Following Local Adsorption Sites through a Surface Chemical Reaction: CH_3SH on Cu(111)

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Studying the interaction of CH_3SH, methanethiol, with Cu(111) as a model system, we demonstrate the ability of chemical-shift normal incidence x-ray standing wave field measurements to identify the local adsorption geometries of coadsorbed reaction products at different temperatures, a technical problem of broad chemical significance. In the present case the local geometries of four distinct S-containing adsorbate species (intact CH_3SH, two thiolate (CH_3S-) reaction intermediates and atomic S) are determined.

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Practical surface chemical reactions, such as those in heterogeneous catalysis, involve several coadsorbed molecular moieties, including reaction intermediates, and while spectral fingerprinting techniques have proved fruitful in identifying these species, little progress has been made so far in determining their local adsorption geometries. One method with the potential to achieve this is to combine the standard method of x-ray standing waves (XSW) [1] with detection of the photoabsorption cross section at different sites through the intensities of the chemically shifted photoemission peaks from the coadsorbates. Although a limited demonstration of this possibility has been performed [2], full exploitation requires a combination of high incident x-ray flux to detect the low absorber concentrations ($\leq 5 \times 10^{14}$ cm^{-2}) and high spectral resolution ($\leq$0.3 eV) to separate the chemically shifted states; we have exploited an undulator beam line on the new third-generation X-Ray European Synchrotron Radiation Facility (ESRF) to satisfy these requirements. Here we demonstrate how this combination of methods and resources allows us to determine the local geometry of the four distinct S-containing species (including two reaction intermediates) present on a Cu(111) surface as a result of interaction with CH_3SH, methanethiol.

The interaction of alkane thiols with surfaces is of interest from both the point of view of desulfurization catalysts and catalyst poisoning and because these species form self-assembled thiolate monolayers (through deprotonation at the interface) which are of potential interest in molecular electronics. Methanethiol is the simplest such species, and its interaction with Cu(111) has recently been characterized by high resolution S $2p$ photoelectron spectroscopy [3]. These experiments show that four distinct S-containing surface species result from this interaction. Aided by other spectroscopic studies of the same species interacting with other noble and transition metal surfaces [especially Ni(111) [4]], these have been assigned to an intact adsorbed methyl thiol molecule (present only at the lowest temperatures $\leq$150 K), two distinct states, both attributed to methyl thiolate (CH_3S-) adsorbed in different geometries, and atomic sulphur, to which all species transform at the highest temperatures ($\geq$400 K). The two thiolate species are conveniently labeled low and high temperature (LT and HT) thiolates; both thiolate species are present at the lowest temperatures, but the LT thiolate transforms to the HT thiolate as the temperature is raised. The chemical shifts of the S $2p$ photoelectron binding energies of the intact molecular thiol, the LT thiolate, and the HT thiolate relative to the atomic sulphur have been identified as 2.3, 0.6, and 1.4 eV, respectively.

Our experiments were performed on the ID32 beam line of the ESRF using the 48 mm period undulator and the double-crystal [Si(111)] monochromator together with a standard surface-science spectrometer end-station equipped with the usual facilities for *in situ* sample cleaning and characterization. In the XSW technique [1] an x-ray Bragg reflection is established in the substrate and the interference of the incident and diffracted beams produces a standing wave field, the intensity of which has a periodicity equal to that of the scatterer planes. The phase of this standing wave shifts as the exact scattering condition is varied, and the x-ray absorption in a particular atomic species as a function of scatterer condition is characteristic of the location of these atoms relative to the scatterer planes. By using normal incidence to the scatterer planes (and scanning the photon energy through the Bragg condition), the experiment becomes rather insensitive to substrate crystal perfection and is applicable to standard metal single crystals [5,6]. We conducted normal incidence XSW (NIXSW) experiments using the (111) and $(\bar{1}11)$ Bragg reflections, which provide absorber-substrate spacings sufficient to triangulate the absorber atom locations [6]. The x-ray absorption at S atoms in the adsorbate species was determined from the S $1s$ photoemission signal measured in a Physical Electronics concentric hemispherical analyzer. Note that independent tests show that

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there is no significant influence on the XSW absorption profiles due to nondipole contributions to the photoelectron angular dependence [7] under these conditions.

