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Abstract. The interaction of methanethiol, CH_3SH, with Cu(100) has been studied by S 1s photoemission, S K-edge near-edge x-ray absorption fine structure and normal-incidence standing x-ray wavefield absorption at both (200) and (111) reflections. The results indicate that a single methanethiolate species, CH_3S-, is formed and this is bonded to the unreconstructed surface via the S atoms which adopt the fourfold symmetric hollow site. This conclusion confirms the results of a recent near-edge and surface extended x-ray absorption fine structure study, but contrasts with the established adsorbate-induced reconstruction produced by this species on Cu(111).

1. Introduction

Studies of thiol–surface interactions are motivated by two distinct issues. One of these concerns the general problem of the interaction of sulphur-containing species with the surfaces of materials relevant as catalysts in the petrochemical industry, because S poisons many such catalysts while the feedstock commonly contains significant levels of S-containing impurities. The second, quite different topic is the interest in 'self-organization' of alkane thiols $(CH_3(CH_2)_nSH)$ which attach themselves to the surfaces of noble metals by deprotonation of the –SH thiol end-group [1]. In the case of the simplest such species, methanethiol (CH_3SH), interaction at room temperature with Cu(111) somewhat surprisingly leads to major reconstruction of the outermost layer(s) of the copper substrate [2]. While the details of this reconstruction remain unclear, both surface extended x-ray absorption fine structure (SEXAFS) and normal-incidence x-ray standing wavefield absorption (NIXSW) show that the S penetrates the outermost Cu atomic layer to produce a local geometry which must involve a significant reduction in the Cu atomic density of this layer [2, 3]. Longer-chain alkane thiols appear to behave in a similar fashion on Cu(111) [4, 5].

More recently, detailed characterization of the interaction of methanethiol with Cu(111) at different temperatures using high-resolution S 2p soft x-ray photoelectron spectroscopy (SXPS) [6] has indicated that if the thiol is adsorbed at low temperatures and the surface slowly heated, one can identify four distinct species; at the lowest temperatures (around 100 K) intact methyl thiol is adsorbed, but heating leads to two distinct intermediates, both believed to be methanethiolate; these coexist, but at low temperatures one is dominant and at room temperature there is total conversion to the second species. At higher temperatures the molecular adsorbate decomposes to leave adsorbed atomic sulphur. A very recent chemical-shift NIXSW study [7] has confirmed this picture and shown that the lower-temperature thiolate

species bonds to an unreconstructed Cu(111) substrate, indicating that this is probably a metastable state which can be seen at low temperature due to kinetic hindrance of the irreversible thiolate-induced reconstruction. SXPS and limited structural investigations suggest that a very similar pattern of behaviour characterizes the interaction of methanethiol with Ni(111) [8, 9].

While the nature of the room-temperature thiolate-induced reconstruction of Cu(111) remains unclear, one possibility is that it not only lowers the density of Cu atoms in the surface layer, but may also change the symmetry of this layer. On Ni(111) atomic S is known to produce a reconstructed surface layer of $(5\sqrt{3} \times 2)$rect. periodicity which is somewhat similar to that of Ni(100) (a so-called pseudo-(100) reconstruction [10]) although there is significant lateral distortion of this layer [11, 12]. Recently, it has also been proposed that the key structural ingredient of the $(\sqrt{7} \times \sqrt{7})$ reconstruction produced by atomic S on Cu(111) also involves Cu_4S clusters having local (100)-like structure [13]. Indeed, it has been suggested in the case of methanethiolate on Ni(111) that the room-temperature phase might also involve a pseudo-(100) reconstruction [9].

In view of this, one obvious question is the behaviour of methanethiolate on Cu(100); does this also involve adsorbate-induced reconstruction, or is the substrate periodicity stable, and is adsorption in the same hollow sites occupied by atomic sulphur? This is the motivation of the present study. In fact a rather recent SEXAFS study of methanethiolate on Cu(100) [14] yields S–Cu bondlengths and bond angles consistent with adsorption in the fourfold symmetric hollow sites of an unreconstructed Cu(100) surface. Here we present the results of an NIXSW investigation of this system, including direct triangulation of the local adsorption site which is potentially a more incisive test of the adsorbate–substrate registry and thus of the presence or absence of lateral reconstruction.

