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The adsorption site and orientation of CH_3S on Ni(111)

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Abstract

The angle-resolved X-ray photoelectron spectra for 0.15 monolayers (ML) of sulfur, and 0.25 ML methyl thiolate formed at 100 K and annealed to 150 and 250 K, on Ni(111) are analyzed to determine the structures of these species. It is found that sulfur adsorbs on the face-centered cubic hollow site on Ni(111) with a S–Ni bond length of 2.20 ± 0.02 Å. The thiolate species formed at 150 K has the C–S bond tilted at ~35° to the surface normal with a C–S bond length of 1.85 ± 0.02 Å and a S–Ni bond length similar to that for adsorbed sulfur (2.2 Å). The methyl group is tilted toward the bridge site and the thiolate appears to be adsorbed on the face-centered cubic site although there may also be adsorption in the hexagonal close packed site. The species formed at 250 K adsorbs on a reconstructed surface where the chemical shift of the S 2p core level indicates that it adsorbs at a four-fold site and the angle-resolved XPS data indicate that the C–S bond is oriented normal to the surface. The calculated angular variations in intensity are consistent with this interpretation but cannot distinguish between the various models proposed for the reconstructed surface. © 1997 Elsevier Science B.V.

Keywords: Chemisorption; Nickel; Photoelectron diffraction; Soft X-ray photoelectron spectroscopy; Sulfur

1. Introduction

The formation of methyl thiolate, CH_3S, has been established as the first step in methanethiol (CH_3SH) decomposition on most metal surfaces [1–11]. Multiple states have been observed in the S 2p core level photoemission from S and CH_3S and it was concluded that these different S 2p signals arise from S or CH_3S in different adsorption sites. An important trend was observed that the S 2p binding energy for sulfur adsorbed on transition metal surfaces becomes lower as the coordination of the adsorption site decreases, so that on W(001) the S 2p binding energy decreases when the S coverage increases [12]. On Ni(111), large S coverages result in a surface reconstruction that changes the S adsorption site from three-fold to four-fold, thus increasing the S 2p binding energy [13]. This correlation between binding energy and S adsorption site has been discussed in detail in a previous publication [14].

The relationship between S 2p peak position and the coordination of the adsorption site has also been applied in interpreting the S 2p spectra of CH_3S on different surfaces. Various S 2p states

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were assigned to CH_3S adsorbed in multiple adsorption sites upon adsorption of CH_3SH on W(001) [7] and Ru(0001) [8] at 100 K.

An unusual transformation was observed for CH_3S on Ni(111) in which the CH_3S changed adsorption sites after annealing [9]. CH_3S adsorbed at 100 K yields a spectrum with a single S 2p state. When the sample is heated to 250 K, the CH_3S partially decomposes producing atomic S that has a lower S 2p binding energy. In addition, a S 2p state appeared at ~1 eV higher binding energy. Applying the relationship between binding energy and adsorption site coordination, it was concluded that the species formed at 250 K was CH_3S in a higher coordination adsorption site than the thiolate formed at 100 K. The simplest explanation consistent with the data is that the thiolate formed at 100 K is in a bridge adsorption site while the thiolate formed upon annealing to 250 K is in three-fold hollow site. Vibrational EELS data suggested that the C–S bond was tilted toward the surface at 100 K and was aligned along the surface normal at 250 K [9]. These assignments of adsorption site and C–S bond orientation were supported by calculations of the total energy of CH_3S in different adsorption sites on a Ni(111) cluster [15]. These calculations indicated that adsorption in the bridge and hollow sites was nearly equi-energetic and that a tilted C–S bond is favored in a bridge site and C–S bond normal to the surface is favored in the hollow site. It was proposed that CH_3S adsorbed in the bridge site at 100 K and then overcame an activation barrier in order to occupy the hollow site at 250 K. Recently, however, Fernández et al. concluded that the thiolate formed at 100 K was adsorbed in a three-fold site based on X-ray standing wave and SEXAFS data [16]. They did not study the species formed at 250 K.

In this report, angle-resolved S 2p photoemission, also known as X-ray photoelectron diffraction (XPD), is used to determine the adsorption site and orientation of S and CH_3S on Ni(111) and follows a protocol that has been successfully applied previously to adsorption on Ni(001) [14]. In addition, a comparison of the S 2p peak positions for S and CH_3S adsorbed on Ni(111) and Ni(001) provides further support for the assignments and provides a test of the relationship between S 2p binding energy and the coordination of the adsorption site. Based on these results, it is established that S adsorbs in the fcc three-fold site at low coverages on Ni(111). Furthermore, CH_3S may adsorb in these same sites at 100 K on this surface. The CH_3S species formed by annealing the Ni(111) sample to 250 K is adsorbed in a four-fold site on a reconstructed surface.

2. Experimental

The Ni(111) sample was aligned by Laué back reflection and mechanically polished. The sample was cleaned using repeated cycles of Ar ion sputtering followed by annealing to 1000 K until no surface contaminants were detected using Auger electron spectroscopy (AES) or soft X-ray photoelectron spectroscopy (SXPS). The clean Ni(111) sample produced a sharp p(1 × 1) LEED pattern with low background intensity.

Atomic S was deposited using H_2S that was dosed at 300 K and then the sample was annealed for one minute at 1000 K. Methanethiol was dosed at a sample temperature of 100 K and then the sample was annealed for one minute at the temperatures indicated.

Photoemission spectra were recorded using a VSW EA125 hemispherical analyzer. The acceptance angle was ±2° based on the manufacturer's specifications. Normal emission was established by sighting the back reflection from the sample through a viewport in the analyzer and was accurate to within ±2°. The sample was oriented as shown in Fig. 1. The emission plane was normal to the surface and contained the $[\bar{1}\bar{1}2]$ and $[11\bar{2}]$ azimuths on Ni(111). Positive emission angles, χ, are from the surface normal toward the $[11\bar{2}]$ direction. Excitation radiation was obtained from beamline U13UA at the National Synchrotron Light Source. The incident radiation was p-polarized in the emission plane and the angle between the incident radiation and the emission direction was fixed at 65°. Angle-dependent X-ray photoelectron diffraction (XPD) data were collected by rotating the sample. The emission angle could be scanned from $-20°$–$+80°$. The excitation

