Structural aspects of the interaction of methyl thiol and dimethyldisulphide with Ni(111)

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Abstract. A combination of near-edge and surface extended x-ray absorption fine structure (NEXAFS and SEXAFS), normal incidence x-ray standing wavefield absorption (NIXSW) and (laboratory-based) x-ray photoelectron spectroscopy and diffraction (XPS and XPD) has been used to investigate the local phases and associated structures resulting from the interaction of methylthiol (CH_3SH) and dimethyldisulphide (($CH_3S)_2$—DMS) with Ni(111). The interaction was followed by adsorbing at low temperature and observing the effects of sequential heating cycles to up to 373 K. At the lowest temperature DMS appears to be intact on the surface, but at slightly higher temperatures, up to at least 223 K, a second molecular species is formed which is also obtained by the thiol adsorption, even at 153 K. This is identified as methylthiolate (CH_3S-) and appears to be bonded (through the S atom) to the hollow sites on the surface with a S–Ni bondlength of 2.24 Å; essentially equal occupation of both (fcc and hcp) hollow sites is found. Both XAFS and XPD indicate that this species shows a substantial tilt angle of the S–C symmetry axis away from the surface normal; the situation is somewhat similar to that reported for the same species on Pt(111) on the basis of C K-edge NEXAFS and vibrational spectroscopy, and comparative S K-edge NEXAFS measurements for Pt(111) are also reported here. The tilted geometry found on both Ni and Pt surfaces contrasts with the perpendicular orientation found on Cu(111). Heating the Ni(111) surface to 373 K converts the thiolate species to a third state which we identify as atomic sulphur. Both SEXAFS and NEXAFS show that this final species has the same local geometry as that found in earlier studies of atomic S on Ni(111): in particular, while the S–Ni nearest-neighbour spacing is similar to that of the thiolate, the S in this phase appears to penetrate the top Ni layer.

1. Introduction

The interaction of sulphur-containing molecules with transition metal surfaces is of significant practical as well as academic interest for both positive and negative reasons. Because S acts as a poison for many heterogeneous catalysts, there is a need to develop desulphurization catalysts [1] as well as to understand the negative role of adsorbed S in other processes. In the case of thiols, there are many examples of partial decomposition at surfaces with the deprotonation of the –SH group to produce surface thiolates [1], an effect

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which is similar to the O–H bond scission at surfaces during interaction with alcohols. Of the relatively small number of quantitative structural studies of surface reaction intermediates, there have been a number of investigations centred on these thiolates [2–5] and alcoxides [6–15], and particularly on the smallest such species, methylthiolate (CH_3S–) [2–4] and the methoxy ($CH3O$–) species [6–15]. Most of these studies have centred around the orientation of the C–S or C–O bond relative to the surface normal, but there are also a very small number of quantitative determinations of the local adsorption site [3, 5, 10, 12, 14, 15].

Here we report the results of experiments which utilize surface extended and near-edge x-ray absorption spectroscopy (SEXAFS and NEXAFS), normal incidence x-ray standing wavefield absorption (NIXWS) and x-ray photoelectron spectroscopy and diffraction (XPS and XPD) to characterize the interaction of methylthiol, CH_3SH, and dimethyldisulphide, $(CH_3S)_2$ (DMS), with Ni(111), and to provide structural information on some of the surface species. The basic characterization of the surface chemistry yields results generally consistent with previous studies of this [16] and closely related systems [17] by other methods. The structural results are discussed in the context of previous determinations of thiolate and alcoxide structures on transition metal surfaces.

2. Experimental details

The experiments reported here were conducted in two different experimental chambers. SEXAFS and NEXAFS studies at the S K-edge and NIXSW measurements at two different {111} Bragg reflections were performed using the surface science chamber installed on beamline 6.3 of the Synchrotron Radiation Source (SRS) at the Engineering and Physical Science Research Council's (EPSRC) Daresbury Laboratory [18, 19]. The subsequent XPS measurements, including emission angle dependence x-ray photoelectron diffraction (XPD) experiments, were made at the University of Warwick in a VSW XPS instrument equipped with the usual twin-anode x-ray source. In both systems, the Ni(111) sample, initially prepared by Laue x-ray orientation, spark machining and mechanical polishing, was cleaned *in situ* by cycles of argon ion bombardment and annealing until the surface showed a well ordered (1 × 1) low-energy electron diffraction (LEED) pattern, and was clean as judged by XPS or Auger electron spectroscopy. The Daresbury chamber was fitted with a Physical Electronics double-pass cylindrical mirror analyser for electron spectroscopy when conducting the SEXAFS and NEXAFS experiments, and latterly with a VSW 100 mm mean radius hemispherical analyser when conducting the NIXSW experiments; the Warwick experiments also used a VSW 100 mm mean radius concentric hemispherical analyser, in this case fitted with multichannel detection. Dosing of the sample with the two reactant species, gaseous methylthiol and the vapour of DMS (which is liquid at room temperature), was effected by direct flooding of the chamber to pressures typically in the 10^{-8}–10^{-7} torr pressure range, with the sample held at low temperature; the exact lowest temperature available in the different experiments was in the range 90–150 K depending on the adsorbate and experimental chamber as described in the next section. All spectroscopic measurements were also made at these low temperatures, although the surface chemistry was followed by subjecting the adsorbed species to brief heating cycles to various temperatures before recooling and remeasuring. The experiments concentrated on relatively high (nominal saturation) initial doses, typically of 10–15 L, particularly because the principal objective of the work was to determine the geometrical structure associated with a surface thiolate species, and an earlier study based on thermal desorption and secondary-ion mass spectrometry (SIMS) [16] had indicated that at lower coverages both S–H and C–S bond scission may occur well below room temperature.
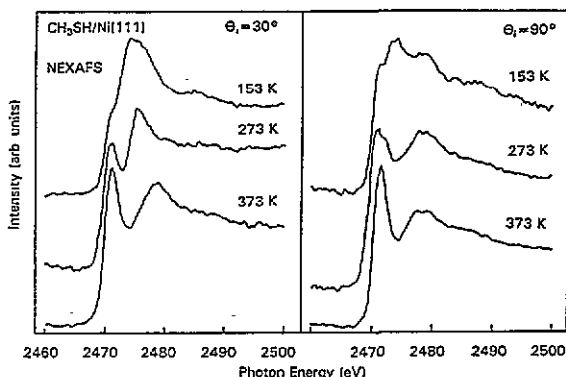
Figure 1. S K-edge NEXAFS recorded at normal and grazing incidence ($\theta_i = 90°$ and $30°$) from a Ni(111) surface exposed at 153 K to a nominal saturation dose of methylthiol and subsequently heated briefly to different temperatures.

