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Characterization of thiolate species formation on Cu(111) using soft x-ray photoelectron spectroscopy

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Abstract. Soft x-ray photoelectron spectroscopy of the S 2p levels at relatively high spectral resolution has been used to characterize the interaction of methanethiol, CH₃SH, ethanethiol, C₂H₅SH and dimethyl disulphide, (CH₃S)₂ with a Cu(111) surface at temperatures from approximately 130 K to 500 K. The results are consistent with previous reports of the formation of a surface thiolate species at intermediate temperatures, but also provide clear evidence for two distinct surface intermediates in addition to the intact molecules and chemisorbed atomic sulphur reported previously for this surface. These two intermediates appear to be similar to the two thiolate species reported in studies on Ni(111). Prior structural studies of the Cu(111)/CH₃S– surface at room temperature show the surface to be reconstructed, and the lower temperature species identified here is assigned to a thiolate species on an unreconstructed surface, reconstruction being hindered at low temperatures. Additional evidence is found for two different atomic sulphur states in a narrow temperature range.

1. Introduction

Atomic S is well known as a poisoner of the surfaces of many catalysts (including those involved in the clean-up of automobile exhaust emissions) and there is therefore significant interest in the surface chemistry of sulphur-containing molecules, in part, as a route to understanding desulphurization catalysts [1]. In addition, however, alkanethiols form the basis of many self-organized organic molecular layers at surfaces [2], with the –SH group commonly suffering deprotonation at the surface to provide a thiolate which can attach to the surface through the S atom. From the point of view of surface science studies, of course, it is simplest to study low molecular mass species as a starting point, and such studies have mainly been conducted with methanethiol, CH₃SH, and dimethyl disulphide (DMS), (CH₃S)₂, the latter also having the possibility of forming the same surface methyl thiolate species by S–S bond scission, although there have also been studies of higher thiols, especially on Cu and Ni surfaces [3–14].

In the case of the Cu(111) surface, there have also been structural studies of the surface in the presence of adsorbed methyl thiolate, CH₃S–, formed at room temperature. X-ray photoelectron diffraction has been used to establish the molecular orientation [9], the S–C bond axis being perpendicular to the surface. A more complete study using a combination of normal incidence x-ray standing waves (NIXSW) and surface extended x-ray absorption

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fine structure (SEXAFS) [6] provided adsorbate registry information. This study led to the surprising conclusion that the methyl thiolate must cause a major reconstruction of this close-packed surface such that the S atoms can penetrate into the surface; although the local S–Cu bond-angles and layer spacings were obtained, no detailed structural model could be obtained from this study. However, the results can only be reconciled with models involving a substantial lowering of the atomic density of the outermost Cu atom layer, and this must be accompanied by substantial atom movement. Moreover, a recent NIXSW study of the species formed by the reaction of a longer chain alkanethiol, 1-octanethiol, $\text{CH}_3(\text{CH}_2)_7\text{SH}$ with Cu(111) led to very similar conclusions regarding the local structure at the S–Cu interface [14].

Most studies of the interaction with surfaces of methanethiol, in particular, have identified the main surface species as an intact physisorbed molecule at the lowest temperatures, a surface thiolate produced by deprotonation at slightly higher temperatures, and atomic S following S–C bond scission and the evolution of hydrocarbon products at temperatures typically above room temperature. However, recent studies of this reaction at Ni(111) surfaces [11] have identified two distinct surface molecular intermediates, both of which have been proposed to be thiolates. A key fingerprint of the two intermediate species is different S 2p photoelectron binding energies, as measured using soft x-ray synchrotron radiation to provide better surface sensitivity and spectral resolution than is usual in conventional laboratory-based x-ray photoelectron spectroscopy (XPS). The two species were initially proposed [11] to correspond to thiolate in differently coordinated (two-fold and three-fold) adsorption sites, possibly also having different molecular orientations.