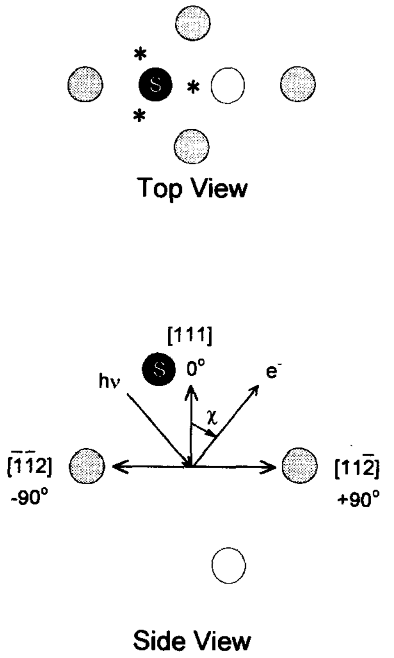

Fig. 1. Experimental geometry for studying the angular dependence of S 2p emission on Ni(001). Second layer Ni is shown in white, first layer Ni in gray and S in black. The emission plane contains the $[\bar{1}\bar{1}2]$ and $[11\bar{2}]$ azimuths for Ni(111). The polar emission angle, χ, is also indicated. (*) indicates the positions of the three bridge sites that are inequivalent with respect to the $[11\bar{2}]$ azimuth.

energy was selected in order to produce the desired photoelectron kinetic energy.

3. Calculation of angle-resolved photoemission data

The method for calculating the variation in photoemission intensity as a function of detection angle has been described in detail in a previous publication [14] and uses the concentric-shell algorithm of Saldin et al. [17]. In that scheme, the calculations are rendered tractable by the division of the cluster into a series of concentric shells centered on the photoemitter. The resulting division of the multiple scattering into intra- and inter-shell portions results in significant savings of computer time, as in analogous calculations of X-ray absorption near-edge structure (XANES) [18] for instance, while not sacrificing accuracy.

4. Experimental results

4.1. Photoemission

The S 2p photoelectron spectrum from 0.15 monolayers (ML) of S on Ni(111) is shown in Fig. 2a. The photon energy was 250 eV giving a photoelectron kinetic energy (KE) of 80–90 eV and the emission angle, χ, was 15°. The S $2p_{3/2}$ binding energy is 161.15 eV. The S 2p spectrum from CH_3S on Ni(111) annealed to 150 K is displayed in Fig. 2b. Only a single S 2p state is seen and the S $2p_{3/2}$ binding energy is 162.30 eV. The spectrum observed after heating to 250 K is shown in Fig. 2c. S 2p states are formed at a lower binding energy than the state observed upon adsorption at 100 K. In addition, a well-resolved

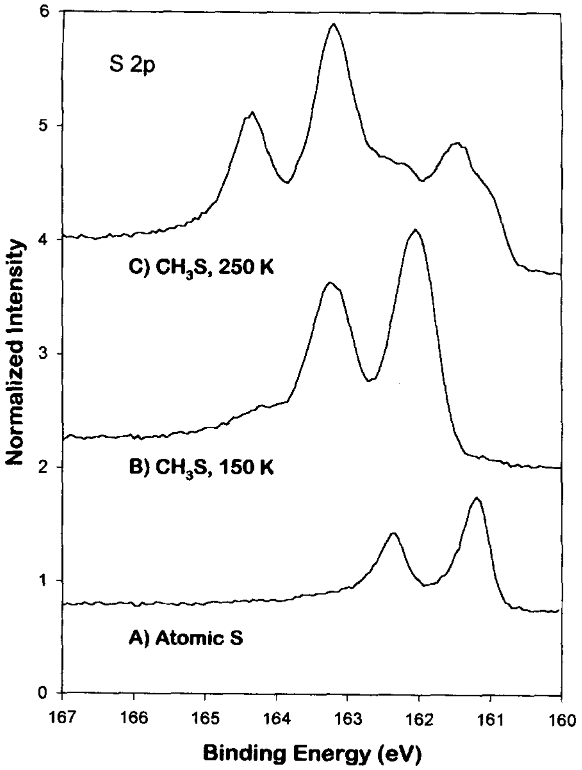

Fig. 2. (a) S 2p photoemission spectra for 0.15 ML of S (b) from 0.25 ML of CH_3S at 150 K on Ni(111) and (c) from 0.25 ML of CH_3S at 250 K on Ni(111). The photon energy was 250 eV.

S 2p state is formed at higher binding energies with a S $2p_{3/2}$ binding energy of 163.30 eV.

4.2. *X-ray photoelectron diffraction*

Several factors were taken into account in order to reliably determine the relative intensities of the S 2p photoemission peaks at different emission angles [14]. The S 2p spectra were normalized to the background intensity in order to account for variations in incident flux. The intensities at different emission angles were then divided by an empirically determined, emission-angle-dependent, instrument function. Finally, the data were scaled so that the minimum between −20° and 60° is equal to 1. The photon energy was 365 eV so that the S 2p kinetic energy was approximately 200 eV.

The angular variation in intensity for 0.15 ML of sulfur on Ni(111) is shown in Fig. 3a. The angular variation in intensity exhibits an intense maximum between 30° and 55°.

Diffraction data for the S $2p_{3/2}$ signal at 162.3 eV BE from CH_3SH on Ni(111) at 100 K and then annealed to 150 K are shown in Fig. 4a. The data again exhibit maxima at ~30° and ~45°. The angular variation in the S $2p_{1/2}$ state at 164.5 eV BE, formed after the sample is heated to 250 K, changes significantly compared to the results at 150 K as shown in Fig. 5a. Most notably, the maxima observed for atomic S and low temperature CH_3S near 40° is absent, and a broad, intense peak appears at normal emission extending from −15 to +15°. Note that, in this case, the intensity of the S $2p_{1/2}$ was monitored because the more intense S $2p_{3/2}$ peak overlaps with other peaks in the spectrum.

5. Analysis and discussion

5.1. *S on Ni(111)*

The angle-resolved photoemission intensities were calculated for sulfur adsorbed at a three-fold hollow site on Ni(111). It has been shown previously that sulfur adsorbs on the three-fold hollow face-centered cubic (fcc) site on Ni(111) with a vertical S–Ni distance of 1.65 Å [19–21].