SEXAFS and NEXAFS studies were conducted around and above the S K-edge at 2472 eV by monitoring the yield of S KLL Auger electrons at 2078 eV while scanning the energy of photons delivered by the ultrahigh-vacuum double-crystal monochromator from the SRS [18, 19]. The monochromator was operated using InSb(111) x-ray reflections for the XAFS studies. NIXSW absorption profiles for the S and Ni species were conducted at normal incidence to the (111) planes (i.e. incidence normal to the surface) and to the ($\bar{1}$11) planes (incidence at 70.5° to the surface in the appropriate azimuth). The appropriate Bragg condition for excitation of these standing waves occurs at a nominal photon energy of 3045 eV, which was obtained using the Ge(111) crystal reflections in the monochromator. Absorption was monitored through the S 1s and Ni 2p photoemission signals. XPS and XPD measurements at Warwick concentrated on the S 2p and C 1s photoemission peaks using Al Kα radiation, leading to photoelectron kinetic energies of approximately 1325 eV and 1200 eV respectively. Some comparative ultraviolet photoelectron spectroscopy (using He I and He II radiation) was also conducted in parallel with the laboratory-based XPS studies and provided a fingerprint of the initial fragmentation of the low-temperature condensed molecular species.

3. Results and interpretation

In this section we present the main experimental results and data analysis according to the techniques used. The NEXAFS, XPS and UPS data were first used to characterize the number and character of the adsorbed species. In addition, NEXAFS data have been used to provide some information on molecular orientations. Further structural information has then been provided by XPD (molecular orientation), SEXAFS (adsorbate–substrate registry and molecular orientation) and NIXSW (adsorbate–substrate registry).

3.1. Adsorption state characterization: NEXAFS, XPS

The basic characterization of the interaction of both species with Ni(111) is provided by the NEXAFS spectra of figures 1 and 2. Figure 1 shows S K-edge NEXAFS recorded at both normal incidence ($\theta_i = 90°$) and grazing incidence from a surface exposed to methylthiol at a sample temperature of approximately 153 K, and subsequently warmed to successively

higher temperatures. There is a clear change of the spectra between the initial low-temperature state and the spectra recorded after heating to the highest temperature of 373 K. At the intermediate temperature of 273 K, the spectra are similar to, but slightly different from, the higher-temperature spectra, and it appears that rather than a third intermediate state being present, this intermediate-temperature result can be understood in terms of an incomplete conversion of the low-temperature state to the high-temperature state.
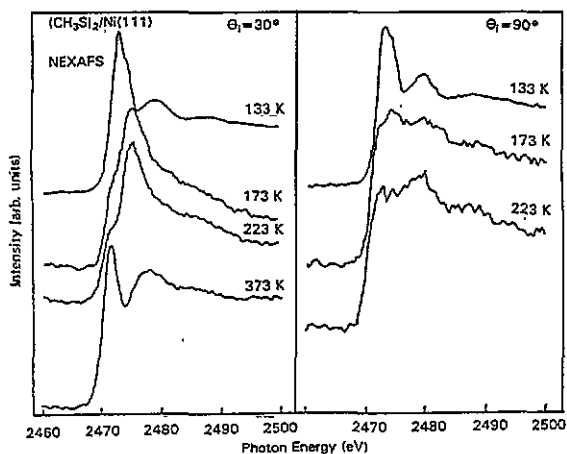

Figure 2. S K-edge NEXAFS recorded at normal and grazing incidence (θ_i = 90° and 30°) from a Ni(111) surface exposed at 133 K to dimethyldisulphide and subsequently heated briefly to different temperatures.

A similar set of S K-edge NEXAFS spectra recorded after exposing the Ni(111) surface to DMS is shown in figure 2. Comparison with the data of figure 1 indicates that the same species are present on the surface after heating to 153–173 K, or to 373 K, independent of which molecule initially interacts with the surface. For the DMS experiments, however, initial exposure at a slightly lower substrate temperature of 133 K was achieved, and in this case a significantly different NEXAFS spectrum is obtained.

On the basis of these spectra we propose three distinct surface species. At 133 K following DMS exposure, a molecular state which is probably intact DMS is present on the surface. At 373 K, essentially complete conversion to atomic sulphur is achieved, while at the intermediate temperatures, a common molecular species is produced from both reactant molecules: this intermediate is proposed to be methylthiolate, CH_3S-, produced by S–S bond scission of DMS, or by deprotonation of methylthiol. This initial set of assignments is consistent with the earlier investigation by Castro and White [16] of methylthiol interaction with Ni(111) conducted using TPD (temperature-programmed desorption) and SIMS. In particular, their TPD spectra indicated that the initial surface deprotonation of the thiol occurred at a sample temperature of 121 K. Moreover, an earlier ultraviolet photoelectron spectroscopic (UPS) study of the interaction of both molecules with Ni(100) [17] indicated that decomposition of the thiol to the thiolate occurred at a sample temperature of 110 K or less, whereas the first stage of DMS decomposition did not occur until a temperature of 144 K was reached.