The objective of the present work was to investigate the possible existence of two or more intermediate molecular species in the interaction of methanethiol, ethanethiol and DMS on Cu(111). In view of the existence of prior structural work indicating that methyl thiolate does produce a major reconstruction of Cu(111) at room temperature, one might suppose that this reconstruction would be suppressed or retarded at low temperatures, leading to the possible existence of thiolate formation on an unreconstructed surface. This might then constitute a second species as seen in soft x-ray photoelectron spectroscopy (SXPS). Indeed, during the preparation of this manuscript this interpretation has now been used to account for the existence of the two distinct thiolate species on Ni(111) [13].

2. Experimental details

The photoemission experiments were performed on beamline 6.1 of the Synchrotron Radiation Source at the CLRC's (Central Laboratories for the Research Councils) Daresbury Laboratory, which is fitted with a Miyake plane grating grazing incidence monochromator [15] and a surface science end-chamber equipped with the usual *in situ* sample preparation and characterization capabilities including LEED (low-energy electron diffraction) and Auger electron spectroscopy (AES). The Cu(111) sample was prepared by the usual combination of x-ray Laue alignment, spark machining, mechanical polishing and *in situ* argon ion bombardment and annealing cycles to produce a clean well-ordered surface as judged by AES and LEED. The reactant gases were introduced into the chamber from a gas handling line via a leak valve, typically to pressures of up to about 4×10^{-8} mbar. The methanethiol gas was of 99.5% purity (CK Gases, UK) while the liquid DMS and ethanethiol were loaded into glass ampoules attached to the gas handling line and purified *in situ* by freeze/pumping cycles before allowing the vapour, in equilibrium with the liquid at room temperature, through the leak valve. Sample cooling was achieved by a copper braid link between a liquid-nitrogen-filled reservoir close to the sample holder, and the

sample holder itself. On the basis of measurements from a thermocouple mounted adjacent to the sample the 'low temperature' measurements reported here were conducted at a sample temperature of approximately 120–125 K.

The SXPS spectra in the region of the S 2p photoemission (with a nominal binding energy of 165 eV) were recorded using a photon energy of 200 eV. A VSW Scientific Instruments HA100 100 mm mean radius concentric hemispherical mirror analyser (CHA) fitted with 16-channel parallel detection, mounted with its axis at 90° to the photon incidence direction, was used to collect the spectra at a fixed pass energy of 5.0 eV. Under these conditions the analyser resolution is about 70 meV but the instrumental resolution is limited to an estimated 300 meV by the monochromator. However, our typical spectral peak widths (FWHM) in the S 2p photoemission data, in keeping with similar studies elsewhere [11], were about 700 meV, indicating that intrinsic broadening effects determine the observed resolution in this system. Indeed, in studies of SO₂ adsorption on Cu(111) conducted during the same experimental run as the current work we noted that our resolution appeared marginally superior to that obtained in recent studies of this system using a high resolution beamline (100 meV quoted) on a third generation storage ring and associated beamline [16]. Because our objective was simply to characterize the number and origin of the different S-containing surface species, no absolute binding energy calibration was performed, and all spectra are shown on a relative binding energy scale, using the S 2p_{3/2} level of the chemisorbed atomic sulphur seen at the highest temperatures as the reference zero. The binding energy associated with this peak has been previously reported to be 160.2 eV on Cu(100) [16] and 161.55 eV on Ni(111) [11].

3. Results

S 2p photoemission spectra were collected for each adsorbate as a function of exposure at the lowest available sample temperature and as a function of the temperature to which the sample was subsequently briefly heated. The latter series of spectra typically started from a low temperature exposure of about 10⁻⁵ mbar s corresponding to close to a nominal saturation coverage, although in the case of DMS, for which multilayer condensation could be achieved at low temperature, the starting coverage was usually that corresponding to a few monolayers. Figure 1(a) shows such a set of spectra recorded after exposure to methanethiol; dotted lines are superimposed at energies corresponding to the S 2p_{3/2} peak energies of the various components discussed below. The spectra can be most readily understood by first considering those recorded at the highest temperatures, which show a single spin-orbit split doublet associated with atomic sulphur. This same state has been seen in many studies of the dissociation of S-containing molecules on Cu and Ni surfaces and is characterized by a binding energy significantly lower than that of any of the molecular states. The spectra recorded at 223 K and 273 K also appear to be dominated by a single doublet, and it is clear that in the 300–400 K temperature range this state is progressively converted to atomic S. This second state is evidently that previously identified as methyl thiolate [5] and studied more extensively through room temperature exposures [6, 9].