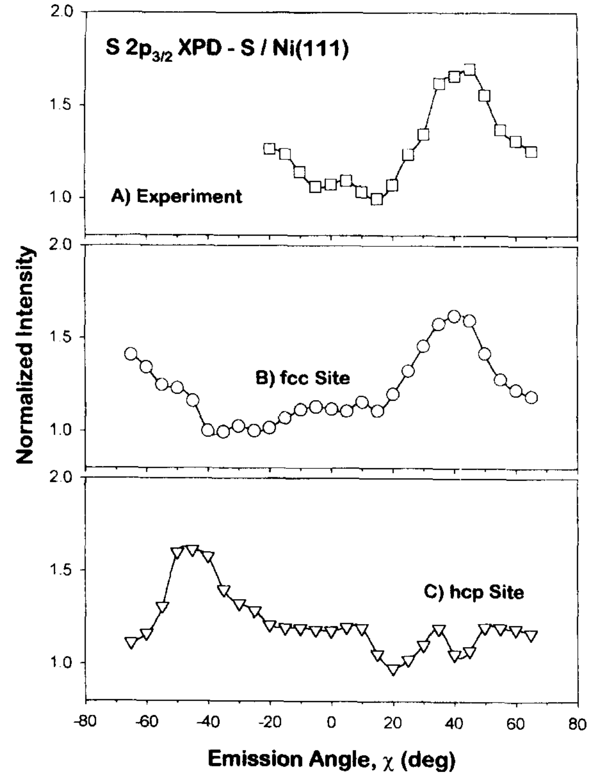

Fig. 3. (a) Sulfur 2p angular dependence at 200 eV kinetic energy for 0.15 ML S on Ni(111). Calculated S 2p angular dependence for S adsorbed 1.65 Å above the first Ni layer in (b) an fcc three-fold site, and (c) an hcp three-fold site.

Calculations were performed for sulfur adsorbed on this site and the substrate geometry was taken to be that of an ideally terminated single crystal of nickel. The only adjustable, non-structural parameter in the calculations is the kinetic energy of the electrons. Although the electron kinetic energy was nominally fixed at 200 eV, there may be slight differences between the kinetic energy determined by the analyzer and the kinetic energy used in the calculations. The kinetic energy for the calculations was determined by optimizing the agreement between the experimental and calculated spectra. In all cases, the correspondence between the experimental and theoretical result was calculated from a D factor:

$$D(\alpha,\beta)=\frac{\sqrt{\sum_i(\alpha+\beta E_i-C_i)^2}}{\sum_i E_i}$$

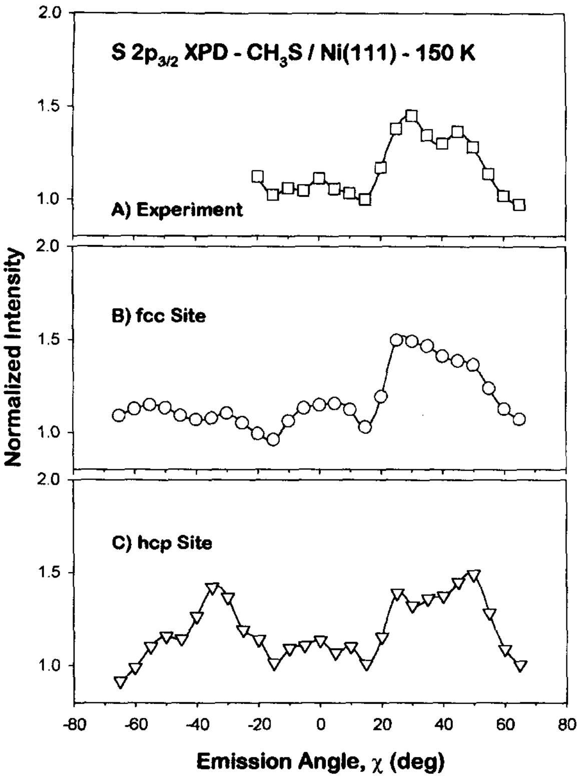

Fig. 4. (a) Sulfur 2p angular dependence at 200 eV kinetic energy for 0.25 ML CH_3S adsorbed on Ni(111) annealed to 150 K. Calculated S 2p angular dependence for CH_3S adsorbed in (b) an fcc three-fold site, and (c) an hcp three-fold site. The S atom was 1.65 Å above the first Ni layer with the C–S bond 1.85 Å long and tilted at 37° to the surface in the [11$\bar{2}$] direction.

where E_i are the experimental data and C_i the corresponding calculated results. β and α represent a scaling factor and an offset correction respectively between the experimental and calculated data and D is minimized with respect to α and β for each adjustable parameter to obtain the best comparison between the experimental data and the calculated angular distribution. The variation in D is shown plotted in Fig. 6 for sulfur adsorbed in a three-fold site on Ni(111) as a function of the distance of the sulfur atom to the Ni(111) surface for various values of the electron kinetic energy between 200 and 210 eV. The minimum in D corresponds to a vertical S–Ni distance of 1.64±0.01 Å and the optimum kinetic energy is 205 eV, close to the nominal experimental value. This value for the electron kinetic energy is used in all subsequent calculations. The S–Ni vertical distance leads to a S–Ni bond distance of 2.20±0.02 Å and this value is in good agreement with measurements on both Ni(111) and Ni(001) using other methods [19–23]. The determination of the error bars has been described in detail previously [14].

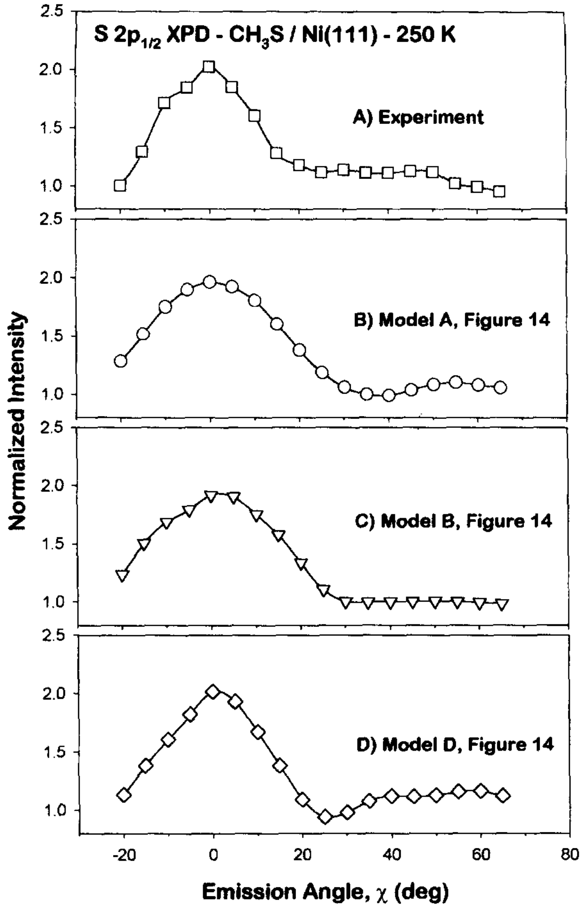

Fig. 5. (a) Sulfur 2p angular dependence at 200 eV kinetic energy for 0.25 ML CH_3S adsorbed on Ni(111) annealed to 250 K. Calculated angular distribution of photoelectrons from CH_3S adsorbed on a reconstructed Ni(111) surface using the models of (b) Edmonds et al. [30], (c) Woodruff [31], and (d) Foss et al. [32]. The S atom was adsorbed in the four-fold sites, the S–Ni bond distances were 2.20 Å, and the C–S bond was 1.80 Å long oriented along the surface normal.