Further evidence for this general picture is provided by XPS and UPS measurements of the effect of exposing Ni(111) to DMS at an even lower sample temperature (95 K) followed by briefly heating to successively higher temperatures. S 2p and C 1s XPS data are shown in figure 3. The S 2p shows a clear shift to lower binding energy by approximately
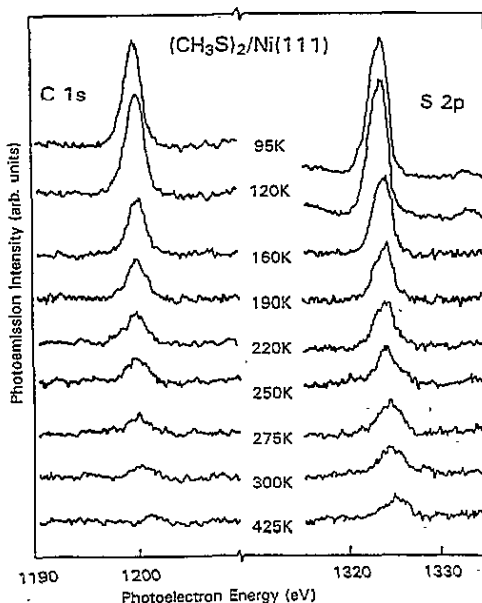
Figure 3. Al Kα C 1s and S 2p XPS spectra recorded from a Ni(111) surface exposed at 95 K to 10 L of dimethyldisulphide and subsequently heated to different temperatures.

0.7 eV between the spectra recorded after heating to 120 K and 160 K, and a further shift of an additional 1.0 eV which is complete after heating to 425 K but is already starting to contribute to the spectrum after heating to 250–273 K. By contrast the C 1s spectrum shows no significant shift in binding energy until the higher temperatures (most notably 300 K or more) are reached. Both sets of spectra can be understood in terms of S–S bond scission and thiolate formation (leaving the C–S bond intact) at around 140 K, and further decomposition leading to chemisorbed S plus some chemisorbed C or CH_n species at the highest temperatures. Note that intensity changes in these XPS spectra also indicate that partial desorption accompanies both dissociation steps; in the case of the initial low-temperature transition, it is probable that the initial DMS film comprises more than one monolayer.

Although these techniques provide a rather clear identification of the three distinct surface phases of intact molecule, molecular intermediate (thiolate) and atomic sulphur, we should also mention that a very recent independent study [20] which came to our notice during the course of preparing this manuscript leads to similar conclusions but with the key difference that they believe there are two different methylthiolate species formed, with a transformation from one to the other occurring as the sample is heated through the temperature range of approximately 200–220 K. They resolve the two states by high-resolution soft XPS, and through differences in relative intensities of vibrational modes seen in electron energy loss spectroscopy, and propose different orientations and local bonding sites may distinguish the two species. We have no evidence to distinguish these states, but have concentrated our studies at the low-temperature end of the stability range of the thiolate to avoid possible dissociation to atomic S. Our results are therefore essentially devoid of quantitative information concerning a possible higher-temperature thiolate.

3.2. NEXAFS and XPD: molecular orientation information

In principle, at least, some structural information is available from the NEXAFS data of figures 1 and 2. Although quantitative interpretation of these data in terms of an adsorbate–substrate site registry is difficult, the orientation of molecular species can be obtained from the polarization angle dependence of NEXAFS spectra providing that clear identification of the symmetries of the final states involved in the excitation can be made [21]. In order to make these identifications we can draw on comparisons with NEXAFS from closely related systems, but must first establish how many peaks we need to consider.

The low-temperature (153 K) S K-edge spectra of figure 1 produced by methylthiol exposure appear to be representative of the thiolate species; they are essentially identical to those produced by DMS exposure followed by heating to 173 K, but the signal-to-noise ratio is somewhat better. If we first consider the grazing incidence spectrum, we note that there is a shoulder on the leading edge which lies below (i.e. at a lower absorption cross-section than) the higher-energy continuum: this suggests that there is actually a peak at approximately 2470.5 eV which lies below the true continuum absorption edge about 1 eV higher in photon energy. (Notice that a correct location of the continuum edge, and particularly whether a peak lies above or below the edge, can be crucial to a correct determination of the polarization dependence of the amplitude of the peak, although this will not prove to be important for our present purposes.) A second clear broad peak, which we assume to be above this edge, is centred at about 2475 eV. Inspection of the normal incidence spectrum, however, shows that this broad feature may be comprised of two peaks, which in the normal incidence spectrum are seen at approximately 2473.5 eV and 2477.5 eV. Even without careful curve fitting, however, it is clear that the feature at 2473.5 eV shows a significant polarization angle dependence, and that the other two features vary much more weakly with polarization direction. A comparison with similar S K-edge spectra for gas phase methylthiol [22] and methylthiolate [23] on Cu(111) indicates that this peak can be attributed to a σ_{C-S} shape resonance. By contrast, we assign the other two features of the thiolate spectrum to substrate scattering effects. Note that a strong substrate scattering feature at the absorption edge (a 'white line') is characteristic of atomic sulphur adsorption NEXAFS spectra—an example is the NEXAFS spectra of figures 1 and 2 taken after heating well above room temperature; these spectra are essentially identical to those published in studies of atomic S adsorption on Ni(111) [24, 25], a fact which strongly reinforces our identification of this high-temperature state as atomic S.

