however, cannot be due to a smaller density of HTP on Ag. The dose necessary for saturation on NaCl agrees well with that for a close-packed layer of HTP molecules with its molecular plane oriented parallel to the surface, assuming an average sticking coefficient around 0.5 at the measured rate of impingement. Neglecting any relaxation effects of HTP and assuming molecules adsorbed in planar orientation, each HTP molecule occupies about 1.5 unit meshes of NaCl(100) (area per unit mesh 15.8 $Å^2$). The saturation concentration on Ag with the molecules oriented out-of-plane cannot be smaller than this value, and must be compensated for by a higher sticking coefficient close to 1. This means that absolute saturation concentrations on both surfaces are roughly equal, in agreement with the results deduced from the damping of XPS intensities mentioned above. Because of the smaller area per unit cell on Ag(100) (8.4 $Å^2$) the relative concentration at saturation is close to 1/3 on this surface.

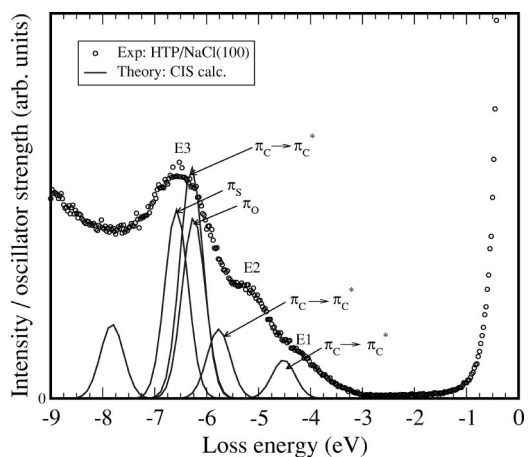The difference in integral intensity of the E3-loss on

both surfaces must be a consequence of different molecular orientations of HTP on both surfaces, in agreement with the conclusion from our UPS-results. For an estimate of the angle of inclination we use the simplest EELS-model of an incoming electron and its space charge in the bulk generating an electric field $\vec{E}$, which interacts with surface dipoles $\vec{d}$ $(I \sim \Theta |\vec{E} \cdot \vec{d}|^2)$.[17] Assuming the planar adsorption of HTP on NaCl(100), the HTP molecule poly-Ag(100) must be inclined at a polar angle of 60° with respect to the surface for this ratio of intensities. This is in good agreement with the angle derived from UPS. Here we implicitly assume that the dipole moment of the E3-loss $\vec{d}$ is perpendicular to the molecular plane of the HTP-molecule, i.e., it is a π-like orbital. Indeed, this is in good agreement with the results from RCIS-calculations, which will be presented now.

Mainly for the purpose of peak identification in EELS we carried out RCIS-calculations, again for isolated HTP molecules. The theoretical results together with the experimental data for HTP/NaCl(100) are shown in Fig. 7. In order to obtain agreement between calculated and observed losses we corrected the calculated loss energies by shifting them by 1.3 eV towards lower energies. This is allowed since the RCIS as a zeroth-order method is known to overestimate excitation energies.[18] In any case, the agreement is sufficient to allow the identification of the various loss contributions, since also the relative intensity ratios between E1, E2 and E3 are reproduced rather well. This comparison shows that the E1 and E2 transitions originate from electronic excitations of the benzene ring, with U1 and U2 as initial states, respectively. The RCIS-result also shows that the E3 peak (initial state also U1) indeed consists of (at least) three peaks with excitations located in different parts of the molecule, namely at the benzene ring, the hydroxyl- and the thiol-group, respectively. This is consistent with our experimental oberservation that the FWHM of the E3 peak is significantly broader than E2 and E1 of HTP/NaCl(100). It agrees also with our conclusion that the interaction between HTP and the NaCl(100) surface is weak. The fact that the FWHM of the E3-loss of HTP/poly-Ag(100) is smaller compared to the adsorption experiment on NaCl(100), reflects the chemical re-

action of sulphur states with the substrate, an effect not included in these simple calculations. Since no other loss peaks appear on poly-Ag(100), the separate peaks of the E3 loss seen in the calculations can only shift slightly so that they merge into a narrower peak in the experiment on poly-Ag(100). This again indicates that the molecule stays intact also on the silver surface, but is chemisorbed with an inclined orientation of the molecular axis, in contrast to the adsorption on the insulating NaCl(100) surface.