The best-fit spectrum is plotted in Fig. 3b for comparison with the experimental result (Fig. 3a). The agreement between theory and experiment is good. Also plotted in Fig. 3 is the calculated

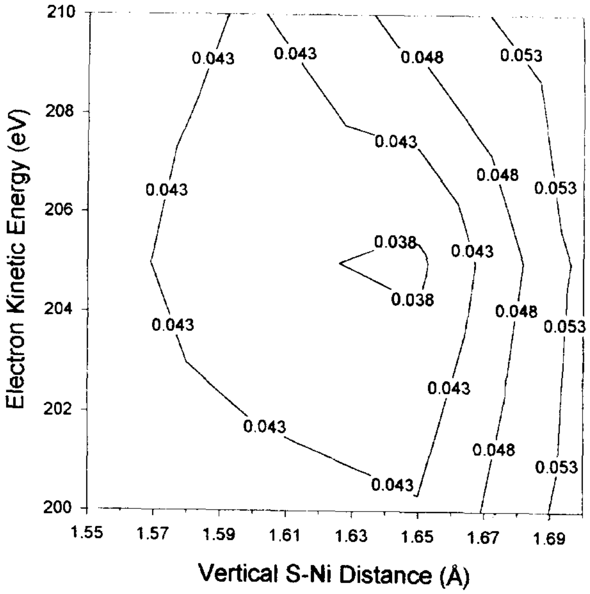

Fig. 6. Plot of the quality of fit parameter, D (see text), versus the vertical S–Ni distance and the electron kinetic energy for the photoelectron angular distribution of S/Ni(111).

spectrum for S adsorbed in the hexagonal close packed (hcp) site (Fig. 3c). This spectrum is essentially the mirror image of the spectrum from S in the fcc site with the maximum at −40° instead of 40°. This is because the structure of the surface Ni atoms around the three-fold site is the same for the fcc and hcp sites, but they are rotated azimuthally by 180° with respect to each other (see Fig. 1). The results in Fig. 3 indicate that angle-resolved XPS can easily distinguish between different adsorption sites even without recourse to calculations. Note that there is no peak at normal emission in the calculated spectrum for S adsorbed in the hcp site even though there is a Ni atom in the second layer below the S. This is different from S adsorbed on Ni(001) where backscattering from second layer Ni was observed [14]. The absence of a S–Ni feature at normal emission in the Ni(111)-hcp calculation can be attributed to the difference in the distance between S and second layer Ni on Ni(111) and Ni(001). The distance from S to the second layer Ni atom is 3.68 Å on Ni(111) and 2.55 Å on Ni(001). The enhancement due to backscattering oscillates as a function of electron KE and internuclear separation [24]. For a 200 eV electron, the oscillations are apparently near a maximum for a 2.55 Å separation and near a minimum for a 3.68 Å separation.

5.2. CH_3S on Ni(111) at 150 K

The S 2p signal from CH_3SH adsorbed on Ni(111) at 100 K and annealed to 150 K has been assigned to methyl thiolate, CH_3S [9]. The experimental angular variation in intensity for this thiolate species is displayed in Fig. 4a. The angular dependence is qualitatively similar to the result from S on Ni(111) (Fig. 3a) in that it shows essentially no enhancement at normal emission and enhanced emission between 30–55°. The absence of enhancement at normal emission implies that the C–S bond is *not* oriented normal to the surface as was found, for example, for CH_3S adsorbed on Ni(100) [14]. Fernández et al. arrived at a similar conclusion based on S 2p XPD data at 1325 eV KE [16]. Furthermore, the peaks at higher emission angles suggest that the CH_3S is adsorbed in a site similar to S on Ni(111), namely the fcc site. Fernández et al. also concluded, on the basis of surface extended X-ray absorption fine structure (SEXAFS) and X-ray standing wave spectroscopy, that the thiolate was adsorbed in a three-fold hollow site. They could not, however, determine the angle of the S–C bond with respect to the surface normal.

As shown in the determination of the adsorption site for S on Ni(111), different internuclear bond directions lead to qualitative differences in the photoemission angular dependence, whereas variations in the bond lengths lead to quantitative differences. Therefore the best strategy for determining the structure of an adsorbate is to first compare calculations for different adsorption sites and orientations with the experimental data using nominal bond lengths and then to optimize the bond lengths in the best configuration.

In order to determine the orientation of the thiolate species on this surface at 150 K, the D factor was calculated as a function of the azimuthal angle, ϕ, and the polar angle, θ, for the C–S bond in the thiolate species adsorbed on the three-fold site. The $[11\bar{2}]$ direction is defined as $\phi = 0$, and $\theta = 0$ is aligned along the surface normal. These angles are shown in Fig. 7. The S–Ni distance in these calculations was taken to be 2.20 Å which is the same as the S–Ni distance determined previously for atomic S. This S–Ni distance has also been found in organometallic complexes [25]. The C–S bond distance was set at the value for gas-phase methanethiol of 1.80 Å [26] and the thiolate was initially assumed to be adsorbed in the fcc hollow site. The resulting D factor is plotted in Fig. 8 for ϕ between -60 and $+60°$ and for θ between 20 and 45°. The minimum value is for $\phi=0\pm5°$ and $\theta=37\pm5°$. This indicates that the molecule is substantially tilted with respect to the surface and that the methyl group is oriented toward the bridge site on the (111) surface which presumably minimizes steric interference between the adsorbed species and the surface.