The attribution of the main polarization-dependent NEXAFS peak to a σ-resonance means that we can use this polarization dependence to evaluate the C–S bond angle. For a resonance of this symmetry, the amplitude should vary as $\cos^2 \Theta$, where Θ is the angle between the C–S symmetry axis and the A-vector of the incident x-radiation. If the C–S axis were to be perpendicular to the surface then we would have $\theta_i = \Theta$, and the amplitude of this feature at normal incidence should be zero. The fact that a significant residual intensity remains implies a tilted C–S axis. To determine this tilt we assume that the species is tilted in at least three symmetrically equivalent azimuths to reflect the symmetry of the substrate; the residual intensity at normal incidence relative to that at 30° grazing incidence then yields a C–S tilt angle relative to the surface normal of approximately 30°. The random statistical error on this quantity is no larger than ±10°, but there can be significant systematic errors. In particular, when using NEXAFS spectra based on the absorption edge of the atom within the molecule which bonds to the surface, significant substrate scattering features can overlap the intramolecular resonances; in an excitation geometry in which the intramolecular resonance is symmetry forbidden, such features can lead to spurious conclusions of symmetry-breaking

tilt angles. This problem has already been found to occur in the case of a similar σ resonance signal from the O K-edge of the methoxy species (CH_3O-) on Cu(100) [6, 10], and indeed for S K-edge data from methylthiolate on Cu(111) [22, 3, 11]: in both cases, tilt angles of about 30° obtained from NEXAFS were subsequently shown to be incorrect, and the species were determined to be untilted.
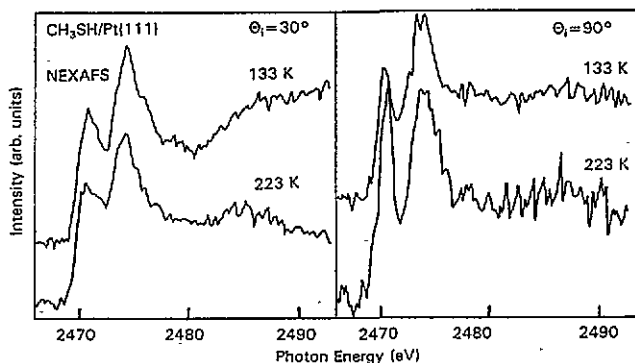

Figure 4. S K-edge NEXAFS recorded at normal and grazing incidence ($\theta_i = 90°$ and $30°$) from a Pt(111) surface exposed at 133 K to a nominal saturation dose of methylthiol and after subsequently heating briefly to approximately 223 K. These two conditions have previously been found to yield surface methylthiolate and thioformaldehyde species respectively [2].

In this regard we should also present briefly some comparable S K-edge NEXAFS data obtained from Pt(111) surfaces exposed to methylthiol at low temperatures and heated in a similar fashion. These data are shown in figure 4. The NEXAFS spectra are dominated by two peaks at essentially identical energies to those identified on Ni(111) (figure 1) as a substrate scattering pre-edge feature and the σ_{C-S} resonance. Vibrational spectroscopy and C K-edge NEXAFS from work on this same system [2] indicate that at the lower interaction temperature (133 K) the surface species is methylthiolate, whereas heating to higher temperatures produces a thioformaldehyde (CH_2S-) surface species; the temperature for this latter transformation appears to have been above 255 K in the earlier work [2], although our measurements indicate a somewhat lower temperature transition. There are two clear differences between the lower-temperature (methylthiolate) spectrum of figure 4 taken from Pt(111), and the equivalent Ni(111)-spectra of figure 1. Firstly, the Pt spectra show significantly stronger (pre-) edge peaks, but the absence of strong polarization dependence is retained. In addition, however, the σ-resonance, which shows a significant dependence on polarization angle for Ni(111), is almost independent of polarization angle on Pt(111). A total absence of polarization angle dependence is expected for a tilt angle equal to the 'magic angle' of 54.7°; in fact the small angular dependence shown in the spectra of figure 4 indicate (ignoring the possible effects of substrate scattering) a C–S bond tilt angle for methylthiolate on Pt(111) of 45°, identical to that obtained in the earlier C K-edge NEXAFS experiment [2] (for which substrate scattering effects can be expected to be much weaker). Indeed, the implied somewhat larger tilt angle for the thioformaldehyde species given by the S K-edge NEXAFS of figure 4 is also consistent with the results of the C K-edge NEXAFS [2].

Of course, the consistency of the S and C K-edge NEXAFS for these strongly tilted species on Pt(111) does not prove the correctness of the tilt angle inferred for methylthiolate on Ni(111) on the basis of S K-edge data alone. Nevertheless, visual comparison of the spectra of figures 1 and 4 reinforces the quantitative deduction that methylthiolate is
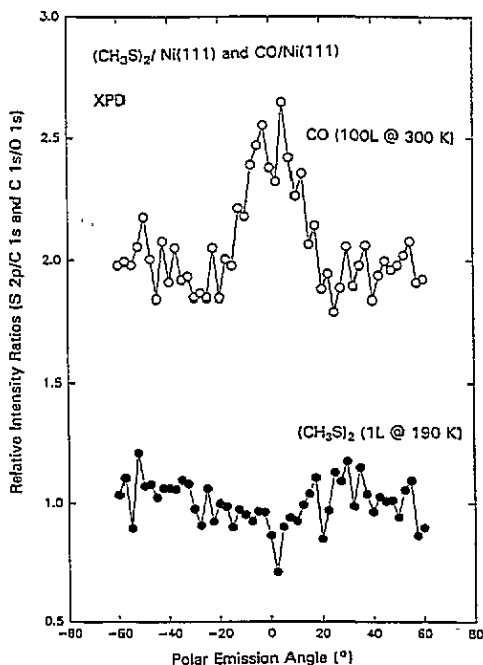
Figure 5. Angular dependence of XPS signals (XPD) from methylthiolate on Ni(111) produced by DMS exposure, and from CO adsorbed on the same surface. For the thiolate the signal plotted is the ratio of the S 2p to C 1s signals; for CO this is replaced by the C 1s to O 1s ratio.

significantly less strongly tilted on Ni(111) than on Pt(111).

