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Local methylthiolate adsorption geometry on Au(111) from photoemission core-level shifts

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Abstract

The local adsorption structure of methylthiolate in the ordered Au(111)(√3x√3)R30º phase has been investigated using core-level-shift (CLS) measurements of the surface and bulk components of the Au $4f_{7/2}$ photoelectron binding energy. The amplitude ratio of the CLS components associated with surface Au atoms that are, and are not, bonded to the thiolate are found to be compatible only with the previously-proposed Au-adatom-monothiolate moiety in which the thiolate is bonded atop Au adatoms in hollow sites, and not on an unreconstructed surface, or in Au-adatom-dithiolate species.

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Despite the very many studies of self-assembled monolayers (SAMs) of thiolate molecules on Au(111) (e.g. [1, 2, 3, 4]), motivated by a range of practical applications including chemical and biochemical sensors, the structure of the thiolate/metal interface in even for the simplest system, namely the (√3x√3)R30º phase of adsorbed methylthiolate, CH_3S-, remains controversial. Until recently, all theoretical total energy calculations have favoured S headgroup atom occupation of hollow, bridge or off-hollow sites on an unreconstructed surface, while the only quantitative experimental structural determinations (using photoelectron diffraction [5]) and normal incidence X-ray standing waves – NIXSW [6]) are consistent only with an atop site. Recent evidence of adsorbate-induced reconstruction offers a potential solution to this dilemma, with two competing models based on Au-adatom-monothiolate [7] and Au-adatom–dithiolate [8] moieties, both of which involve local atop sites for the thiolate. A recent X-ray diffraction study provides some support for a complex mixed bridge-plus-dithiolate model generated by molecular dynamics calculations, but did not consider any other models [9].

In view of this absence of a definitive quantitative experimental surface structure determination, we present here the results of a simpler spectroscopic fingerprinting approach, namely the measurement of photoelectron core-level shifts (CLS), that has previously been shown [10] to be capable of identifying the local coordination site of an adsorbate on a surface in a qualitative fashion. We show that our results exclude adsorption on an unreconstructed surface, and clearly favour the Au-adatom-monothiolate model over that of the Au-adatom-dithiolate moiety.

It is well known that photoemission from the atoms in the surface layer(s) of an elemental solid may show a different core-level binding energy than emission from atoms in the bulk, due to differences in the structural and electronic environment. Moreover, if a surface atom is bonded to an adsorbate species, a different CLS is observed. Predicting the magnitude and sign of these shifts is complex, because they derive from a combination of initial (ground-state) and final (core-ionised) state effects. However, these shifts provide a spectral fingerprint of the differently-bonded surface atoms, and the relative intensities of their associated photoemission peaks are quantitatively related to

their relative occupancy on the surface. Thus, in the case of Rh(111)(√3x√3)R30°-CO [10], for example, one can readily distinguish between CO adsorption in the three-fold-coordinated hollow sites which would lead to all surface Rh atoms being bonded to CO, with none showing the core-level shift of the clean surface, and atop adsorption in which one third of the surface Rh atoms are bonded to CO and the remaining two thirds retain a core-level shift characteristic of the clean surface.

Here we present the results of the application of this method to the Au(111)(√3x√3)R30°-CH_3S (methylthiolate) surface phase, monitoring the core-level shifts of the Au $4f_{7/2}$ emission. Fig. 1 shows the five distinct local structural adsorption geometries considered here, namely adsorption on an unreconstructed surface in hollow, bridge and atop sites, plus the two competing reconstruction models. The Au-adatom-monothiolate moiety, with an Au adatom in a hollow site and the S-headgroup adatom atop this adatom, was proposed on the basis of NIXSW studies of longer-chain thiolates at high coverage [7]; the Au-adatom-dithiolate moiety has an Au adatom in a bridging site midway between two thiolate species in local atop sites, and has been identified in STM studies at very low coverages of methylthiolate [8]. For the ordered (√3x√3)R30° phase, with one thiolate species per surface unit mesh, the expected results of the CLS experiment are clear for most of these models. If we denote emission from surface Au atoms bonded to a thiolate as T, and surface-layer Au atoms not bonded to a thiolate as S, then simple counting of surface atoms leads one to expect the following S:T intensity ratios for these models: hollow, 0:3; bridge, 1:2; atop, 2:1; Au-adatom-monothiolate, 3:1. The one structure for which the application of these simple arguments is less clear is the Au-adatom-dithiolate model. In this case there are two different types of surface Au atom bonded to the thiolate species, namely the Au adatom (bonded to two thiolate species) and the surface layer Au atoms directly below the thiolates. If we label these two Au atoms as T_{ad} and T_S, respectively, and we note that a coverage of 0.33 ML of thiolate corresponds to a coverage of Au-adatom-dithiolate moieties of only 0.16 ML, then the ratio of these $S:T_{ad}:T_S$ should be 4:1:2; if these two distinct types of Au bonded to thiolate have the same CLS the S:T ratio is 4:3. Notice that it is not actually possible to form an ordered Au(111)(√3x√3)R30° phase with a coverage of 0.33 ML of thiolate species from the Au-