A similar set of calculations were performed for the thiolate adsorbed in the hexagonal close packed site and the resulting *D* factors are displayed in Fig. 9. These results point to a similar conclusion, namely that the methyl group is oriented at ~35° away from the normal and along the $[11\bar{2}]$ azimuth. However, in this case, the methyl group is tilted toward the atop site rather than the bridge site. The minimum *D* factor is slightly worse for the hcp site compared to the fcc site (0.013 versus 0.010) which may imply that the thiolate adsorbs in the latter site. However, the similarity between these two values means that no firm conclusion can be arrived at on the basis of differences between them.

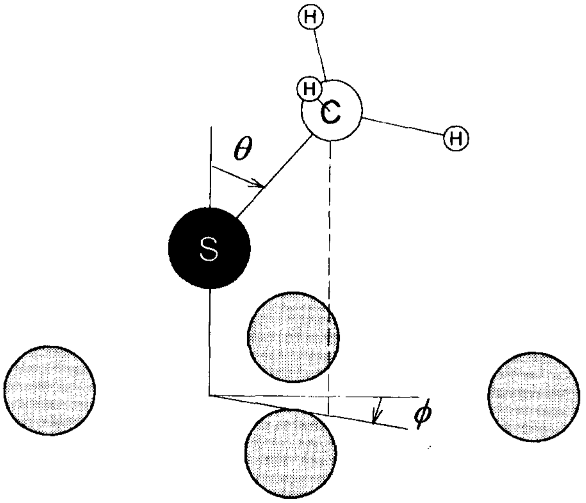

Fig. 7. Schematic diagram showing a thiolate adsorbed on Ni(111) indicating the tilt angle, θ, and the azimuthal angle, ϕ, used in the calculation of the angular variation in photoemission intensity.

The thiolate species has also been proposed to adsorb on the bridge site on the (111) surface at low temperatures [9,15]. In order to test for this possibility, the angular variation in photoemission intensity was calculated for a tilted (35°) species adsorbed on the bridge site using a S–Ni distance of 2.2 Å and a S–C bond length of 1.80 Å. There are six locally equivalent configurations that need to be averaged in order to calculate the expected S 2p angular dependence. The thiolate can be adsorbed in any of the three bridge sites that are inequivalent with respect to the $[11\bar{2}]$ azimuth (indicated by * in Fig. 1). In each of these bridge sites, the methyl group could be tilted toward either the fcc or the hcp site giving a total of six possible configurations. The resulting calculated angle-resolved data (Fig. 10b) are compared with the experimental data (Fig. 10a). There are clearly significant differences between the calculated and experimental data, in particular the calculated maximum is sharper and shifted to a smaller angle so that there is no peak at 45° as in the experimental data. The *D* factor is also two times worse in Fig. 10 compared to Fig. 4. On this basis we conclude that adsorption in the bridge site is unlikely.

In order to further refine the molecular geometry, the *D* factor was calculated as a function of C–S and S–Ni distance in the fcc site using the azimuthal and polar angles determined previously. Shown in Fig. 11 is the calculated dependence of the *D* factor on carbon–sulfur distance and sulfur–nickel distance. The minimum in these curves corresponds to a C–S distance of 1.85±0.02 Å, close to the gas-phase value and the vertical S–Ni distance is 1.65±0.02 Å, very close to that for atomic sulfur in nickel, leading to a S–Ni bond length of 2.20±0.03 Å, and also identical to the value measured on Ni(001) [14]. Similar results were obtained for a thiolate adsorbed in the hcp site (Fig. 12), although again the minimum *D* factor was worse for the hcp site compared to the fcc site. The corresponding bond lengths determined by Fernández et al. [16] were 2.25±0.04 Å

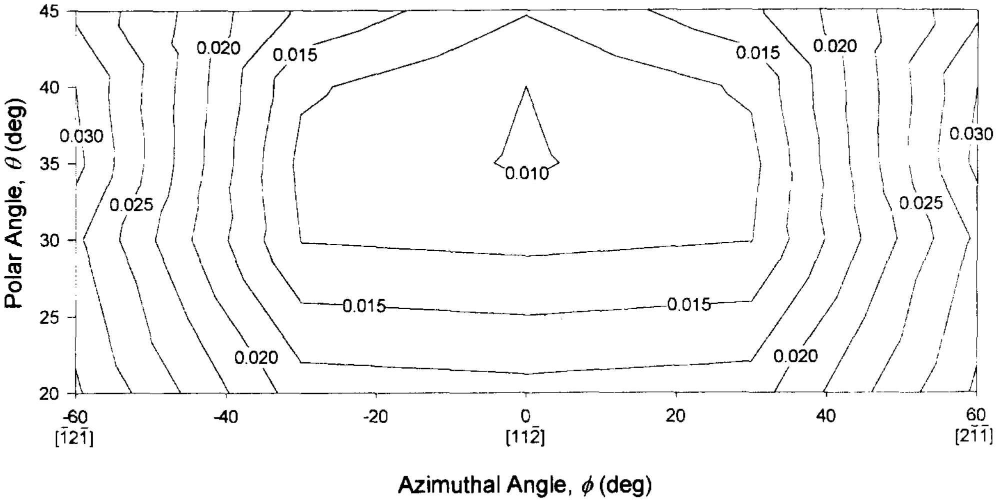

Fig. 8. Plot of the quality of fit parameter, D (see text), versus the angle of the C–S bond with respect to the surface normal, θ, and the azimuthal angle, ϕ, (see Fig. 7) for CH_3S/Ni(111) at 150 K adsorbed in an fcc site.

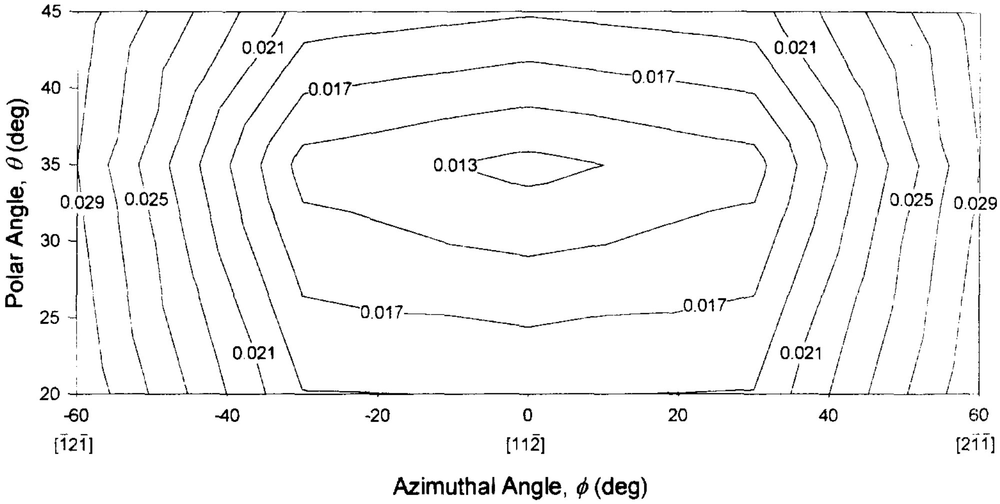

Fig. 9. Plot of the quality of fit parameter, D (see text), versus the angle of the C–S bond with respect to the surface normal, θ, and the azimuthal angle, ϕ, (see Fig. 7) for CH_3S/Ni(111) at 150 K adsorbed in an hcp site.