Although the species of greatest interest from the point of view of the surface chemistry is the thiolate which is the reaction intermediate, we should also note that the polarization dependence of the NEXAFS from the low-temperature DMS phase should provide some orientational information on this adsorbed molecule. In fact, as may be seen in figure 2, there is little change in the NEXAFS from this species when the incident x-ray direction is changed. The most probable assignment of the dominant peak at the edge (at approximately 2470.5 eV) is the σ_{C-S} resonance—the shift in energy relative to the thiolate can be attributed to a chemical shift in the threshold binding energy. It is possible that the second peak at approximately 2478 eV is associated with a σ_{S-S} final state, but there is no clear basis for any assignment. The overall implication of the lack of polarization angle dependence, of course, is either that the molecules are randomly oriented, or that the key symmetry axes are oriented relative to the surface normal by the magic angle of 54.7°. For a single monolayer of DMS, we might expect the molecule to 'lie down' with its S–S axis approximately parallel to the surface, although this could leave the C–S bond directions in a mixture of orientations. For a multilayer, of course, a more random, 'orientationally amorphous' structure could be envisaged, but on the basis of the relative x-ray absorption edge jumps, we estimate the coverage studied to be only about 2–3 ML. We must conclude, therefore, that either strongly tilted or mixed orientation DMS species are involved. This statement is most clear for the C–S bonds because of the relatively reliable σ_{C-S} peak assignment; the S–S orientation may be more reliably deduced from the SEXAFS as discussed in the next section.

A far less ambiguous but somewhat less general method of determining adsorbate

molecular orientations is provided by the technique of x-ray photoelectron diffraction. At high ($\gtrsim$500 eV) photoelectron kinetic energies, atoms scatter electrons in a predominantly forward direction, and peaks in the angular distribution of high-energy photoelectrons emitted from atoms within an adsorbed molecule can be attributed to emission along forward-scattering intramolecular bond directions [26–28]. In order to obtain an independent measurement of the S–C bond orientation for methylthiolate on Ni(111), we have therefore made measurements of the angular distribution of the XPS peaks of figure 3 from a surface exposed to DMS at low temperature and subsequently heated briefly to 160 K. The results of these measurements are shown in figure 5 in the form of the polar angle dependence of the ratio of the S 2p to C 1s emission intensities, normalized to an average value of unity well removed from normal emission. The normalization to the C 1s signal introduces some additional noise, but removes most of the instrumental angular effects. Because the C 1s signal cannot be forward scattered (except from the very weakly scattering H atoms), its angular dependence is not expected to show any XPD effects. For comparison, figure 5 also shows the results of a similar experiment on CO adsorbed on the same Ni(111) surface, in this case plotting the ratio of the C 1s to O 1s photoemission intensity. The CO molecules are well known to adsorb with their C ends bonded to the surface and the C–O axis perpendicular to the surface, and this leads to a substantial forward scattering of the C 1s photoelectrons at the O atoms in the C–O axis direction: the XPD data thus shows a clear peak along the surface normal defining the molecular axis. By contrast, no such peak is evident in the thiolate XPD. This clearly indicates that the S–C axis is not perpendicular to the surface. For a tilted species, we expect an XPD peak along the intramolecular axis, but we must also recognise that, on a highly symmetric surface, a range of azimuthal orientations of the tilt are equally probable. In the case of the 3m symmetry Ni(111) surface, at least three such equivalent azimuths must be involved, but we also note that on this 'atomically smooth' surface, it is quite possible that the azimuthal angle of the tilt is random: indeed, it is likely that the tilted species may rotate freely. Averaging over all such possible tilts leads to a strong attenuation and broadening of the XPD forward-scattering peak to be seen in any specific azimuth. The absence of an observable forward-scattering peak is therefore clearly attributable to a tilted species, but the exact limits of the possible tilts are not very well defined. In fact the XPD data of figure 5 appear to show a broad minimum along the surface normal, with a faint indication of a weak peak around +30°, but with the signal at negative polar angles rising to a plateau around −40°. It is clear that the signal-to-noise ratios do not allow us to make any positive assignment of a definite tilt angle; if, on the other hand, we accept that there is no evidence for any forward-scattering peak(s) in the data we estimate that, at the measured signal-to-noise level, the tilt angle should be not less than 30°. Either of these conclusions is broadly compatible with the NEXAFS result for the tilt angle.

3.3. SEXAFS

Of the methods we have applied in this study, only SEXAFS and NIXSW are capable of determining the adsorbate–substrate registry in these adsorption systems, and the information given by the two methods is somewhat complementary. In SEXAFS the primary information is the nearest-neighbour bondlengths, while additional information may include the bondlengths of more distant neighbours as well as bond directions relative to the surface normal. S K-edge SEXAFS were recorded at both normal and grazing incidence from the three distinct surface phases which we have so far identified as molecular DMS, methylthiolate and atomic sulphur. A set of raw spectra from each of these states at each

