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## The orientation of mercaptide on Cu(111) studied by x-ray photoelectron diffraction polar angle scans

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**Abstract.** The orientation of mercaptide ( $\text{CH}_2\text{S}$ -), and the closely similar methoxy ( $\text{CH}_3\text{O}$ -) species on Cu single-crystal surfaces, has been the subject of some controversy. Some near-edge x-ray absorption fine structure results indicate substantially tilted C–S or C–O molecular axes relative to the surface normal, but reflection–adsorption infrared spectroscopy of methoxy on Cu(111), scanned-energy mode photoelectron diffraction of methoxy on Cu(100), and S K-edge surface extended x-ray absorption fine structure of mercaptide on Cu(111) all indicate perpendicular molecular orientations. A technique that provides particularly clear information on molecular orientations is polar angle scanned x-ray photoelectron diffraction, and we have applied this method to a study of the molecular orientation of mercaptide on Cu(111). The results show clearly that the mercaptide molecular axis is oriented perpendicular to the surface, a result which is found to be true over a wide range of surface coverages. The origins of the discrepancies between the various techniques are discussed.

### 1. Introduction

Many surface techniques are capable of providing information on the orientation of molecules on surfaces, but few of these methods yield quantitative values for this parameter. For example, reflection–absorption infrared spectroscopy (RAIRS) can, through the application of strict selection rules, associate zero intensity of specific vibrational excitations with specific orientations, although if a band is predicted to be excited, no simple assessment of its quantitative intensity can be made. Similar (but more complex) arguments apply to the study of vibrational excitations by electron energy loss spectroscopy, for which both dipole and impact mechanisms apply. One method, which does have the potential for quantitative orientation information, is near-edge x-ray absorption fine structure (NEXAFS) for which rather simple quantitative analysis of the intensity of transitions between initial and final states of known symmetry within an adsorbed molecule is possible [1]. Recent work has, however, stressed that one of the underlying assumptions of NEXAFS analyses of this type, namely that the spectral structure seen is entirely due to intra-molecular effects, is almost certainly a source of significant error in many results of this kind [2].

A particularly simple method of molecular orientation determination, which appears to be free of such complications, is x-ray photoelectron diffraction (XPD) [3]. In this technique the angular dependence of the emission of relatively high kinetic energy (typically  $>500$  eV) electrons photoemitted from a core level is studied. By fixing the

angle between the incident x-radiation and the detector (which removes all atomic angular dependence from contributing directly to the measurement), the main variations of interest are due to the coherent interference of the directly emitted photoelectron wavefield with components of this wavefield elastically scattered by the surrounding atoms (photoelectron diffraction). At these high kinetic energies, only elastic scattering in the near-forward direction has substantial cross section, and because the scattering phase shifts for these high-energy forward scattering events are small ( $\ll \pi$ ) the scattering always reinforces the signal in the directions associated with those intramolecular bonds for which the emitting atom lies behind a scattering atom within the molecule relative to the photoelectron detector. The technique thus provides a method of measuring the directions of intramolecular bonds in real space.

Many adsorbed molecules adopt rather simple, high symmetry orientations on low-index single-crystal surfaces, so that most linear diatomic molecules (e.g. CO, NO, N<sub>2</sub>) usually adsorb perpendicular to the surface. The mercaptide (CH<sub>3</sub>S-) and methoxy (CH<sub>3</sub>O-) species, formed at surfaces of appropriate solids by the catalytic deprotonation of methyl thiol and methyl alcohol, have, however, been proposed to adopt tilted orientations on a number of surfaces on the basis of NEXAFS measurements. In the case of methoxy, O K-edge NEXAFS appears to indicate a tilted (by  $\approx 30\text{--}40^\circ$ ) conformation on both Cu (100) [4] and Cu(110) [5]. On Cu(100), however, a scanned-energy-mode photoelectron diffraction study has contradicted this conclusion [2], whilst C K-edge NEXAFS indicates that a substrate scattering effect is probably the cause of the misinterpretation of the O K-edge data, and that the molecule actually adopts an essentially perpendicular orientation on this surface [2]. However, XPD measurements of methoxy on Cu(110) do indicate tilted species on this surface, although the detailed interpretation differs from that of the NEXAFS data [6].

In the case of mercaptide, S K-edge NEXAFS from mercaptide on Cu(111) [7] and C K-edge NEXAFS from this species on Pt(111) [8] both indicate C-S bond tilt angles of order  $40^\circ$ . On Cu(111), however, S K-edge SEXAFS (surface extended x-ray absorption fine structure) has been interpreted as consistent with a perpendicular C-S bond [9]. Here we present XPD measurements from this mercaptide/Cu(111) system which clearly support the view that the molecule is not tilted in this case, indicating that the S K-edge NEXAFS must suffer from similar substrate scattering effects.