Methanethiol was adsorbed onto the Cu(111) surface to saturation coverage at a sample temperature of 140 K; Fig. 1 shows S 1*s* photoelectron energy spectra recorded from such a surface, and after heating to 300 K. It is clear that each spectrum contains at least two distinct peaks, and indeed that the dominant peak of the higher temperature spectrum occurs at an energy which does not correspond to either of the main contributions to the low temperature spectrum. More careful fitting with Doniach-Sunjic line shapes with Shirley backgrounds reveals a total of four different peaks; each of the two spectra contains contributions from three of these four, and two of the peaks are common to the two spectra. Figure 1 shows these components obtained in this fitting. Possible ambiguities in this fitting procedure are removed by the constraint that the same four binding energies were used to fit both a set of spectra recorded after heating to seven different temperatures, and spectra recorded at each of 29 different photon energies within the $\{111\}$ XSW photon energy scans at 140 and 300 K. Figure 2 shows a subset of such spectra recorded at four different photon energies with the surface at 140 K for the (111) reflection; the relative intensities of the different chemically shifted S 1*s* components varies significantly, greatly constraining the fitting but also demonstrating that different adsorption sites are associated with each state. The locations of these four photon energies relative to the substrate XSW absorption wave profile are shown in the right-hand panel of Fig. 2. The relative S 1*s* photoelectron binding energies of the four peaks used to fit all of these spectra were identical to the relative S 2*p* energies measured previously [3] and are labeled accordingly.

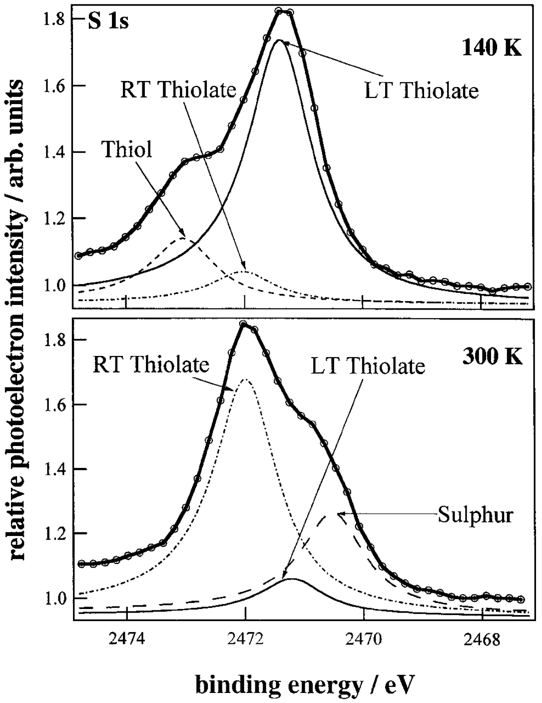

FIG. 1. Experimental photoelectron energy spectra (circles and bold line) in the region of the S 1*s* binding energy recorded at a photon energy of 3000 eV from a saturation dose of CH_3SH on Cu(111) at 140 K, and after heating to 300 K. The other lines show the individual chemically shifted components fitted to these spectra.

The S chemical-shift XSW measurements comprised a full set of photoemission energy spectra similar to those shown in Fig. 2 but recorded at photon energies in 0.2 eV increments through both the (111) and the $(\bar{1}11)$ normal incidence Bragg conditions; data of this kind were obtained from samples treated at both the low (140 K) and high (300 K) temperatures. Fitting each photoemission spectrum by the four contributing states described above yielded separate (111) and $(\bar{1}11)$ NIXSW absorption profiles for the four species at each temperature. The NIXSW absorption profile for each state was found to be independent of temperature, and these were then fitted using our standard procedures [6,8] to yield the XSW structural fitting parameters, the coherent position, and the coherent fraction. The resulting structural parameter values are shown in Table I.