incidence angle is shown in figure 6. Notice that in the case of the thiolate and atomic S states, data were taken from surfaces prepared by both DMS and methylthiol reaction, with no significant differences being seen. One experimental difficulty experienced in collecting the SEXAFS data was a tendency to get a slight spill-over of the incident radiation onto the Mo sample holder, with attendant appearance of the Mo L_2 absorption edge in the spectrum. By careful alignment of the sample and beam, this effect was reduced to a small peak (much narrower than the sample EXAFS) on the normal incidence spectra alone, and this was removed from the spectra prior to processing by treating it as a noise spike. The raw SEXAFS spectra taken from the thiolate and atomic S states are shown in figure 6: what is immediately obvious from these raw data is that, in addition to pronounced changes in the near-edge region as discussed above, there is also a significantly larger-amplitude SEXAFS in the atomic S spectra than in the data from the molecular adsorbates, particularly at normal incidence. This must be attributed to the atomic sulphur chemisorption state having either a higher-coordination Ni neighbour, a different local geometry, lower Debye–Waller factors or some combination of all three.
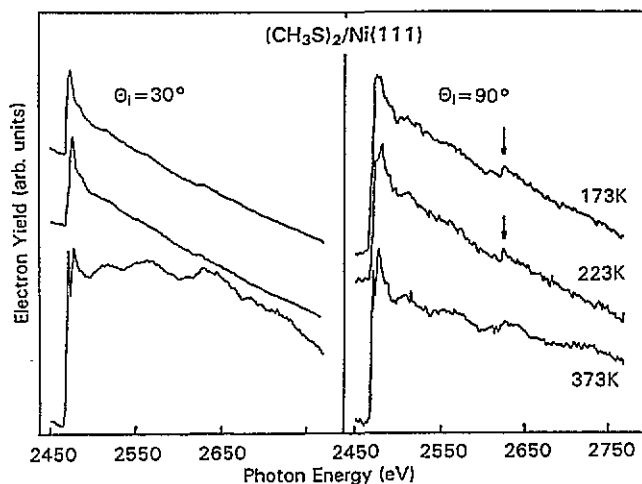

Figure 6. S K-edge SEXAFS spectra in their 'as-recorded' state at grazing and normal incidence conditions ($\theta_i = 30°$ and $90°$) from a Ni(111) surface exposed to DMS at low temperature and then heated to either 173 K or 373 K to produce the thiolate and atomic sulphur adsorption states. The arrows on the normal incidence spectra indicate a feature associated with the Mo L_2 absorption edge from the sample holder as discussed in the text.

In order to obtain quantitative information from these data, the fine-structure functions were extracted in the usual way and subjected to fitting by model calculations using the EXCURV suite of computer programs developed for Daresbury Laboratory [29]. In view of the quality of the data, no attempt has been made to fit the data to a large number of scattering shells: fits concentrated on only one or two scattering shells, and the primary objective was to establish the absolute near-neighbour shell distances around the S absorbers, and the polarization angle dependence of the relative effective number of scatterers in each shell. The experimentally derived fine-structure functions and representative fits to them are shown in figure 7 for the thiolate and atomic sulphur states.

In the case of the SEXAFS data from the surface thiolate, the dominant first-shell contribution is found to be from Ni, although significant improvements in the quality of the fits, particularly at low photoelectron momentum, are achieved by adding a C scatterer shell.

The Ni–S nearest-neighbour distance is found to be 2.25 ± 0.04 Å, while the C–S distance is significantly less reliable, but is found to be in the range 1.82–1.96 Å, generally consistent with its distance in methylthiol (1.81 Å) [30]. The S–Ni nearest-neighbour distance is very similar to that found in chemisorbed S phases on Ni surfaces, as we discuss below. Further information on the structure is obtained from the polarization angle dependence of the SEXAFS amplitudes. For the Ni shell, the grazing to normal incidence ratio was found to be 2.6 ± 0.7. For adsorption in the principal high-symmetry adsorption sites of an unreconstructed Ni(111) surface with a nearest-neighbour distance of 2.25 Å, this ratio is predicted to be infinite (atop), 3.6 (bridge) or 2.4 (hollow). Clearly the experimental result agrees well with the hollow site, and we can exclude the other high-symmetry sites. For the C backscattering shell, the grazing to normal incidence amplitude ratio is found to be 1.3. This implies a C–S bond axis relative to the surface normal of some 50°; the errors involved in this second-shell information are difficult to assess very precisely, because its contribution is weak and is concentrated only in the low energy part of the SEXAFS spectrum. For bond angles close to the 'magic angle', a given fractional error in the measured polarization dependence leads to much smaller errors in the bond angle, but in the present case an error of as much as 50% in the polarization dependence is possible. This would lead to an angular precision of approximately $\pm 10°$. A S–C bond angle relative to the surface normal of about 40° is therefore consistent with both the SEXAFS and NEXAFS conclusions as well as the XPD data.

In the case of the SEXAFS data from the high temperature atomic sulphur state, the data are well fitted by a single Ni shell with a S–Ni nearest-neighbour distance of 2.26 ± 0.03 Å, and a grazing to normal incidence amplitude ratio of 1.0 ± 0.2. Clearly this value is incompatible with any of the simple adsorption sites on an unreconstructed surface mentioned above. Specifically, this ratio implies an average S–Ni bond angle relative to the surface of 54.7°, placing the S too low on the surface to be compatible with any simple overlayer site. This result is, however, perfectly consistent with SEXAFS studies of the $(5\sqrt{3} \times 2)$rect. phase produced on Ni(111) by heating a surface after exposure to H_2S, and has been attributed to S penetration into a reconstructed top layer of the surface [24, 25, 31, 32], a conclusion which further reinforces the idea that the surface phase produced in our experiments by the highest temperature treatments is essentially an atomic sulphur chemisorption state.