2. Experimental details and results

The experiments were conducted in a purpose-built UHV surface science end-station at the CLRC Daresbury Laboratory installed on the SRS (Synchrotron Radiation Source) behind a UHV double-crystal monochromator and prefocusing optics. The instrument is equipped with a concentric hemispherical electron energy analyser at a fixed angle of 40° to the incident synchrotron radiation, a LEED optics and a sample manipulator allowing azimuthal rotation as well as polar angle rotation about a vertical axis (perpendicular to the horizontal plane containing the incident radiation, its principal polarization vector and the direction of detection of the emitted electrons). The Cu(100) sample was prepared by the usual combination of x-ray Laue orientation, spark machining, mechanical polishing and *in situ* argon ion bombardment and annealing cycles until a clean well ordered surface was obtained as indicated by Auger electron spectroscopy and LEED. Dosing of the surface was effected by exposing the sample at a temperature of 100 K to methanethiol gas introduced into the chamber to a typical pressure of 5×10^{-8} mbar. 5×10^{-6} mbar s of exposure appeared to ensure saturation coverage within a single layer; the temperature was not low enough to allow multilayer condensation. The effect of heating the surface briefly to different annealing temperatures was then investigated, measuring the photoelectron energy spectrum in the vicinity of the S 1s photoemission peak using a nominal photon energy of 3450 eV after each heating cycle. Measurements were made at a nominal sample temperature of 100 K.

A sequence of such spectra is shown in figure 1. Although the overall spectral resolution is only about 2.0 eV (FWHM), it is clear from these data that there are (at least) three distinct chemically shifted states. Following the highest temperature anneal (to 480 K) the spectrum is dominated by a single peak attributed to atomic S at a nominal binding energy of 2469.8 eV. No careful absolute energy scale calibration was undertaken, but relative binding energies should
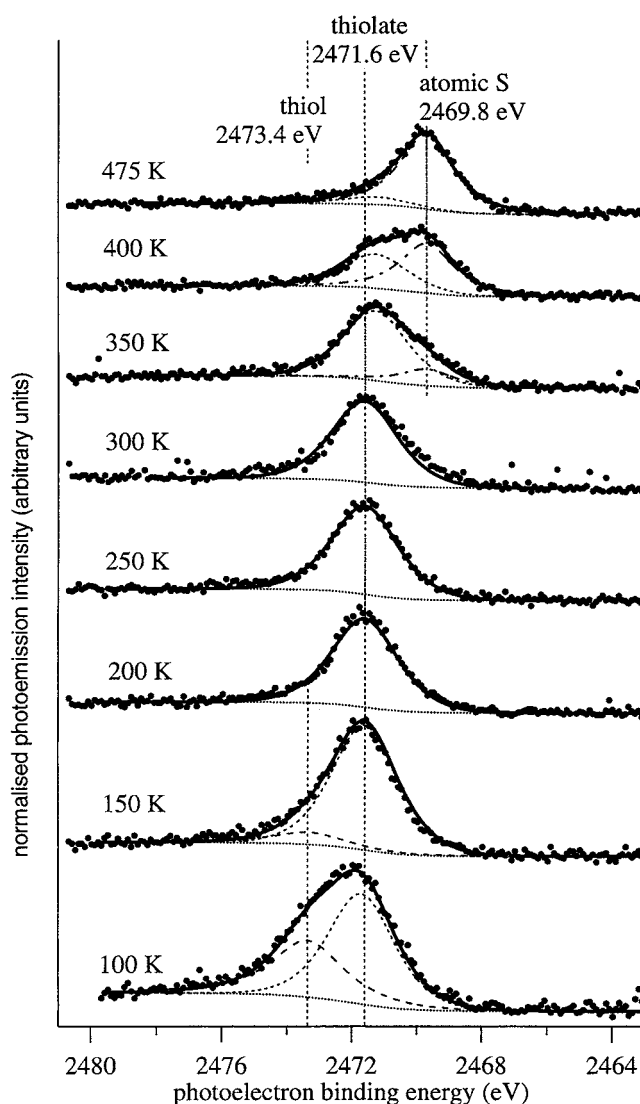
Figure 1. Photoelectron emission energy spectra in the vicinity of the S 1s peak recorded from a Cu(100) surface exposed to methanethiol at 100 K and then heated briefly to successively higher temperatures. Also shown are fits to these data based on three possible photoelectron binding energies. Note that the energy scale has not been calibrated in an absolute fashion.