At the lowest temperature, however, the spectrum is more complex. Bearing in mind that all the spectra must be composed of S 2p doublets with the same spin-orbit splitting (1.18 eV), the presence of outlying peaks at relative binding energies of about 0.5 eV and 3.5 eV clearly indicates the presence of two species in addition to the thiolate seen at around 250 K, one having a S 2p_{3/2} relative binding energy of about 0.5 eV while this value for the other state must be approximately 2.3 eV (the feature at 3.5 eV being the associated S 2p_{1/2} peak). The individual components obtained in a full fitting for the

lowest temperature spectrum (see also figure 2) are superimposed in figure 1(a) to clarify this point. Heating this surface to 173 K (see figure 1(a)) removes the deepest binding energy state, while the shallow binding energy state is also strongly suppressed. Additional spectra recorded at intermediate temperatures in a separate experiment confirm this trend. Some further information on these low-temperature states is provided by additional spectra recorded at the lowest temperature (124 K) as a function of increasing exposure, and these are shown in figure 1(b). At the lowest exposures there is little evidence for the deepest binding energy state, and the spectrum appears to be dominated by the thiolate species seen at higher temperatures, but with a significant contribution from the shallow binding energy state. Increasing exposures leads to an increase in intensity in both the low and high binding energy states, with the higher temperature thiolate state being essentially unchanged. On the basis of these spectra and previous work on this system we attribute the deepest binding energy doublet to the presence of intact methanethiol on the surface which is desorbed by only a small increase in temperature. Note that an earlier characterization of methanethiol on Cu(111) [5] using ultraviolet photoemission indicated a desorption temperature for the intact molecule of 116 K, broadly consistent with our findings bearing in mind the problems of absolute temperature measurement of the sample in such experiments. This earlier study also found no evidence for this intact molecular species on Ni(100) down to 110 K, indicating a lower reactivity of the copper surface, consistent with the fact that the more recent work on Ni(111) down to 100 K did not show evidence for this species on the surface [11].