SEXAFS data were also recorded from the low temperature DMS species, and the fine-structure functions are shown in figure 8. Quite reasonable fits to these data were achieved using only a single S nearest-neighbour shell: including a Ni scattering shell, in particular, led to no significant improvement in the quality of the fits. The S–S nearest-neighbour distance obtained in these fits was 1.98 ± 0.02 Å for both spectra, consistent with appropriate S–S bondlengths of, for example, 2.04 Å in S_2Cl_2 [30]. This provides further evidence that this low-temperature adsorption state is intact DMS, with the dominant electron backscatterer to the S atoms being the adjacent nearest-neighbour S. The very similar amplitude of the SEXAFS recorded at different polarization angles from this state shows clearly that the effective coordination number is only weakly dependent on polarization angle: we deduce a grazing to normal incidence ratio of 1.2 ± 0.3, which would imply an average S–S bond angle relative to the surface normal of approximately $50 \pm 5°$. This conclusion reinforces the result implied by the NEXAFS data that there is some significant average tilting of the molecule, although we cannot exclude the possibility that the first layer does have a S–S bond nearly parallel to the surface and that the apparent average tilt arises from the contribution of differently oriented molecules in the second (and third) layers.
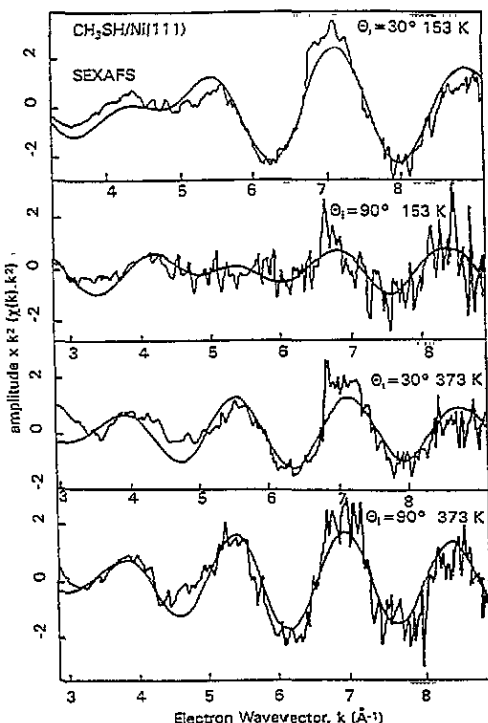
Figure 7. S K-edge SEXAFS fine-structure functions at normal and grazing incidence from the thiolate (153 K) and atomic sulphur (after heating to 373 K) states on Ni(111) obtained from raw data as shown in figure 6. The smooth-line fits are the results of simulations as described in the text.
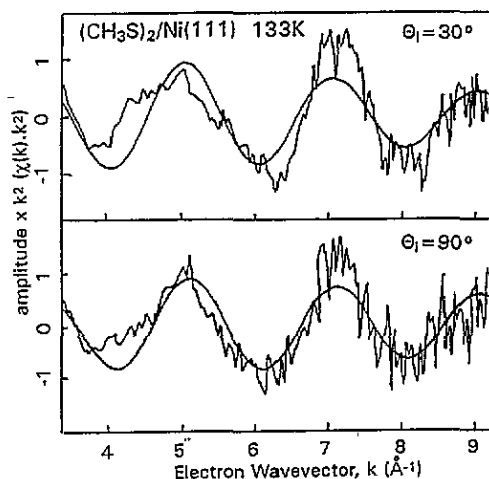
Figure 8. S K-edge SEXAFS fine-structure functions at normal and grazing incidence from the low-temperature (133 K) molecular DMS state on Ni(111); the smooth-line fits are the results of simulations based on a single S scattering shell as described in the text.

3.4. NIXSW

The NIXSW method is a variant of the usual standing x-ray wavefield method which is especially effective in the study of normal metal crystals which have a mosaicity too poor to allow the standard method to be used [33, 34]. The basic information to emerge from the technique is the layer spacing of an adsorbate atom relative to some set of scatterer planes of the underlying bulk crystal. The technique involves the measurement of the relative absorption at an adsorbate atom site of the x-ray standing wavefield established in a Bragg reflection from the substrate: this absorption is measured as a function of the exact scattering condition by scanning the photon energy through the Bragg condition, and the resulting absorption profile is fitted by two structural parameters, the coherent position and the coherent fraction. In the case of a simple single atomic adsorption site, the coherent position is the adsorbate–substrate layer spacing, and the coherent fraction (which in this case will be close to unity) is a measure of the degree of static and dynamic disorder. A fuller discussion of the structural interpretation of these parameters is given elsewhere [35].

In the present case, our objective is to establish the adsorption site of the S atom in the thiolate species relative to the Ni(111) substrate, by measuring the XSW absorption profiles at the (111) and ($\bar{1}$11) Bragg reflection conditions. Typical experimentally measured
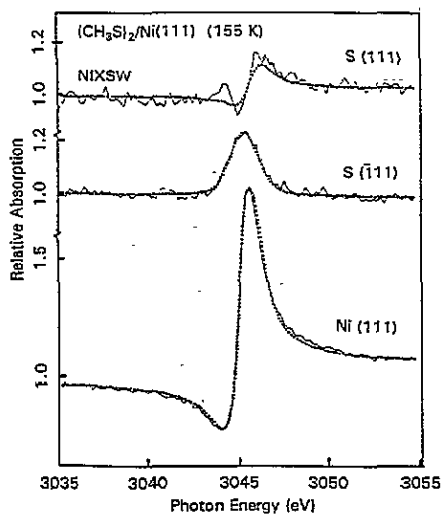
Figure 9. NIXSW absorption profiles around the (111) and ($\bar{1}$11) Bragg reflection conditions from thiolate on Ni(111) produced by dissociation of DMS. The upper curves show the S absorption signal for both reflections, while the lower curve shows the Ni absorption signal for the (111) reflection only; the Ni absorption signal at the ($\bar{1}$11) condition is essentially identical. The dotted lines represent fits to the experimental data using coherent position and fraction values as quoted in the text.