## 2. Experimental details and results

The experiments were conducted in an ultra-high vacuum (UHV) chamber equipped with facilities for low-energy electron diffraction, Auger electron spectroscopy, x-ray and ultraviolet photoelectron spectroscopy (UPS) as well as the usual ion bombardment cleaning and sample-heating facilities of a surface science spectrometer. Typical background pressures were in the low  $10^{-10}$  Torr region. The geometry of the x-ray source and its associated electron spectrometer is slightly unusual in order to optimise its performance for XPD in that the sample polar angle rotation is effected about an axis perpendicular to the axis of the electron spectrometer but in the plane defined by the incidence direction and this collection direction (figure 1). In this way this crystal rotation changes the polar angle of emitted electron collection, but keeps constant not only the angle between the collection and incidence directions, but also the incidence direction relative to the crystal surface. This reduces the influence of essentially instrumental factors on the measured polar angle scans of the emitted photoelectron flux, so that

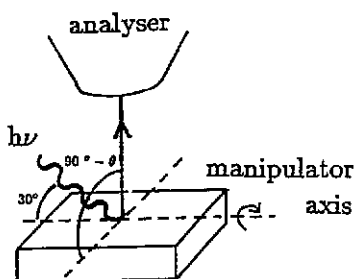
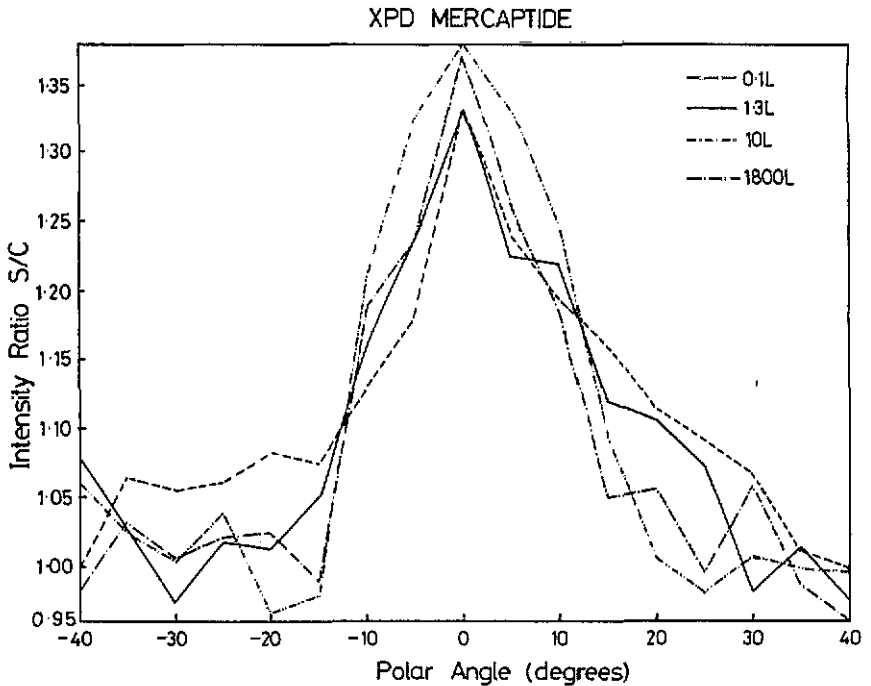


Figure 1. Schematic diagram of the experimental geometry for the XPD measurements of this study. Note that as the sample manipulator is rotated, the polar collection angle varies, but the incidence angle and the angle between the incident photons and the collection direction both remain constant.

only those factors specifically related to the changing polar emission angle should be measured, these are photoelectron diffraction and the role of the different inelastic scattering path lengths, which increase with increasing polar angle.

The Cu(111) sample was prepared by the usual combination of Laue x-ray scattering orientation, spark machining, mechanical polishing and *in situ* argon-ion bombardment and annealing cycles until XPS spectra indicated a clean surface and LEED showed an ordered ( $1 \times 1$ ) diffraction pattern. The formation of the mercaptide overlayer was effected by exposing the sample at room temperature to dimethyl disulphide,  $(\text{CH}_3\text{S})_2$ . We have shown previously using UPS and NEXAFS [10, 7] that this species is formed by such treatment and also by similar exposure to methyl thiol,  $\text{CH}_3\text{SH}$ , but the disulphide is considerably easier and safer to handle. XPD measurements involved successive measurements of the S 2p and C 1s photoemission peaks using Mg  $K\alpha$  radiation at a series of polar emission angles, typically from  $-40^\circ$  to  $+40^\circ$ , in steps of either  $5^\circ$  or  $2.5^\circ$ . The areas of these peaks were then evaluated and plotted against polar angle. Following the approach used in the pioneering work with this technique of Fadley and co-workers (e.g. [3]) we have concentrated on plotting the *ratio* of the S and C peaks, as this ratio should essentially remove all angular dependence factors other than photoelectron diffraction. Strictly, some energy dependent instrumental and inelastic scattering effects remain, but the ratio certainly suppresses much spurious variation in normal experiments. In fact we find in our geometry that only relatively weak underlying angular effects are seen, even in the raw peak area plots although there is a slight asymmetry about the surface normal emission direction present in the experimental data of figure 2 which violates the formal symmetry of the experiment and must be instrumental in origin; these effects are probably due to slight misalignments as the sample is rotated.