be reliable and we refer the chemical shifts in the S 1s photoelectron binding energy to this state. By contrast in the intermediate temperature range from around 150 to 300 K the spectra are all dominated by a different single peak with a chemical shift of 1.8 eV to greater binding energy. At the very lowest temperature the spectrum clearly contains two components and can be fitted by a sum of this second state and a third one with a chemical shift of 3.6 eV relative to that of atomic S. By comparison with the known chemistry of methanethiol on a range of metal surfaces we attribute this low temperature state to adsorbed intact methanethiol, and the intermediate temperature state to the deprotonated species, methanethiolate. These chemical
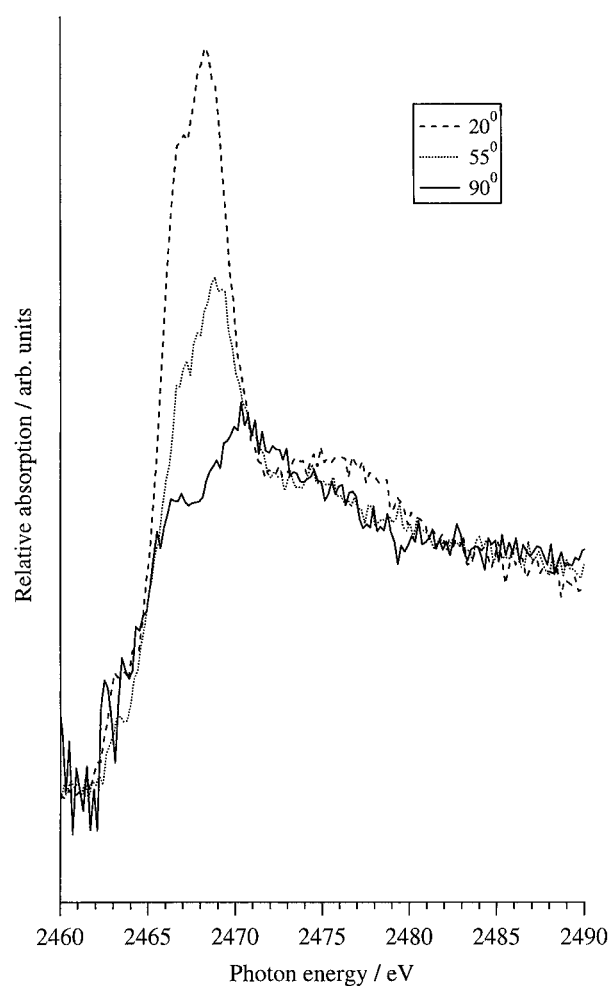
Figure 2. S K-edge NEXAFS spectra from the methanethiolate species on Cu(100) at three different angles of the principal x-ray polarization vector relative to the surface normal.

shifts may be compared with those seen for the interaction of methanethiol with Cu(111). In this case for both S 1s [7] and S 2p [6] the chemical shifts relative to the adsorbed atomic S for the intact thiol and the room-temperature (reconstructed surface) thiolate were 2.3 eV and 1.4 eV respectively. Evidently the chemical shift of the intact molecule relative to the atomic S is significantly different on the two surfaces of different substrate symmetry, but the ordering of the states is the same and the relative photoelectron binding energy of the thiolate and atomic S is quite similar on the two surfaces. On Cu(111) a third state with a chemical shift of 0.6 eV relative to the atomic S was observed at low temperatures, attributed to thiolate adsorbed on the unreconstructed surface. Despite the modest resolution of these present measurements it is clear that none of the lower temperature spectra of figure 1 show any indication of a high kinetic energy shoulder which could be attributed to a similar state, and all spectra are fitted quite well by a sum of the three states identified above, modelled by Gaussian-broadened Doniach–Sunjic lineshapes. We therefore conclude that there is no evidence for two distinct thiolate species on Cu(100) and note that even at the relatively poor resolution used here, such

an additional state would be detectable if its associated chemical shift were similar to that seen on Cu(111).

The thiolate species was then studied by NEXAFS and NIXSW to obtain structural information. In the case of NEXAFS, the intensity of the electron emission at the kinetic energy corresponding to the low energy S LVV Auger electron signal at 145 eV appeared to give the best signal-to-background ratio and this was recorded as the photon energy was stepped through the S K edge for three different incidence angles for which the polarization vector of the x-radiation was at 90°, 55° and 20° to the surface normal (note that the first of these corresponds to normal incidence, the last to grazing incidence). These are shown in figure 2.