adatom-dithiolate model, but it has been suggested that the true structure has a high degree of disorder [9]; the implication is that sufficient vestige of (√3x√3)R30° ordering remains, but in considering this model we must assume a (2√3x√3) unit mesh.

One further complication in applying this simple analysis to adsorption on Au(111) is that the clean surface is reconstructed to a higher-density close-packed 'herring-bone' structure, while the thiolate adsorption lifts the reconstruction. We may therefore anticipate that the CLS associated with the surface component on the clean surface (S_C) may differ from the value associated with surface Au atoms *not* bonded to the thiolate on the thiolate-covered unreconstructed surface (S).

Our experiments were conducted at beamline MPW6.1 of the Synchrotron Radiation Source at the CLRC's (Central Laboratories for the Research Councils) Daresbury Laboratory. This beamline has been described in detail elsewhere [11]; the source is a multi-pole wiggler and is fitted with a grazing incidence grating monochromator and a surface science end-chamber equipped with the usual *in situ* sample preparation and characterisation facilities. A concentric hemispherical analyser (with the axis of the entrance lens at 60° to the incident photon beam in the horizontal plane) was used to measure the energy distribution curves (EDCs) of photoemitted electrons at fixed pass energy. The Au(111) crystal sample was cleaned *in situ* by the usual combination of argon ion bombardment and annealing cycles to produce a clean well-ordered (22x√3)rect. 'herring-bone' reconstructed surface as assessed by the synchrotron radiation X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy and LEED. The methylthiolate surface phase was formed by exposures in the range 8-20 × 10^{-6} mbar.s of dimethyldisulphide (CH_3S-SCH_3) vapour with the sample at room temperature. S 2p XPS measurements showed these exposures led to saturation coverage, whilst LEED showed the expected (√3×√3)R30° pattern. Much higher exposures (up to $3x10^{-3}$ mbar.s) were tested and yielded essentially identical photoemission spectra and LEED patterns, clearly indicating that our procedure led to saturation coverage. The Au $4f_{7/2}$ photoemission spectra were recorded at normal incidence, and thus at a polar emission angle of 60°, using a photon energy of 135 eV. This geometry, combined with

the associated kinetic energy of ~50 eV, close to the minimum in the attenuation length, leads to a very high degree of surface specificity. S 2p spectra were also recorded using a higher photon energy of 210 eV; no evidence of more than a single component S 2p photoelectron binding energy was seen, consistent with earlier reports [12].

To extract quantitative information on the CLS values and relative intensities, the Au $4f_{7/2}$ photoemission spectra were fitted by the computer program FitXPS2 [13] to a sum of Doniach-Sunjic lineshapes, convoluted with Gaussian functions, together with a low-order polynomial background. The upper panel of Fig. 2 shows a typical spectrum recorded from the clean Au(111) surface together with the two components to the fit corresponding to emission from the bulk (B) and clean reconstructed surface layer (S_C). The binding energy shift of the surface component is -0.34±0.02 eV relative to that from the bulk , in perfect agreement with the original report of this surface CLS which gave a value of -0.35 eV [14], and very close to the value of -0.31 eV found in a later high-resolution study [15]. The main difference between the spectrum of Fig. 2 and that of the original study is that here the surface component is larger in amplitude than that of the bulk. This is due to the very high degree of surface specificity in our experiment. The intensity ratio of the surface and bulk peaks is 2.67, implying an attenuation length of 6.5 Å. One feature of this spectral fit is a slightly larger value of the overall width of the surface peak relative to that of the surface peak, with FWHM (full-width half-maximum) values of 0.48 eV and 0.43 eV respectively, although it is unclear whether this difference is due to the Lorentzian and Gaussian contributions. This same effect and the uncertainty in fitting has been reported in a detailed study of Al 2p emission from Al(111), the enhanced width of the surface component being attributed to a combination of crystal field splitting and inhomogeneous broadening to be expected at the imperfectly-ordered surface [16]. The absolute value of the binding energy of the Au $4f_{7/2}$ bulk component is shown in Fig. 1 as 84.00 eV; small variations in this value (<0.10 eV) in a number of measurements were seen, but may be due to limitations in exactly defining the location of the Fermi level in measurements of the Fermi cut-off which were recorded after each Au 4f spectrum.