for the S–Ni distance, 1.89±0.07 Å for the C–S distance and 1.63±0.10 Å for the vertical S–Ni distance in good agreement with the values established here.

The best fit spectra for CH_3S adsorbed in an fcc site and in an hcp site are plotted in Fig. 4b and c, respectively. The agreement between either calculated curve and the experimental curve is good. We note again that Fig. 4c is for a thiolate in an hcp site with the methyl group tilted toward a top site. Calculations on Ni(111) [15] and Pd(111) [27] have indicated that the preferred tilt direction for a thiolate adsorbed in a hollow site is toward the bridge site. Therefore we conclude that at least some of the thiolate present after annealing to 150 K is adsorbed in the fcc site. However, adsorption in a mixture of sites, as proposed by Fernández et al. as a result of the coherent positions and

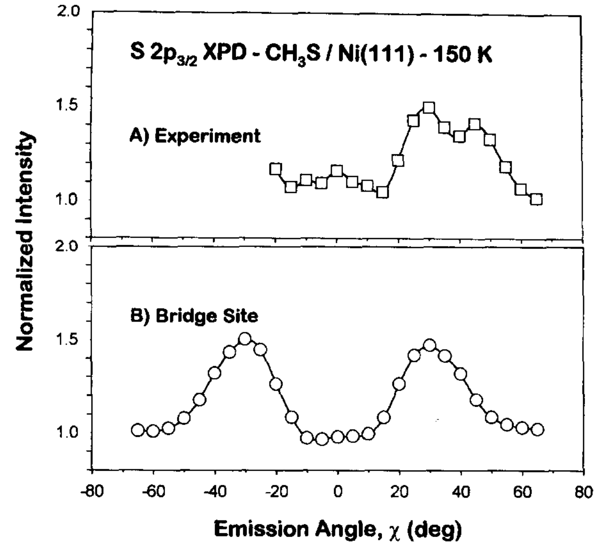

Fig. 10. Comparison of (a) the experimental X-ray photoelectron diffraction data with (b) the results of a calculation for a tilted thiolate species adsorbed on a bridge site. The S–Ni bond distance was 2.20 Å and the C–S bond was 1.85 Å long and tilted at 37° toward the three-fold sites.

coherent fraction in XSW [16], cannot be ruled out. If the CH_3S is adsorbed at the hcp site with the methyl group tilted in the $[\bar{1}\bar{1}2]$ direction, it would contribute little structure to the angular dependence from −20° to 70° (see the variation at the fcc site in Fig. 4b from −70° to 20°). Additional experiments along the $[\bar{1}\bar{1}2]$ azimuth would indicate whether the thiolate was adsorbed in the hcp sites as well.

Our conclusion that CH_3S is adsorbed in a hollow site and that the methyl group is tilted toward the surface at 150 K is consistent with the results obtained by Fernández et al. The tilted configuration is also consistent with angle-dependent EELS results [9]. A tilted CH_3S species was also observed on Pt(111) [28]. However, this result disagrees with calculations for CH_3S on Ni(111) which indicate that the C–S bond should be normal to the surface for adsorption on the hollow site [15]. These calculations showed only a small variation in total energy as a function of C–S bond angle, ~5 kcal mol^{-1} between 0°–35°, which suggests that a tilted configuration is not strongly precluded. Using a different computational method, Sellers calculated that CH_3S will adsorb with the C–S bond normal to the surface on Pt(111) but tilted on Pd(111) [27]. It is not clear whether this method would predict that CH_3S would bond to Ni(111) more like it does to Pt(111) or Pd(111). Neither of these methods considered inter-adsorbate interactions which might also influence the adsorbate configuartion. Note that Sellers calculation on Pt(111) disagrees with the experimentally determined orientation of

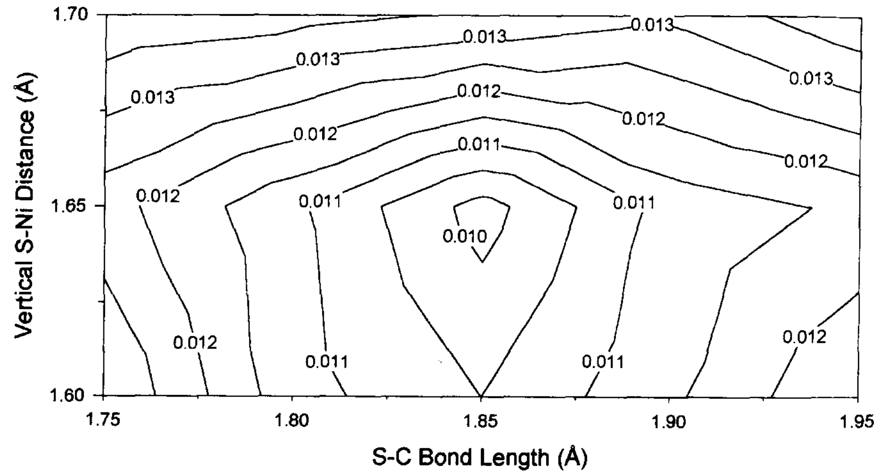

Fig. 11. Plot of the quality of fit parameter, *D* (see text), at the minimum of the graph of *D* versus tilt and azimuthal angles for a thiolate adsorbed in an fcc site (Fig. 8), versus the vertical S–Ni distance and C–S bond length for the photoelectron angular distribution of CH_3S/Ni(111) at 150 K.