In the simplest case of adsorption in a single high symmetry site, which yields high coherent fractions (typically ≥ 0.8), the coherent positions can be equated with layer spacings and the adsorption site deduced from triangulation of the two different $\{111\}$ spacings. This situation applies to the S atom in the intact thiol; the (111) S-Cu layer spacing of 2.38 Å given by the coherent position should lead to a $(\bar{1}\,11)$ coherent position of 0.79, 1.48, or 2.18 Å, depending on whether the S atom occupies atop, hcp hollow (above a second layer Cu atom) or fcc hollow (above a third layer Cu atom) sites. The experimental value is in perfect agreement with the prediction for the atop site, so we deduce that the intact thiol is bonded to the Cu(111) surface through its S atom which is directly atop an outermost layer Cu atom. The implied Cu-S bond length is 2.38 Å (neglecting any possible outermost layer relaxation), identical to the value obtained more directly for the RT thiolate, when isolated as the sole surface species, by surface x-ray absorption fine-structure (SEXAFS) analysis [9]. This bond length clearly implies true chemisorption rather than weak van der Waals bonding; the fact that the values are identical is somewhat surprising as one would expect the intact molecule to be more weakly bound, but may be related to the fact that the Ni coordination for the S in the intact methanethiol bonding is lower (onefold) than for the thiolate (threefold or fourfold).

If the LT thiolate occupied a high symmetry site, the measured (111) layer spacing of 1.88 Å should lead to $(\bar{1}11)$ coherent positions of 0.63 Å (atop), 1.32 Å (hcp hollow) and 2.01 Å (fcc hollow). The measured value

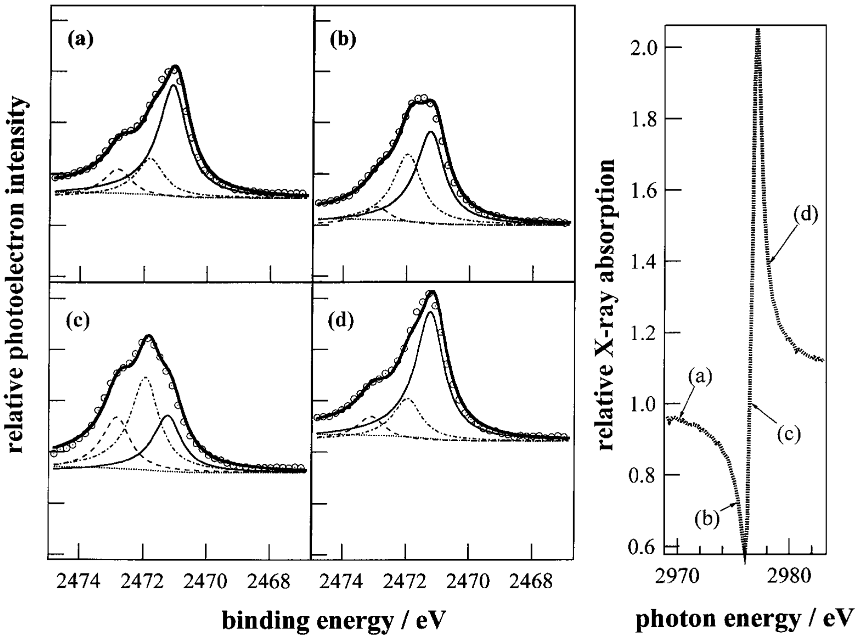

FIG. 2. Experimental S 1*s* photoelectron energy spectra (and their fitted components as in Fig. 1) from Cu(111) exposed to a saturation dose of CH_3SH at 140 K, recorded at different photon energies through the (111) NIXSW condition. Also shown is the bulk (Cu) absorption profile through this region showing the relative locations of these four photon energies (*a*) to (*d*).

of 1.55 Å is intermediate between the last of these two, and is most easily reconciled with mixed occupation of the two hollow sites, the best fit corresponding to 65% occupation of the hcp sites. This mixed site occupation would also lower the $(\bar{1}11)$ coherent fraction to an upper limit of 0.5. The implied S-Cu bond length in this case is again 2.38 Å. An alternative interpretation is that the S of the LT thiolate is in a bridge site; this lower symmetry site would reduce the expected $(\bar{1}11)$ coherent fraction to 0.33, in better agreement with the experiment, but the associated coherent position would be 1.66 Å, marginally outside our error estimates for the experimental measurement. The mixed hollow site model therefore appears more likely. Notice that the implied Cu-S bond length for this site is 2.38 Å, identical to that found for both the intact thiol and the RT thiolate; if the bridge site is occupied, this is reduced to 2.27 Å. Figure 3 shows schematically the local structure for these two low temperature species.