profiles are shown in figure 9, together with the fits used to establish the associated structural parameters. In particular, the figure shows the S absorption profiles for both reflections, and the Ni absorption profile for the (111) reflection (the Ni profile for the ($\bar{1}$11) reflection is essentially identical). As in our previous applications of this method, the Ni (substrate) profile was fitted by adjusting the non-structural parameters of the absolute energy and the energy broadening, and the S absorption profiles were fitted using these same non-structural parameter values, but fitting the coherent position and coherent fractions. The structural parameter values obtained in this way were, for the (111) and ($\bar{1}$11) reflections respectively: coherent positions, 1.63 ± 0.10 Å, 1.63 ± 0.15 Å; coherent fractions, 0.58 ± 0.10 and 0.25 ± 0.10. If we assume that the (111) coherent position can be interpreted as the S to bulk Ni layer spacing for a single site, one can calculate the coherent position values to be expected in the ($\bar{1}$11) reflections for the atop, hcp and fcc hollow sites as 0.54 Å, 1.22 Å and 1.90 Å. Evidently, none of these values match the experimentally determined coherent position. A further possibility, however, is that both fcc and hcp hollow sites are occupied equally; in this case the coherent position for the ($\bar{1}$11) reflection would be the mean of the individual sites; i.e. 1.57 Å, in agreement with the measured experimental value. In this case, however, the coherent fraction to be expected for the ($\bar{1}$11) reflection is reduced by a factor of two relative to that expected for individual sites [35]. Thus, if we interpret the measured coherent fraction of the (111) reflection (0.58) as being due to some form of disorder of the S atoms, the expected coherent fraction for the ($\bar{1}$11) reflection should be 0.29, in good agreement with experiment. While this provides a rationale for the very low ($\bar{1}$11) coherent fraction, the value for the (111) reflection is surprisingly low. The origin of the implied static or dynamic disorder perpendicular to the surface is far from clear. Nevertheless, the basic site assignment provided by the NIXSW data is in agreement with, but enlarges upon, the conclusions derived from the SEXAFS data.

4. General discussion and conclusions

The information concerning the basic characterization of the interaction of DMS and methylthiol with Ni(111) which emerges from this study is entirely consistent with previous characterization of the interaction of both species with Ni(100), and methylthiol with Ni(111). In particular, both molecules react at temperatures of 150 K or greater to form a surface methyl thiolate species, while heating to higher temperatures (above about 250 K) leads to further dissociation, with atomic sulphur being left on the surface, apparently with some coadsorbed C (or possibly, within the constraints of our measurements, CH_n species). Below about 140 K DMS remains intact on the surface, while we know only that methylthiol is not intact for sample temperatures above 153 K.

Structural studies of the chemisorbed S state produced by the highest-temperature treatments are also consistent with a local (reconstructed) structure similar to that of the Ni(111)($5\sqrt{3} \times 2$)rect.–S structure [24, 25, 31]. We did not make any LEED measurements of any of the adsorption phases because our previous experience indicated that these S-containing molecules are very sensitive to electron beam damage, so we do not know whether the S phase formed shows any long-range order.

In the case of the adsorbed intact DMS species at low temperature, the results are unable to identify any well defined local adsorption site, and indicate no single simple molecular orientation although it appears that both the S–S and S–C bond angles are, on average, well displaced from both the surface and the surface normal; this may be a result of different geometries in the two to three layers of the phase studied, but may also be due to an intrinsically low-symmetry orientation for the molecule.

The most interesting new data concern the thiolate species. We find that the SEXAFS data are consistent with this species being bonded to the surface by the S atoms which occupy simple threefold symmetric hollow sites on an unreconstructed surface. More specifically, NIXSW data indicate that rather than a single type of hollow site being occupied, both hcp and fcc sites, probably with essentially equal probability, are occupied. This occupation of a high-coordination hollow site is consistent with previous studies of methylthiolate on Cu(111) [3] and thiophenolate on Ni(100) [5], although in the case of Cu(111) there was also clear evidence of adsorbate-induced surface reconstruction; the present data indicate that this does not occur on Ni(111). The orientation of the methylthiolate, on the other hand, is consistently indicated by NEXAFS, SEXAFS and XPD to involve a S–C axis which is significantly tilted: the best estimate of this tilt on the basis of the three techniques is approximately 40°, relative to the surface normal. This result is quite different from the perpendicular molecular orientation found on Cu(111). It is, on the other hand, more similar to the situation on Pt(111), although in this case the local bonding geometry is not known; the significant difference between the polarization angle dependence of the S K-edge NEXAFS for the thiolate on Ni and Pt (111) surfaces, however, does indicate that there are differences in these two systems, although whether this is simply a difference in the exact molecular orientation, or whether there are different substrate scattering contributions to the two spectra is not known. The combination of a strongly tilted molecular axis and a high-symmetry adsorption site is superficially rather surprising, but there is still not a real body of structural studies of this kind to judge it against.

Finally, we should make some remarks concerning the results described here and those of a parallel study [20] of the same adsorption systems by different methods which has come to our notice. The key difference found in this work is evidence (through high-resolution SXPS) for the existence of two distinct thiolate species, nominally low- and high-temperature states with a transformation occurring from the low- to high-temperature

form as the sample temperature was raised through the range 200–220 K. On the basis of vibrational spectroscopy the low-temperature species is believed to be a tilted thiolate, and the high-temperature state to be a more nearly perpendicularly orientated thiolate. None of these conclusions actually conflict with our findings, in that our structural studies of the thiolate have all been conducted on samples which were not allowed to warm to these higher temperatures: our rationale for this was to avoid possible partial conversion to atomic S. It is, of course, possible that a third species does coexist in our NEXAFS warming spectra, which we mistakenly assigned to a mixture of the (low-temperature) thiolate and atomic sulphur. The change in S 2p chemical shift seen in the high resolution SXPS on conversion from one intermediate to the other has been attributed by Mullins *et al* [20] to a change in local site from bridge at low temperature to hollow at higher temperature: these actual sites are purely speculative, and while an associated structural change is possible, our own results provide quantitative evidence to support our assignment of the hollow site to the low-temperature thiolate phase.

Acknowledgments

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