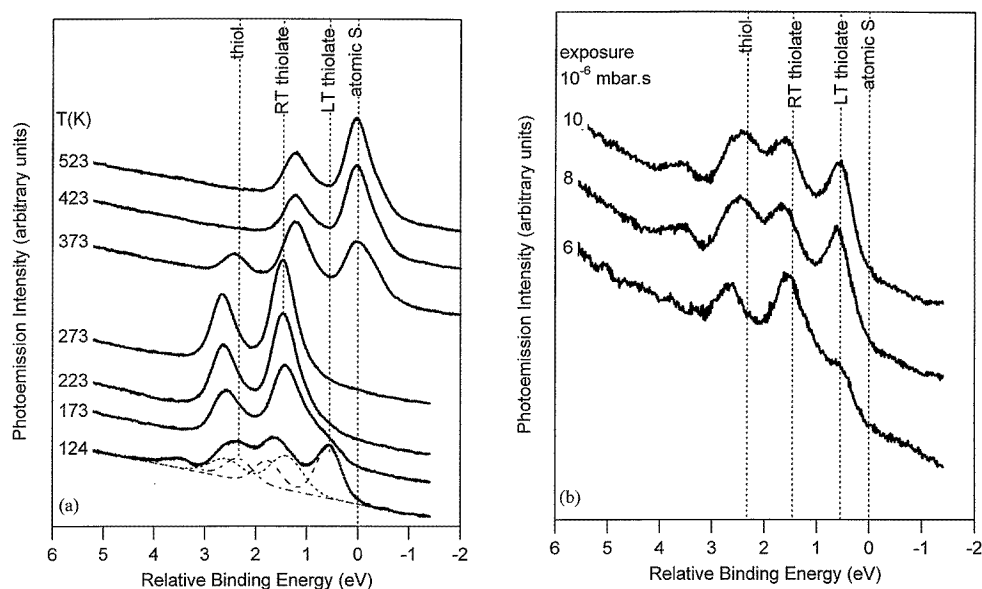


Figure 1. (a) Photoelectron energy spectra in the region of the S 2p peak obtained from Cu(111) exposed at 124 K to 10^{-5} mbar s of methanethiol and subsequently heated briefly to increasingly higher temperatures. The spectra were recorded using a photon energy of 200 eV, but the binding energy scale is shown relative to the S 2p_{3/2} peak corresponding to atomic S on the surface at the highest temperatures. The dashed lines show the S 2p_{3/2} peak energies of the individual components obtained by detailed curve-fitting as described in the text at relative binding energies of 0.55 eV, 1.46 eV and 2.33 eV. (b) Photoelectron energy spectra in the region of the S 2p peak obtained from Cu(111) exposed at 124 K to increasing doses of methanethiol. Otherwise as figure 1(a).

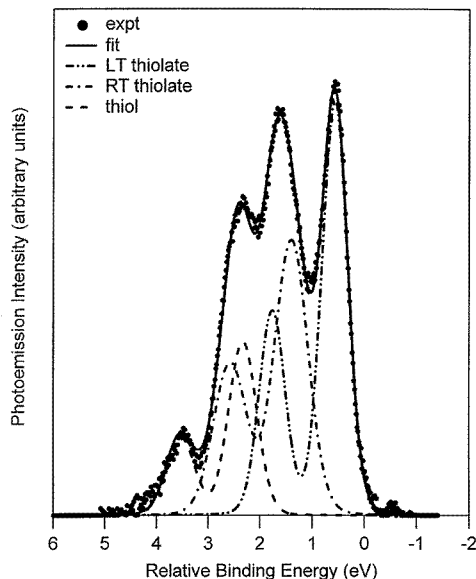


Figure 2. Example of spectral fitting, showing the photoemission spectrum recorded after exposure of the Cu(111) surface to 10^{-5} mbar s of methanethiol at 124 K (bottom spectrum of figure 1(a)) after background removal, and the fit obtained from the sum of the three states attributed to the intact thiol molecule and the two different methyl thiolate species.

The shallow binding energy state seen at low temperatures we then assign to a second methyl thiolate species. The ordering of the relative binding energies of the chemisorbed atomic sulphur and the two species each attributed to methyl thiolate is the same as that found for the same species on Ni(111). With the aid of some simple curve-fitting, constraining the fits to comprise doublets of known splitting and with relative intensities close to the anticipated atomic value of 1:2 (e.g. figure 2), we find the binding energies of the thiolate seen at room temperature (hereafter referred to as the RT thiolate) and that seen only at low temperature (LT thiolate) relative to the atomic species to be 1.46 eV and 0.55 eV. The equivalent values on Ni(111) are 1.75 eV and 1.17 eV [11], significantly different quantitatively, but with the same peak ordering, the LT thiolate having a binding energy intermediate between those of the RT thiolate and the atomic S. Notice, of course, that the LT and RT labels we use here are only partially descriptive; the LT thiolate is only seen at low temperatures, but the RT thiolate state is partially occupied even at the lowest temperatures and also appears to be the first state to be occupied at low exposures, even at the lowest temperatures.

Very similar behaviour is seen in the experiments involving ethanethiol exposure as seen in figure 3, and we infer that there are two inequivalent intermediate ethyl thiolate species with essentially identical S 2p photoelectron binding energies to those seen for methyl thiolate. Finally, in figure 4 we show a similar set of spectra obtained following sequential heating cycles of the Cu(111) surface exposed at low temperature to approximately 5×10^{-5} mbar s of DMS. This molecule can be condensed onto the surface to form multilayers at this temperature, so high exposures lead to spectra dominated by the doublet with a S 2p_{3/2} relative binding energy of 3.2 eV which is characteristic of these multilayers. Notice, however, that even at low temperature the initial DMS arriving at the surface