TABLE I. Values for the NIXSW fitting parameters of coherent position (CP) and coherent fraction (CF) for the four distinct chemically shifted S 1*s* states associated with CH_3SH interaction with Cu(111).

S 1*s* absorber	CP (111) (Å)	CF (111)	CP $(\bar{1}11)$ (Å)	CF $(\bar{1}11)$
Thiol	2.38(5)	0.90(10)	0.79(5)	0.80(10)
LT thiolate	1.88(5)	0.90(10)	1.55(5)	0.30(10)
RT thiolate	1.07(5)	0.70(10)	0.31(10)	0.15(10)
Atomic S	1.56(5)	0.70(10)	1.97(5)	0.30(10)

The RT thiolate shows a much smaller (111) coherent position, and the $(\bar{1}11)$ coherent fraction is close to zero. This result is consistent with those of an earlier but less complete study which isolated this state alone on Cu(111) by NIXSW [using only the (111) reflection] and SEXAFS [9], a recent NIXSW study of the room temperature octane thiolate on Cu(111) [10], and a SEXAFS study of C_6 and C_{12} alkane thiols on this surface [11]. As discussed

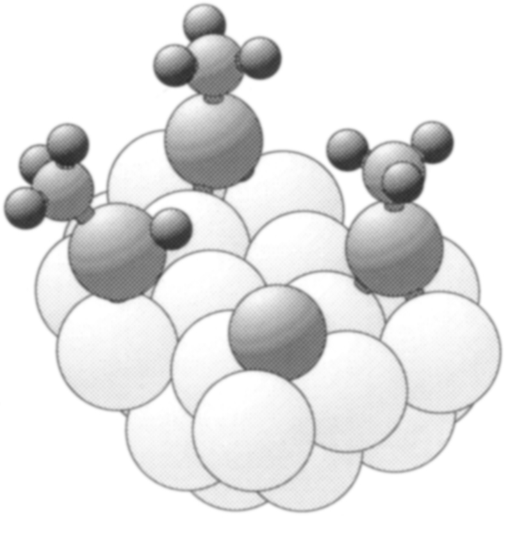

FIG. 3. Schematic diagram showing the local adsorption geometries at low temperature of the coadsorbed intact thiol (left) and LT thiolate on Cu(111); also shown is the HT atomic S species. The molecular orientation is not determined here but is inferred from general considerations of chemical bonding.

in these earlier papers, the data can only reasonably be reconciled with a local reconstruction of the outermost Cu atom layer to a more open packing, allowing the S atoms of the RT thiolate to penetrate deeper into this top layer. The very low $(\bar{1}11)$ coherent fraction is consistent with this reconstruction being incommensurate or having a large unit mesh with many nonequivalent local site registries.

Finally, we note that the measured coherent positions for the atomic S triangulate quite well to the occupation of fcc hollow sites; the measured (111) coherent position of 1.56 Å would lead to an expected $(\bar{1}11)$ coherent position for this site of 1.91 Å, close to the measured value. However, the coherent fractions for this species are too low for a single high symmetry adsorption site, and the implied Cu-S bond length for a single hollow site is 2.15 ± 0.05 Å, significantly shorter than that (2.30 Å) seen in a pure Cu(111)/S structure [12]. We note, however, that S is known to cause complex reconstructions of the Cu(111) surface, and partial reconstruction of this kind could account for the low coherent fractions. Moreover, a mixture of an unreconstructed overlayer and a partially penetrated reconstructed surface could account for the low implied (111) layer spacing and apparent bond length.