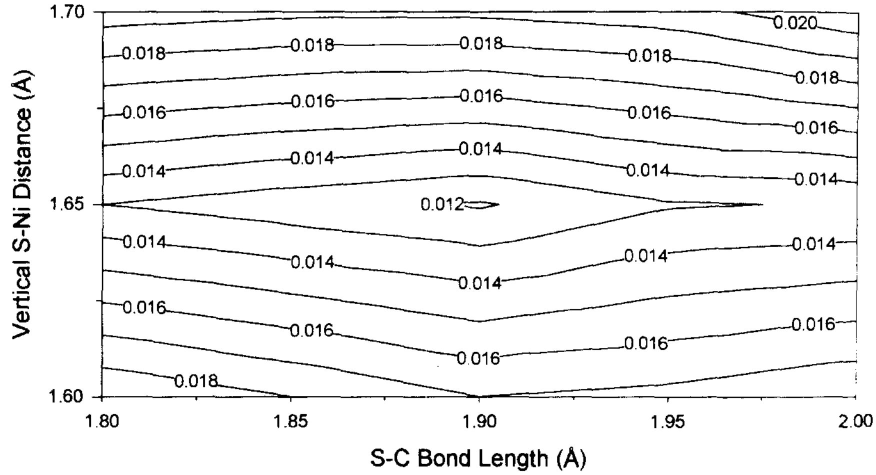

Fig. 12. Plot of the quality of fit parameter, D (see text), at the minimum of the graph of D versus tilt and azimuthal angles for a thiolate adsorbed in an hcp site (Fig. 9), versus the vertical S–Ni distance and C–S bond length for the photoelectron angular distribution of CH_3S/Ni(111) at 150 K.

CH_3S on Pt(111) by Kollin et al. [28]. Evidently more experimental and theoretical work need to be done on the orientation of CH_3S on various surfaces before a clear pattern can be established.

5.3. CH_3S on Ni(111) at 250 K

The thiolate species formed on Ni(111) at 250 K has a 1 eV shift in the S $2p_{3/2}$ peak position from 162.30 eV to 163.30 eV compared to the species formed at 150 K. This shift suggests that the thiolate has moved from a three-fold adsorption site to a higher coordination adsorption site. The S 2p spectrum from CH_3SH at 250 K on Ni(111) is plotted along with spectra of CH_3S and S on Ni(001) and S on Ni(111) in Fig. 13. The S 2p signal from CH_3S on Ni(111) at 250 K is in the same position as CH_3S on Ni(001) which has been shown to be adsorbed in the four-fold site [14]. In order for adsorption to occur in a four-fold site on Ni(111), the surface must be reconstructed at 250 K. The S 2p spectra provide additional evidence for a three-fold to four-fold reconstruction. C–S bond scission also occurs at 250 K on Ni(111) producing atomic S on the surface. The structure and S 2p photoemission from atomic S on Ni(111) [13] and Ni(001) [14] have been reported previously. The S $2p_{3/2}$ peak position for S adsorbed

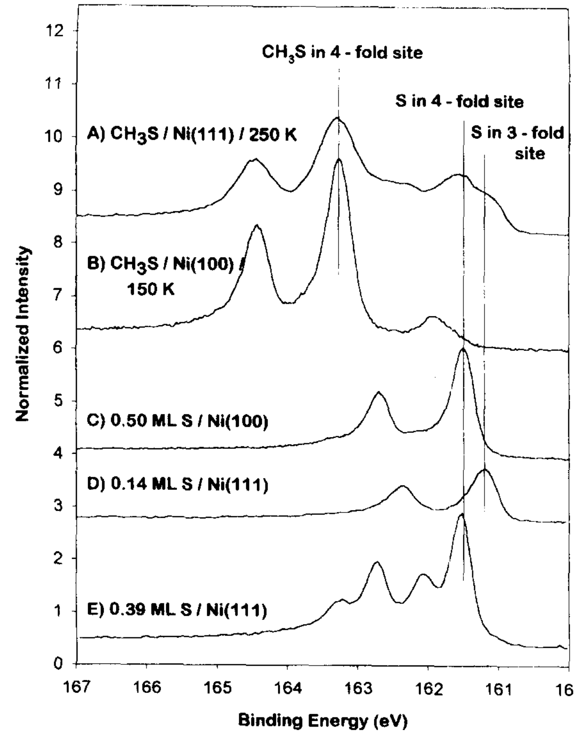

Fig. 13. S 2p photoemission spectra for (a) 0.25 ML of CH_3S adsorbed on Ni(111) and annealed to 250 K (b) 0.40 ML of CH_3S adsorbed on Ni(001) (c) 0.50 ML of S adsorbed on Ni(001) (d) 0.15 ML of S on Ni(111) and (e) 0.40 ML of S on Ni(111). The photon energy was 250 eV.

in a three-fold site on Ni(111) is 161.15 eV. There is some S adsorbed in this site following the decomposition of CH_3S on Ni(111) at 250 K as shown in Fig. 13. However, the S $2p_{3/2}$ peak position for S adsorbed in a four-fold site on Ni(001) [14] or in a "closed" four-fold site on reconstructed Ni(111) [13] is 161.55 eV. Therefore, some of the atomic S is also in this site following decomposition of CH_3S at 250 K on Ni(111) indicating reconstruction. Further, the LEED pattern at this temperature is consistent with a surface reconstruction and S–Ni vibrational frequency of the atomic S from decomposed CH_3S on Ni(111) is consistent with atomic S adsorption in four-fold sites on Ni(111) [13,29].

Models have been proposed by Edmonds et al. [30], Woodruff [31] and Foss et al. [32] for the S-induced reconstruction of Ni(111). All of these models have a surface layer of nickel atoms with four-fold adsorption sites as shown in Fig. 14. In order to determine whether adsorption of CH_3S on these surfaces is consistent with the angle-resolved XPS, we have calculated the angular variation in intensity for thiolates adsorbed on these reconstructed surfaces. Unfortunately, the point group symmetry of the photoemitting atom in these surfaces is not high enough to allow a full calculation for a large cluster of atoms surrounding each photoemitter. In order to circumvent the problems associated with carrying out the calculation for a large, low-symmetry cluster, the angular variation in photoemission was calculated for a thiolate species adsorbed in each of the individual local four-fold sites contained in each of the models in Fig. 14. The results were then added together in the proportion of their relative abundances on the surface to yield the angular dependence for the larger unit cell.