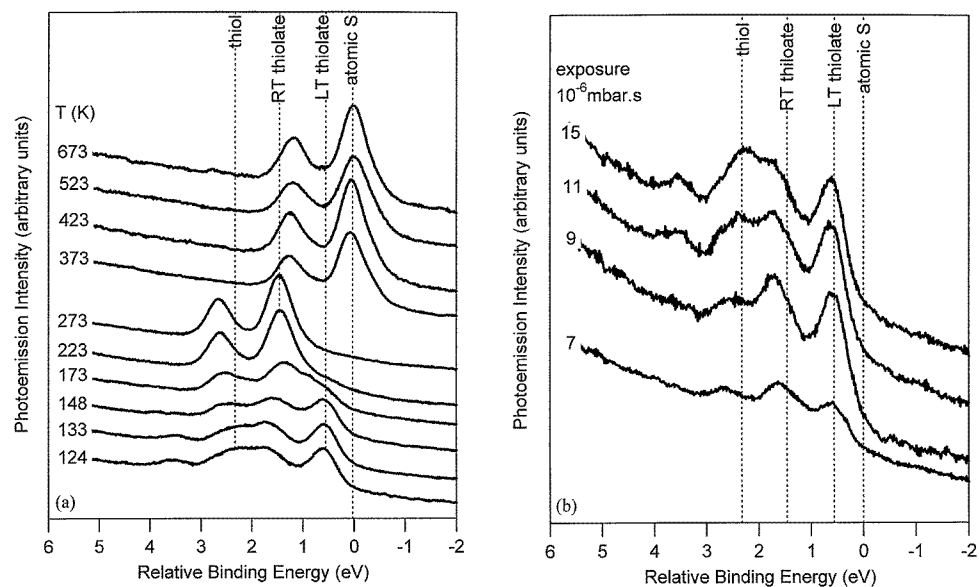


Figure 3. (a) Photoelectron energy spectra in the region of the S 2p peak obtained from Cu(111) exposed at 124 K to 10^{-5} mbar s of ethanethiol followed by successive heating cycles and (b) similar spectra obtained after successively higher doses of ethanethiol at 124 K. Otherwise as in figure 1.

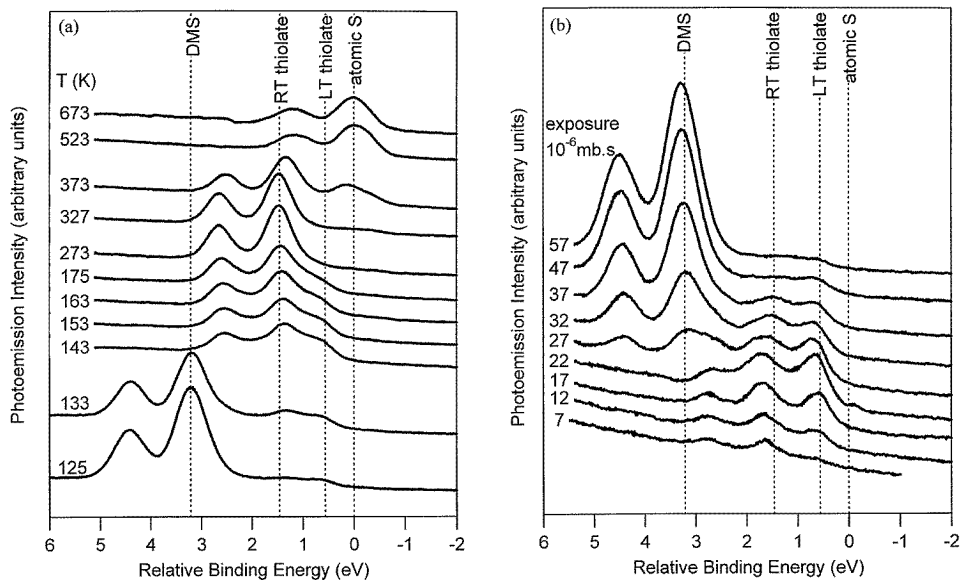


Figure 4. (a) Photoelectron energy spectra in the region of the S 2p peak obtained from Cu(111) exposed at 124 K to 5×10^{-5} mbar s of dimethyl disulphide (DMS) followed by successive heating cycles and (b) similar spectra obtained after successively higher doses of DMS at 124 K.