In conclusion, therefore, the ability to obtain chemical-state resolution in local adsorbate structure determination has allowed us to build a rather complete picture of the reaction of CH_3SH with Cu(111), despite the fact that some species, notably the thiol and the LT thiolate, could *only* be found on the surface as coadsorbates. At the lowest temperatures the intact molecular thiol bonds through the S atom which occupies a local atop site on the surface. Even at 140 K, however, significant deprotonation of this molecule occurs. There are two distinct states of the resulting methyl thiolate, CH_3S- species. The state ("HT thiolate") which appears to be most stable and which dominates at higher temperatures occupies a high coordination site penetrating a reconstructed top Cu atom layer, but at low temperature this reconstruction is kinetically hindered, and some of the thiolate species ("LT thiolate") are thus adsorbed on unreconstructed areas of the surface, most probably occupying the two nonequivalent hollow sites with similar probability. We attribute the partial occupation of the higher temperature thiolate state at low temperature to partial thiolate-induced reconstruction at more facile sites, presumably associated with surface defects. At the highest temperatures the molecule suffers C-S bond scission, the atomic S then occupying geometries broadly consistent with earlier studies of pure atomic S adsorption phases on this surface.

The main features of this behavior are quite similar to the conclusions of an investigation of CH_3SH interacting with Ni(111) [13] although in this case no intact adsorbed thiol was seen. In this paper, chemical shifts in the photoemission were also used to distinguish the two thiolate species, while photoelectron diffraction angular scans provided limited structural information. In a different system full coadsorption site determination has been shown to be possible through chemical-shift photoelectron diffraction [14]; our results show that, with the aid of new third-generation synchrotron radiation sources, chemical-shift XSW provides an alternative complementary approach to this chemically important general problem.

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[1] J. Zegenhagen, Surf. Sci. Rep. **18**, 199 (1993).

[2] M. Sugiyama, S. Maeyama, S. Heun, and M. Oshima, Phys. Rev. B **50**, 14 778 (1995).

[3] M. S. Kariapper, G. F. Grom, G. J. Jackson, C. F. McConville, and D. P. Woodruff, J. Phys. Condens. Matter **10**, 8661 (1998).

[4] T. S. Rufael, D. R. Huntley, D. R. Mullins, and J. L. Gland, J. Phys. Chem. **99**, 11 472 (1995).

[5] D. P. Woodruff, D. L. Seymour, C. F. McConville, C. E. Riley, M. D. Crapper, N. P. Prince, and R. G. Jones, Phys. Rev. Lett. **58**, 1460 (1987).

[6] D. P. Woodruff, Prog. Surf. Sci. **57**, 1 (1998).

[7] C. J. Fisher, R. Ithin, R. G. Jones, G. J. Jackson, D. P. Woodruff, and B. C. C. Cowie, J. Phys. Condens. Matter **10**, L623 (1998).

[8] A copy of the automated fitting program, written as an IGOR-PRO macro by R. G. Jones, is obtainable from Robert.G.Jones@Nottingham.ac.uk

[9] N. P. Prince, D. L. Seymour, D. P. Woodruff, R. G. Jones, and W. Walter, Surf. Sci. **215**, 566 (1989).

[10] H. Rieley, G. K. Kendall, A. Chan, R. G. Jones, J. Lüdecke, D. P. Woodruff, and B. C. C. Cowie, Surf. Sci. **392**, 143 (1997).

[11] A. Imanishi, K. Isawa, F. Matsui, T. Tsuduki, T. Yokoyama, H. Kondoh, Y. Kitajima, and T. Ohta, Surf. Sci. **407**, 282 (1998).

[12] N. P. Prince, D. L. Seymour, M. J. Ashwin, C. F. McConville, D. P. Woodruff, and R. G. Jones, Surf. Sci. **230**, 13 (1990).

[13] D. R. Mullins, D. R. Huntley, T. Tang, D. K. Saldin, and W. T. Tysoe, Surf. Sci. **380**, 468 (1997).

[14] K-U. Weiss, R. Dippel, K-M. Schindler, P. Gardner, V. Fritzsche, A. M. Bradshaw, D. P. Woodruff, M. C. Asensio, and A. R. González-Elipe, Phys. Rev. Lett. **71**, 581 (1993).