IV. SUMMARY AND CONCLUSIONS

In this paper we have presented results of the electronic structure of HTP on NaCl(100) and on poly-Ag(100) obtained with UPS and EELS. As seen by these experiments, the line widths of characteristic emissions of the adsorbed molecule, even in the case of only weak interaction studied here, is so large that a unique separation of peaks was not possible. Only with the help of DFT- and RCIS-calculations of the isolated molecule we have been able to identify the emissions characteristic of the HTP molecule and to separate them from emissions characteristic of the substrates. This demonstrates the importance of a combination of experiment and calculations for the interpretation of the electronic properties of larger adsorbed molecules. Because of the relatively weak interactions of HTP on both surfaces studied here, and because of the low saturation densities in the first monolayers, respectively, the information from calculations of single isolated molecules turned out to be sufficient. It is obvious that for stronger interactions with the substrate these must also be taken into account.

HTP on NaCl(100) forms a typical van der Waals bond to the surface, as indicated by the essentially unchanged energetic positions compared with the DFT-calculations of a single HTP molecule. The interaction with the surface is maximized by a planar adsorption geometry. The well defined energetic alignment between HOMOs of adsorbed small molecules of organic acids and the valence bands of insulator material found for several systems seems to be due to some additional interaction of the phenolic OH-groups with the valence bands of the insulating films, since they are energetically in resonance. If the molecule is not oriented exactly planar to the surface, it is this group that will be closest to the surface.

In contrast, the electronic interaction of the thiol-group with mainly the silver $4d$-band seems to be responsible for HTP/poly-Ag(100), indicating the formation of an Ag–S bond. It causes a nonplanar adsorption geometry. Both UPS and EELS have shown that HTP on Ag(100) is bound in a close to upright orientation.

Although lateral ordering of HTP was not found, the molecules grow in a well defined orientation with respect to the surface normal. In that sense they still form a self-assembled monolayer. Thus such a molecular layer of HTP still might act as a buffer layer in, e.g., metal–insolator hetereoepitaxy.

[1] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, and H. v. Löhneysen, Phys. Rev. Lett. **88**, 176804 (2002).

[2] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, Science **278**, 252 (1997).

[3] S. K. Nielsen, M. Brandbyge, K. Hansen, K. Stokbro, J. M. van Ruitenbeek, and F. Besenbacher, Phys. Rev. Lett. **89**, 066804 (2002).

[4] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).

[5] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rin Sethna, H. D. Abruna, P. McEuen, and D. C. Ralph, Nature (London) **417**, 722 (2002).

[6] W. Liang, M. P. Shores, M. Blockrath, J. R. Long, and H. Park, Nature (London) **417**, 725 (2002).

[7] S. R. Forrest, Chem. Rev. **97**, 1793 (1997).

[8] E. Umbach, K. Glöckler, and M. Sokolowski, Surf. Sci. **402−404**, 20 (1998).

[9] F. Schreiber, A. Eberhardt, T. Y. B. Leung, P. Schwartz, S. M. Wetterer, D. J. Lavrich, L. Berman, P. Fenter, P. Eisenberger, and G. Scole, Phys. Rev. B **57**, 12476 (1998).

[10] S. W. Joo, S. W. Han, and K. Kim, J. Colloid Interface Sci. **240**, 391 (2001).

[11] U. Malaske, C. Tegenkamp, M. Henzler, and H. Pfnür, Surf. Sci. **408**, 237 (1998).

[12] C. Tegenkamp and H. Pfnür, Phys. Chem. Chem. Phys. **4**, 2653 (2002).

[13] C. Tegenkamp, H. Pfnür, W. Ernst, U. Malaske, J. Wollschläger, D. Peterka, K. M. Schröder, V. Zielasek, and M. Henzler, J. Phys.: Condens. Matter **41**, 9943 (1999).

[14] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.

[15] M. T. Ashby, Inorg. Chem. **34**, 5429 (1995).

[16] C. Tegenkamp and H. Pfnür, ''Changes in the valence band structure of NaCl(100) due to electron bombardment,'' (unpublished).

[17] H. Ibach and D. L. Mills, Electron energy loss spectroscopy and surface vibrations, Academic Press, London, 1982.

[18] J. B. Foresman and Æ Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd edition, Gaussian, Inc., Pittsburgh, PA.