interacts with the copper to produce a spectrum characterized by three peaks which can be attributed to a mixture of the LT and RT methyl thiolate species seen from interaction with methanethiol. It appears, therefore, that the intact molecule only condenses in multilayers after the most active surface sites have been covered with reacted species. Spectra taken after low-temperature saturation of the surface with or without thick multilayer molecular layers confirm that the general sequence of formation of the two methyl thiolate species, in this case by S–S bond scission, is similar to that obtained from methanethiol interaction and deprotonation. Notice, however, that these spectra show no evidence for the doublet peak with a S $2p_{3/2}$ relative binding energy of 2.33 eV, reinforcing the assignment of these peaks in figure 1 to the presence of intact methanethiol on the surface.

While all of these general semi-quantitative deductions are rather clear from inspection of the raw spectra, we have also undertaken more detailed curve fitting in an attempt to ensure that these four general states, intact molecule, two distinct thiolate species, and atomic S are able to provide a complete description of all of the spectra. This did lead to the identification of one intermediate additional state with a binding energy less than that of the chemisorbed sulphur in the temperature range between about 300 K and 380 K. Some evidence of this can be seen in all of the spectra recorded at 373 K in the form of a high kinetic energy shoulder on the atomic S $2p_{3/2}$ peak at a relative binding energy of 0.0 eV which leads to an apparent asymmetry in this peak. A separate set of spectra recorded after heating in smaller temperature increments in this temperature range, obtained from a surface initially exposed at low temperature to ethanethiol (figure 5), show far more clearly a quite distinct additional peak in this region associated with this 'new' state with a binding energy of some 0.37 eV less than the reference peak at 0.0 eV. We attribute this peak to a second atomic sulphur state as discussed below.

4. Discussion

The S 2p photoelectron energy spectra obtained from the interactions of these three S-containing molecules with Cu(111) at different temperatures provide clear fingerprints of the different surface species formed through the chemical interaction with the surface. However, despite the previous general consensus for this surface that only two types of surface species are formed, a thiolate and atomic S, our data show clear evidence for 4 distinct species. The existence of two distinct methyl thiolate species has previously been inferred on Ni(111) [11] (and on W(100) [17] and Ru(0001) [18]) through S 2p photoemission but also aided by vibrational and thermal desorption spectroscopy. This seems to be the most probable origin of the two lower temperature intermediates identified in our spectra which we have labelled as the LT and RT thiolates. Mullins *et al* [12, 13] have argued that there is evidence in several systems (including atomic sulphur of Ni(111) [19]) for a correlation between S atomic coordination at transition metal surfaces and the S 2p photoelectron binding energy, this energy increasing in magnitude as the coordination increases. The simplest physical basis for such a correlation is a systematic change in the one-electron binding energy with a changed coordination, i.e. a pure initial state effect or 'true' chemical shift. The importance of changes in the final state relaxation in determining the observed chemical shift is well known, however, and such correlations of photoelectron binding energy and adsorption geometry need to be treated with extreme caution. Nevertheless, it is clear that one possible reason for the two distinct photoelectron binding energies for the two proposed thiolate species is that they correspond to two different local adsorption geometries. Based on the empirical correlation of S 2p binding energy and coordination number, Rufael *et al* [11] initially suggested that on Ni(111) the LT thiolate