Figure 2 shows the results of these experiments in which the normalized S 2p/C 1s peak intensity ratio is plotted as a function of polar emission angle for four different exposures of dimethyl disulphide. Note that small misalignment effects led to weak ( $\leq 10\%$ ) variations in the underlying polar angle variation and in the absolute S/C peak ratios for different experiments, which have been removed by linear background subtraction and by normalizing all values to unity well away from normal emission. In addition, the lowest exposure experiment yielded very weak C 1s signals, so in this case the S 2p signal variation alone is plotted after a simple linear background subtraction and a similar normalization. It is clear that there is a strong photoelectron diffraction forward-scattering peak along the surface normal in all the data, indicating that the S-C axis lies perpendicular to the surface. One effect we were interested to investigate in these experiments was the role of surface coverage on these angular plots. It is certainly conceivable that at high coverages (the saturation coverage of mercaptide appears to be of the order of  $\frac{1}{4}$  to  $\frac{1}{2}$  monolayer) there may be steric intermolecular effects which might



**Figure 2.** Experimental results for the polar emission angle dependence of the ratio of the S 2p and C 1s photoemission intensity, normalized as described in the text, for CH<sub>3</sub>S- on Cu(111) following different exposures of the clean surface to (CH<sub>3</sub>S)<sub>2</sub>.

influence the molecular orientation. Most obviously this might force a tilted species into a more nearly perpendicular orientation, although in the case of CO on some FCC(110) surface it appears that at the highest (1 monolayer) coverage the CO molecules are forced to tilt away from their preferred perpendicular orientation by steric effects (e.g. [11]). In the present case, we find no evidence of any orientation coverage dependence; in fact we found that most of our exposures gave coverages close to saturation; the coverage based on the XPS signal was essentially identical for the 10 L and 1800 L exposures, and was only about 20% lower after the 1.3 L exposure (previous measurements indicating these saturation coverages to be in the 0.3–0.5 ML range [9]). However, after the 0.1 L exposure (which corresponded to approximately  $\frac{1}{4}$  of the saturation coverage or about 0.1 ML) the XPD results still show a perpendicularly oriented adsorbate, and indeed show no obvious XPD peak broadening, which might result from larger amplitude wagging vibrations in the absence of constraining near-neighbours.

### 3. Discussion and conclusions

The clear conclusion to be drawn from our results, that the mercaptide species adopts a perpendicular orientation on Cu(111) at all coverages, is consistent with the structural deductions of a previous SEXAFS analysis of the saturation coverage phase, but inconsistent with the conclusions of an earlier NEXAFS study. In the near-edge spectral region of XAFS it is known that structure can result from both intramolecular and substrate

electron scattering, and in the case of mercaptide (and of methoxy), which shows only a shape resonance of  $\sigma$ -symmetry, the rather broad peak resulting from this feature is difficult to separate in a reliable way from possible substrate scattering effects. The structural deductions from NEXAFS are particularly sensitive to any residual intensity at the energy of a shape resonance at the incident geometry for which the resonance should be symmetry forbidden, and residual substrate scattering features can be very misleading under these conditions, particularly for the broader  $\sigma$ -resonances. This same problem has been identified rather clearly in the case of methoxy on Cu(100) for which both C and O K-edge NEXAFS have been measured [2]. In this case the residual intensity at the  $\sigma$ -resonance energy is visible in the O K-edge spectrum (the oxygen bonding directly to the substrate), but not in the C K-edge spectrum. The C in the CH<sub>3</sub> group, of course, lies much further from the Cu substrate, so that substrate scattering effects are expected to be much weaker.

In contrast to these two cases, in which the original assignment of a tilted molecule was deduced from NEXAFS but is now believed to be attributable to a perpendicular species, there are at least two cases of methoxy and mercaptide for which this technique appears to have established a tilted species more reliably. In one of these (methoxy on Cu(111)), XPD results also indicate tilted molecules [6]; this surface is relatively 'rough' on an atomic scale, and the tilt could therefore be due to a bonding configuration that is locally symmetric (i.e. effectively perpendicular to a locally bonded Cu cluster). The other example, however, is more curious in that C K-edge NEXAFS from mercaptide on Pt(111) also indicates strong tilting [8]. Pt(111) is a close-packed, atomically smooth surface, and this result would imply a true adsorbate-substrate 'bent bond'. As has been remarked above, the C K-edge NEXAFS is not expected to be strongly influenced by substrate scattering, so this simple origin for misassignment is not possible. In view of our clear conclusion of perpendicular mercaptide on Cu(111), this Pt(111)/mercaptide system would seem worthy of further investigation.

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