The NIXSW technique involves the measurement of the x-ray absorption in the adsorbate S atoms as the photon energy is scanned through a normal incidence Bragg scattering condition. Within this range the incident and reflected x-rays interfere to produce a standing wave, the phase of which is dependent on the exact energy. The shape of this absorption profile is characteristic of the layer spacings of the S absorbers relative to the scatterer planes [15]. By recording NIXSW for two non-parallel sets of scattering planes the location of the absorber in space can be triangulated exactly for a substrate having threefold symmetry or higher. NIXSW data were obtained by first establishing near-normal emission to each of the two sets of Bragg scattering planes of interest, (200) (parallel to the surface) and (111). This was achieved by recording the XSW absorption profile in the Cu(100) substrate and adjusting the incidence geometry to obtain the lowest photon energy for this profile; at near-normal incidence the Bragg condition is only very weakly dependent on the exact incidence angle, so the measurement is very tolerant of the slight mosaicity expected for a typical metal single crystal [16, 15] and is well suited to these studies. At each of these Bragg reflection conditions both the S and Cu NIXSW absorption profiles were then measured by monitoring the amplitude of the S 1s photoemission signal and the Cu LMM Auger electron signals, together with suitable electron emission background signals at a few eV higher kinetic energy, at each photon energy as this was stepped in 0.2 eV increments through the XSW energy range. After background subtraction and normalization of each signal to the average value far from the XSW condition, this led to a set of normalized NIXSW absorption profiles for each species at each XSW condition. We note that while NIXSW monitored by the photoemission signal can be influenced by the asymmetry of non-dipole excitations [17] this does not appear to be a significant problem in the case of S 1s emission in the photon energy range of interest here (around 2980 eV for {111} and 3440 eV for (200)), as we have established in comparative studies of S NIXSW profiles obtained from the S 1s photoemission and S KLL Auger electron emission.

The form of NIXSW profiles is influenced by two non-structural experimental parameters (the absolute photon energy calibration and the energy broadening introduced by the finite resolution of the monochromator) and two structural parameters, the coherent position, d, and coherent fraction, f. In the simplest case of an absorbing atom occupying a single well defined site, the coherent position corresponds to the layer spacing of this site relative to the extended bulk scatterer planes, while the coherent fraction provides some measure of the degree of local order, including the influence of thermal vibrations [15]. In our standard analysis methodology we use the substrate absorption profiles to determine the non-structural parameters and then fix these to fit the adsorbate absorption profiles by adjusting the structural parameters. The substrate absorption coherent positions are expected, for this fcc substrate, to be zero (i.e. the absorbers lie in the scatterer planes being the scatterer atoms themselves), and good fits could be obtained consistent with this expectation. The associated substrate coherent fraction values were in the range 0.85–0.95 (with an estimated precision of ±0.05) with the lower values being found for the (200) reflection; these are generally consistent with a well ordered substrate

although the (200) value is a little lower than we have found typical for (111) reflections from (111) surfaces. Notice, however, that the somewhat higher energy of the (200) reflection does mean that it suffers more serious instrumental broadening than the (111) NIXSW; at the higher energy the intrinsic width of the standing wave range is narrower while the monochromator resolution is worse. This enhanced influence of broadening leads to the weaker modulation of the Cu absorption profile seen in (200) relative to (111) (figure 3). Using this procedure, the structural parameters obtained for the S absorption profiles were: (200), $d = 1.37 \pm 0.05$ Å, $f = 0.66 \pm 0.07$; (111), $d = 1.83 \pm 0.05$ Å, $f = 0.80 \pm 0.10$. These are the key results on which our quantitative determination of the S adsorption sites is based as discussed below. Figure 3 shows the associated fits to the experimental absorption profiles. Notice that the S 1s (200) experimental data show an extremely weak modulation which means that the figure looks very noisy. The superficial impression is therefore of poor quality data which should not provide reliable structural information, but this is not the case. This absence of strong modulation is an important piece of information which actually defines the coherent position; at other coherent positions one expects a much stronger modulation as seen, for example, in the Cu substrate absorption profile.

3. Discussion

The data presented in the previous section provide us with three distinct pieces of information. The XPS characterization of the interaction of adsorbed methanethiol at different temperatures provides a spectral fingerprint of the progress of the interaction, clearly identifying three different S-containing species and certainly indicating that *only* three such species occur. By comparison with the behaviour of methanethiol interaction with other metal surfaces, including that of Cu(111), as characterized by a wider variety of methods, we can be reasonably sure that these three species correspond to intact methanethiol at the lowest temperatures, atomic sulphur at the highest temperatures and methanethiolate at intermediate temperatures.