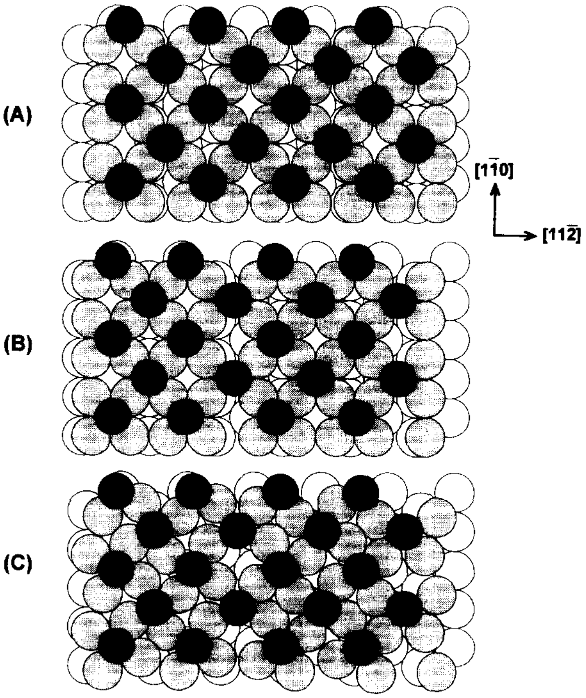

Fig. 14. Models for the S-induced reconstruction on Ni(111) proposed by (a) Edmonds et al. [30] (b) Woodruff [31] and (c) Foss et al. [32]. The white circles are second layer Ni, the gray circles are first layer Ni and the black circles are S.

The experimental data (Fig. 5a) exhibit a strong peak at normal emission, with little variation in photoemission intensity for larger angles. The large enhancement at normal emission suggests that the C–S bond is oriented normal to the surface or that the S is bonded atop a Ni atom. Calculations have excluded adsorption on the atop site on Ni(111) [15], Pt(111) and Pd(111) [27]. In addition, adsorption in the four-fold site is suggested by the S 2p photoemission discussed previously. Therefore, for the present calculations, the thiolates were placed in the four-fold sites with the C–S bond oriented perpendicular to the surface. The C–S bond length was set at 1.80 Å and the S–Ni bond length at 2.20 Å as was done for the species formed at 150 K. The results are depicted in Fig. 5b, c and d for the structures shown in Fig. 14a, b and c, respectively. All of the models reproduce the strong normal emission in accord with the proposal that the thiolate is oriented normal to the surface. This is the same conclusion reached on the basis of the EELS angular dependence [9]. None of the models show much fine structure at higher emission angles in agreement with the experimental data. The lack of structure at higher emission angles can easily be understood by examining the models in Fig. 14. When CH_3S is adsorbed in a four-fold site, a bridge site is behind the S atom for emission in the [11$\bar{2}$] direction so backscattering features are likely to be weak. Variations in the angular dependence are further diluted by the inhomogeneity of the reconstructed surface.

The angle-resolved XPS data and a comparison of the S 2p binding energies with known structures on Ni(001) and Ni(111), lead us to conclude that the thiolate formed at 250 K on Ni(111) is oriented perpendicularly in a four-fold site on a reconstructed surface. Unfortunately, the variations in the photoemission intensity at higher angles are too weak for it to be possible to distinguish between the various models for the surface reconstruction, nor is it possible to further refine the C–S and S–Ni bond distances.

CH_3S adsorbs exclusively in the highest coordination sites available on Ni(001), Ni(111) and reconstructed Ni(111). CH_3S therefore behaves the same as atomic S on these surfaces. This is different than CH_3S on W(001) [7] and Ru(0001) [8] where adsorption in bridge sites as well as hollow sites has been proposed. In light of the current results, perhaps the structure of CH_3S on W(001) and Ru(0001) should be investigated further to see if some previously unsuspected surface reconstruction could be causing the different S 2p states for CH_3S on these surfaces.

The C–S bond in CH_3S is oriented normal to the surface when the thiolate is adsorbed in a four-fold site on Ni and is tilted toward the surface when the thiolate is adsorbed in a three-fold site. Steric interactions do not appear to be the explanation for the difference between the two sites since the methyl group can tilt toward a bridge site in either case and the (001) surface is actually more "open" than the (111) surface. Intermolecular interactions also do not appear to influence the orientation since the saturation coverage of CH_3S at 100 K is the same on both the Ni(111) and Ni(001) surfaces (0.5×10^{15} cm^2). Perhaps the coordination of the S to four Ni atoms in the four-fold site and three Ni atoms in the threefold site results in a different hybridization in the thiolate leading to a different orientation of the C–S bond.

The combined coverages of CH_3S, S and C are apparently sufficient to induce reconstruction of the Ni(111) surface even though the S coverage alone is below what is normally required to induce reconstruction [13]. This is not surprising since the same three-fold to four-fold reconstruction has been proposed for high coverages of C on Ni(111) [33]. If the total coverage of S and C is reduced, the reconstruction can be lifted. When the Ni(111) surface is annealed to >800 K, the S $2p_{3/2}$ shifts from 161.55 eV to 161.15 eV for some of the atomic S indicating that the S is moving back into a three-fold site. Presumably this occurs as a result of the C diffusing into the bulk which reduces the surface concentration.

6. Conclusions

The core level S 2p photoelectron diffraction pattern from atomic S on Ni(111) is consistent with S adsorbed in the three-fold hollow site. This is confirmed using calculations of the electron angular distribution from a sulfur atom adsorbed in a three-fold site on a Ni(111) surface. The angular distribution of photoemitted electrons is calculated using a model where the surface is described by a concentric shell of atoms. This yields a result that is in very good agreement with experiment and indicates that the surface S–Ni bond is 2.2 Å long and that S adsorbs in the face-centered cubic site.

A similar strategy reveals that methyl thiolate adsorbs on Ni(111) at 150 K in the three-fold hollow site with the C–S axis tilted at ~35° to 40° with respect to the surface with the methyl group pointing in the $[11\bar{2}]$ direction. This thiolate has a C–S bond length of 1.85 ± 0.02 Å in good agreement with the corresponding gas-phase value of 1.82 Å. The data suggest slightly better agreement with adsorption in the fcc site. However, adsorption in the hcp site as well cannot be precluded. The orientation of the CH_3S changes on heating to 250 K so that the C–S axis is oriented perpendicularly to the surface. XPS data indicate that the thiolate adsorbs at a four-fold site in this case which is interpreted as being due to reconstruction of the Ni(111) surface. Comparison of the calculated and experimental angle-resolved data is consistent with this view.

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