The lower graph of Fig. 2 shows the Au $4f_{7/2}$ photoemission spectrum after forming the $(\sqrt{3}x\sqrt{3})R30°$-CH_3S surface phase. Clearly the intensity at an energy corresponding to the S_C peak is reduced and new intensity appears at higher binding energy; this qualitative behaviour has been reported previously for thiolate adsorption on Au nanoparticles [17]. The spectrum can be satisfactorily fitted, as shown, by three components, B, S and T. In conducting this new three-peak fit, a number of spectral parameters were fixed. Most obviously, all the shape parameters and the absolute binding energy (to within a few meV) of the B component were fixed to the value obtained from the clean surface. In addition, the shape parameters of the two surface components, S and T, were constrained to have the same values as those of the clean surface component, S_C. The core-level binging energy shift values, relative to that of the bulk component, resulting from fits to a large number of different spectral measurements from separate surface preparations, were -0.23±0.02 eV for the S_T peak and +0.34±0.02 eV for the T peak. The surface-to-bulk peak area ratio S+T:B retains a value closely similar to that of the clean surface in the range 2.6-2.8. The integrated peak intensity ratio, S:T was 3.1±0.2, a value in excellent agreement with the expectation for the Au-adatom-monothiolate model. Clearly, this value is not compatible with any high-symmetry adsorption site on an unreconstructed surface.

For the Au-adatom-dithiolate model, as discussed above, one may expect three distinct surface components, S, T_{ad}, and T_S in the intensity ratio 4:1:2. The fact that we can fit the data satisfactorily by a bulk component and just two surface peaks does not, of course, exclude the possibility that an even better fit may not be achieved with more peaks, although the issue of uniqueness in the fitting becomes much more severe. However, the fact that just two surface components gives a good fit suggests that, if more peaks are present, at least two of them must have rather similar energies; i.e. one of our two surface peaks could itself comprise two components of closely-similar energy. In this case one might expect this unresolved pair of peaks to be represented by a single peak with an increased wider. To explore this possibility, we have therefore conducted additional tests in which the constraints on the widths of the two surface component peaks were relaxed. Slightly improved fits can be achieved in this way, with the following consequences: (i)

the T peak (but not the S peak) width increases by 0.12 eV; (ii) the S:T peak area ratio falls to 2.2±0.2; (iii) the surface-to-bulk peak area ratio, S+T:B, also falls to approximately 2.2. This alternative fit cannot be reconciled with the Au-adatom-dithiolate model. The only combination of peak components that could be compatible with this S:T ratio is if the S and T_{ad} components are unresolved, giving $S+T_{ad}:T_S=2.5:1$. In this case, however, it is the S peak that should have an enhanced width, not the T peak. It is also difficult to see how a decrease in the surface-to-bulk intensity ratio should *decrease* relative to the value of the clean surface as a result of adding Au adatoms to the surface component. A ratio of S:T of 2.0:1 is, of course, consistent with atop adsorption on an unreconstructed surface, but in this case there is no obvious rationale for either the T peak width change or the decrease in the surface-to-bulk intensity ratio. We therefore conclude that the slight improvement achieved by the less-constrained fit is simply a result of an increased number of fitting parameters, but has no physical significance. However, in view of this apparent correlation between peak widths and relative peak areas, we also ran further tests in which all peaks (B, S_c, S and T) were constrained to have the same widths (the optimum width parameter being determined by refitting the clean surface spectra. While this led to tolerable fits with different relative intensities of the bulk and surface peaks, the S:T ratio was found to retain the value of 3.0 found in our original fits. One further effect which might influence the measured intensity ratios of the component peaks is photoelectron diffraction (e.g. [18]). At the low electron energies used here the dominant effect is of strong backscattering; the resulting diffraction is sensitive to the emitter site, but this is the same for all the surface Au atoms (other than the adatoms). Forward scattering from the adsorbed S atoms can also occur, but is unlikely to significantly modify the intensity at the 60° polar angle of the measurement. Neither effect is therefore likely to change the measured relative intensities of the Au 4f signal from surface atoms by the large factors needed to lead to incorrect identification of the correct structural model.