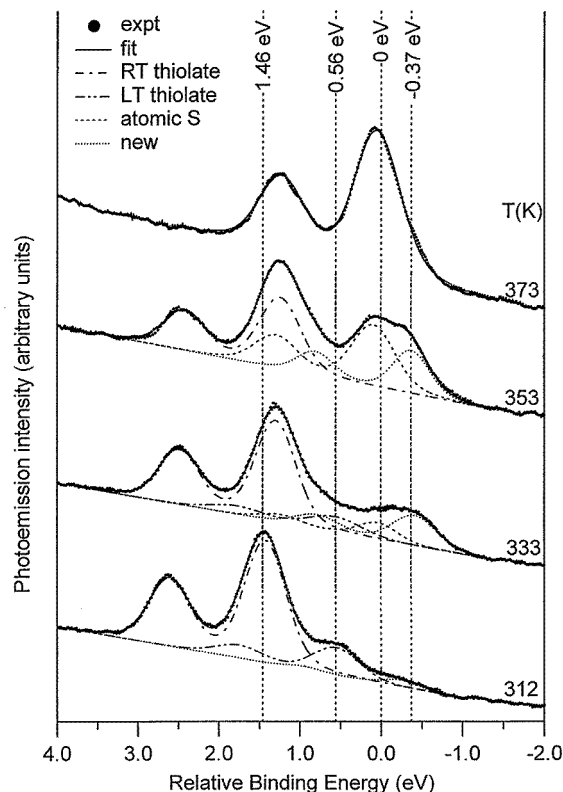


Figure 5. Photoelectron energy spectra in the region of the S 2p peak obtained from Cu(111) exposed at 124 K to 10^{-5} mbar s of ethanethiol followed by successive heating cycles in a narrow temperature range around room temperature, together with fits to these spectra.

was bridge bonded and the RT thiolate three-fold coordinated in a hollow site. In the present case, however, we already know from prior structural work that at room temperature methyl thiolate is adsorbed on a reconstructed Cu(111) surface, the reconstruction being induced by the thiolate adsorption. This reconstruction appears to involve a large change in the outermost Cu layer atomic density, and must therefore involve substantial transport of atoms on the surface; at sufficiently low temperature we can therefore expect that this reconstruction would be hindered and that some methyl thiolate may be adsorbed on unreconstructed regions of the surface. This appears to offer a more reasonable explanation for our results, the RT thiolate corresponding to adsorption on reconstructed regions of the surface, while the LT thiolate is on unreconstructed regions. Indeed, a very recent paper [13] reinterprets the Ni(111) results in this way, speculating on a similar thiolate-induced reconstruction of the Ni(111) surface at elevated temperatures, and assigning the LT thiolate to three-fold coordinated hollow site adsorption as found in another study [20].

A very similar explanation is likely to account for the state identified in the 300–380 K temperature range which appears in the early stages of the growth of the atomic sulphur state. Cu(111) is also known to form surface reconstructions in the presence of atomic sulphur, notably in a $(\sqrt{7} \times \sqrt{7})R19^\circ$ phase; the detailed structure of this phase remains a matter of some controversy [21–23] but there is general agreement that it does not comprise

a simple atomic S overlay. This phase is the one to be expected at high S coverages and after annealing to the somewhat elevated temperatures which characterize the main atomic sulphur state in our spectra. In the first stages of atomic S deposition associated with thiolate fragmentation, however, the S is likely to be adsorbed onto a surface which is either unreconstructed or which still adopts the reconstruction characteristic of the RT thiolate phase.

While the SXPS spectra presented here provide a clear spectral fingerprint of the number of distinct states of sulphur formed at the surface during the interaction, the formal assignment of these to specific molecular or atomic species with specific local geometries is clearly more speculative. In the case of the molecular assignments we are greatly aided by the published work on other surfaces, notably on Ni(111), for which other probes of the species and the associated surface chemistry (vibrational spectroscopy and thermal desorption) were applied. The formal structural assignments, however, must remain more speculative until proper quantitative structural studies are performed. The fact that several of the species are only seen on the surface coadsorbed with at least one other species clearly makes structural studies more difficult, but techniques which exploit the photoelectron binding energy shifts to provide chemical state specificity, such as chemical shift photoelectron diffraction [24] may offer a route to a unique solution of this complex problem.

Nevertheless, the availability of at least partial quantitative structural information in the present case for the more elevated temperature methyl thiolate and atomic sulphur states on Cu(111) does provide key evidence for the most probable explanation of the new data, namely that distinct states for both the thiolate and atomic sulphur seen in narrow temperature ranges can be attributed to adsorption on regions of the surface which have not fully adopted the substrate reconstructions induced by these two distinct adsorbates.

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