The S K-edge NEXAFS data from the adsorbed methanethiolate provide a limited molecular fingerprint and added information on the molecular orientation. The spectra and the strong polarization dependence are essentially identical to those presented in the prior XAFS study by Imanishi *et al* [14] on Cu(100), and indeed are similar to those reported for methanethiolate on Cu(111) [18]. The near-edge peak which dominates at grazing incidence is attributed mainly to a σ(C–S) shape resonance which should have its highest intensity when the polarization vector of the incident radiation lies along the S–C axis and should vanish when the polarization vector is perpendicular to this axis. The fact that this feature is very weak or absent at normal incidence when the polarization vector lies parallel to the surface indicates that the S–C axis is near-perpendicular to the surface. Imanishi *et al* have quantified this S–C molecular tilt angle as $10 \pm 10°$.

Finally, our NIXSW data allow us to determine the S adsorption site. For the simplest case of adsorption in a single well defined (high symmetry) site, it is straightforward to triangulate the site from the (200) and (111) coherent positions, $d_{(200)}$ and $d_{(111)}$. The angle between these two sets of scatterer planes is 54.73°, or $\cos^{-1}(1/\sqrt{3})$. If the adsorbate is atop an outermost layer substrate atom then we would expect that $d_{(111)} = d_{(200)}/\sqrt{3}$. For adsorption in a fourfold symmetric hollow site, the adsorbate now occupies a position which is atop a second layer substrate atom, so in effect the true value of the (200) layer spacing is not $d_{(200)}$, but $d_{(200)} + D_{(200)}$ where $D_{(200)}$ is the bulk layer spacing of the (200) scatterer planes. If we note that the bulk layer spacing of the (111) scatterer planes is $D_{(111)} = 2D_{(200)}/\sqrt{3}$, then it is clear that the expected (111) coherent position for hollow site adsorption is $d_{(111)} = (d_{(200)}/\sqrt{3}) + (D_{(111)}/2)$.
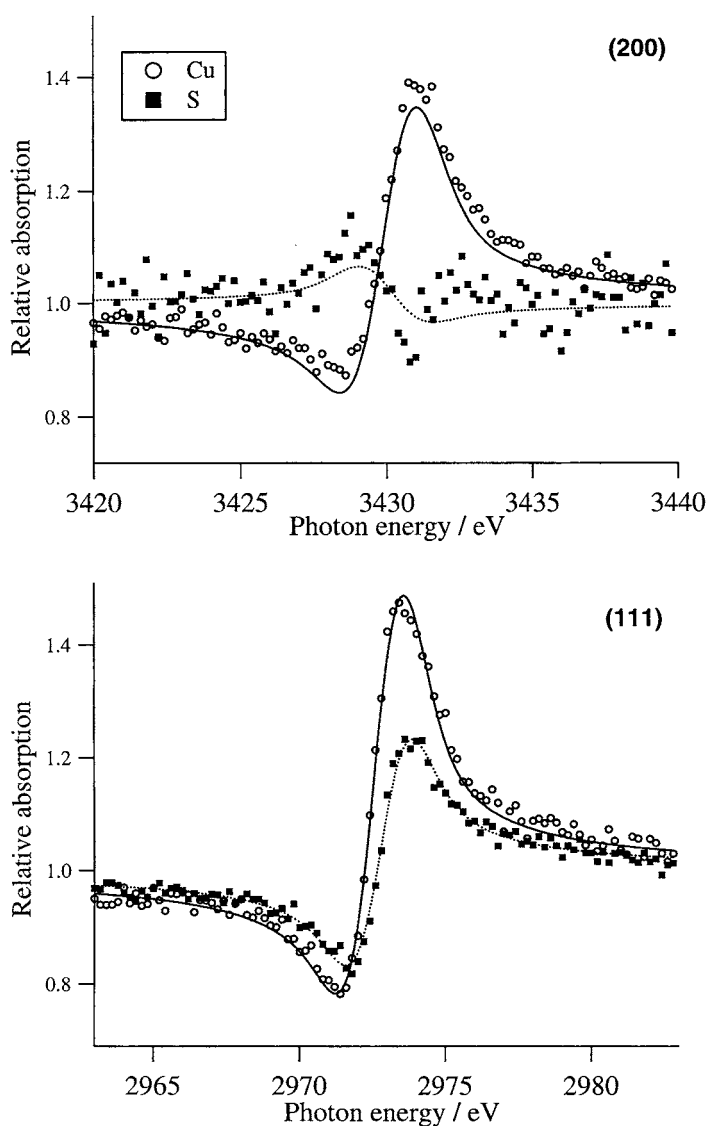
Figure 3. (200) and (111) NIXSW data recorded by monitoring the Cu LVV and S 1s electron emission signals from methanethiolate adsorbed on Cu(100). The full lines show fits to these data for the optimum structural parameter values as given in the text.