Thiolate-induced changes in Au 4f photoemission have previously been investigated for longer-chain alkylthiols on both small particles and on Au(111). In the former case, adsorption appeared to quench the surface component, with the appearance of a thiol-

related peak at higher binding energy than the bulk component; no multi-component analysis of these complex adsorbate-covered surfaces was undertaken [19]. In the case of dodecanethiol on Au(111), the Au 4f spectrum after dosing appeared to show a strong shift of the surface component to within 0.06 eV of the bulk peak, but only a weak shoulder on the high binding energy side [15]. The shape of the resulting spectrum was thus quite different from that reported here. The clear implication is that the interface structure in this system, in which a (2√3x3)rect. phase commonly arises, differs significantly from that in the methylthiolate (√3x√3)R30° phase investigated here.

However, the clear conclusion of our results is that, of the different structural models considered from the ordered Au(111)(√3x√3)R30°-CH_3S surface phase, only that based on the Au-adatom-monothiolate moiety is consistent with these new spectroscopic data. This conclusion needs to be tested against experimental data from more quantitative structural methods. It is known to be consistent with the NIXSW data [6, 7], and is broadly consistent with the original photoelectron diffraction results [5] (which are sensitive primarily to the local adsorption site) but as yet this model has not been evaluated relative to data from surface X-ray diffraction [9]. We stress that the fact that these data from the high-coverage ordered 'standing-up' thiolate phase need not be, in any way, incompatible with the STM evidence for the Au-adatom-dithiolate moiety [8] at very low coverage.

Figure Captions

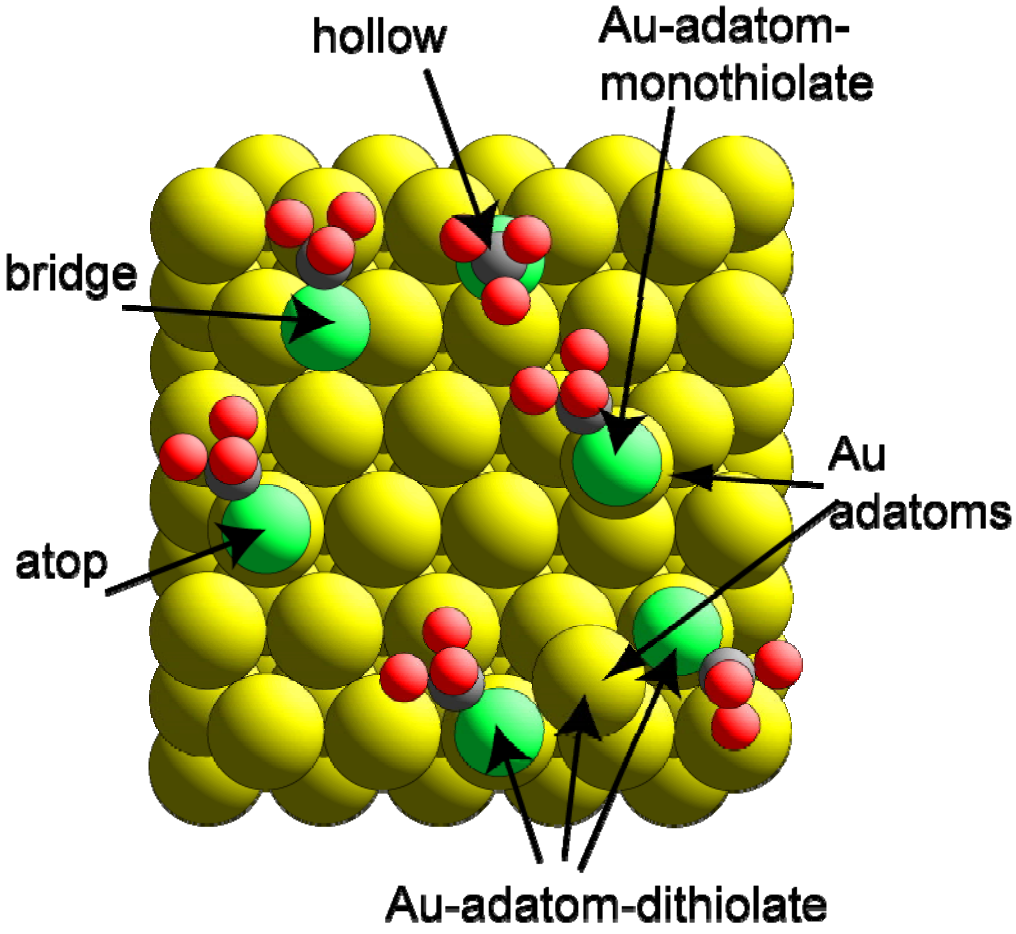

Fig. 1 Schematic plan view of the Au(111) surface showing the five different local adsorption structure models for methylthiolate discussed in the text.

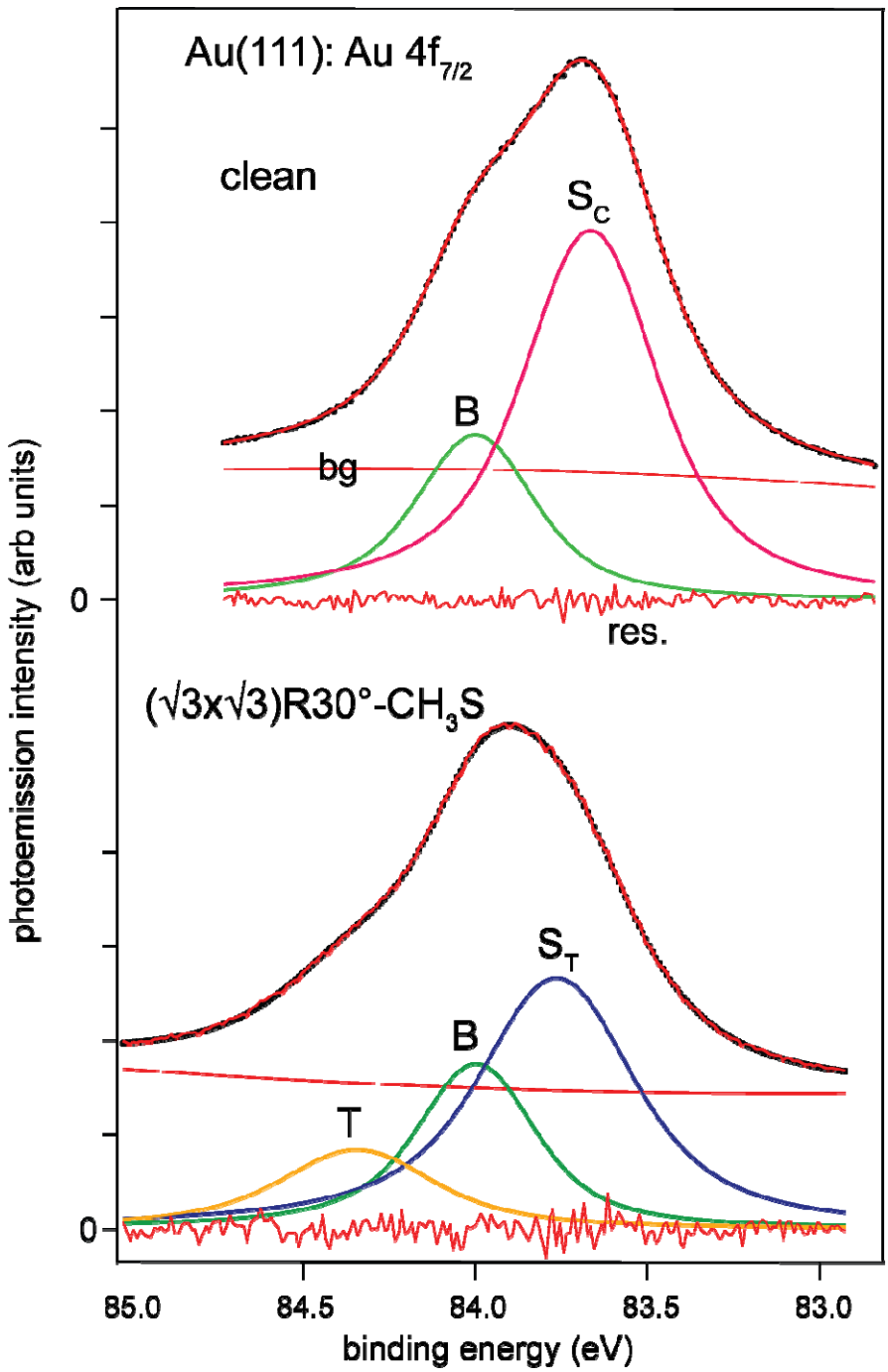

Fig. 2 Au $4f_{7/2}$ photoemission spectra from the clean Au(111)(22x√3)rect. surface and from the Au(111)(√3x√3)R30ºCH_3S adsorption phase. In each case the upper spectrum is the experimental data (individual points) and the spectral fit (continuous line) made up of a sum of the individual components peaks and the background (bg). At the bottom of each group is shown the residual in the fitting with an enhanced amplitude scale (x5).

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