For our experiment we measured $d_{(200)} = 1.37 \pm 0.05$ Å so the expected values of $d_{(111)}$ for atop and hollow adsorption respectively are 0.79 ± 0.03 Å and 1.83 ± 0.03 Å; the measured value of 1.83 ± 0.05 Å is in perfect agreement with that expected for the hollow site. Notice, incidentally, that if bridging sites were occupied, these sites are of lower symmetry than the substrate and two inequivalent sites are expected to be occupied with equal probability. One of these leads to a (111) coherent position which is the same as for the atop site, the other is the same as for the hollow site. The result is an expected (111) coherent position which is the mean of these (1.31 Å in the present case) but with a coherent fraction reduced by a factor of 0.71 relative to that expected for either one of the two bridge sites in isolation.

While this triangulation of the coherent positions clearly provides an excellent match for the hollow site, the measured coherent fractions are somewhat lower than might be expected for a well ordered system with only a single high symmetry adsorption site. More typically these values are around 0.9. The origin of this reduction is unclear. As remarked earlier, even the substrate absorption profile for the (200) reflection is only 0.85. We should stress, however, that the slight lowering of the coherent fractions cannot be attributed to lateral strain or reconstruction induced by adsorbed methanethiolate, such as that seen on Cu(111). Lateral mis-registry would, in the present case, lead to a lowering of the coherent fraction for the (111) NIXSW (for which the scatterer planes are inclined relative to the surface) and *not* for the (200) NIXSW (for which the scatterer planes are parallel to the surface and thus insensitive to lateral registry). Indeed, in the case of the methanethiolate-covered Cu(111) surface the coherent fraction for the NIXSW having the scatterer planes parallel to the surface ((111) for this surface) was high [2, 7], whereas that obtained for scatterer planes inclined to the surface (($\bar{1}$11) was measured) is close to zero [7], consistent with an essentially incommensurate overlayer reconstruction. Clearly our data strongly indicate that methanethiolate does not produce any significant modification of the Cu(100) surface layers. In this regard we can also learn more from a comparison of our NIXSW results with those of the prior SEXAFS study. The XSW technique actually measures the position of the x-ray absorbing adsorbate atom relative to the extended bulk scatterer planes, so the (200) coherent position is only the same as the local S–Cu layer spacing if the outermost Cu layer is not expanded or contracted relative to this extended bulk structure. SEXAFS, on the other hand, measures the true local S–Cu bondlength and bond angle, leading to a true local layer spacing. The values obtained from SEXAFS for the bondlength (2.29 Å) and bond angle (52°) lead to a true S–Cu outermost layer spacing of 1.41 Å, in good agreement with our NIXSW layer spacing relative to the extended bulk scatterer planes of 1.37 ± 0.05 Å. Evidently, within the precision of our measurements, there is also no significant relaxation of the outermost Cu(100) layer perpendicular to the surface.

4. Conclusions

By a combination of S 1s XPS, S K-edge NEXAFS and NIXSW site triangulation using (200) and (111) reflections, we have characterized chemically and structurally the interaction of methanethiol with Cu(100). The results indicate that, unlike the case of methanethiol interaction with Cu(111), only a single adsorbed methanethiolate species is identified, and this does not induce any reconstruction of the surface. The local geometry of this adsorbed species has the S–C molecular axis essentially perpendicular to the surface, while the S atom occupies a fully symmetric hollow site, in excellent agreement with the results of an earlier SEXAFS study. The NIXSW data exclude, in particular, any significant lateral reconstruction of the surface. In addition, by comparing our data with the complementary SEXAFS data we are also able to conclude that there is no significant relaxation perpendicular to the surface.

Acknowledgments

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