

$$\frac{1}{T_1} = \frac{3}{7} \frac{\gamma^4 \hbar^2}{15} B(\tau_1) \sum_{ij} (2\delta_{ij} - 1) R_i^{-3} R_j^{-3} P_2(\cos \Omega_{ij}) \quad (17)$$

where a factor 3/7 is added for intramolecular spin diffusion and δ_{ij} is Cronecker's delta.

Then we consider the relaxation for **2**, where rotation and inversion processes of the amino group should be taken into account. Figure 3 illustrates the six sites of the amino group in **2**. We assume that the rotation occurs with a single jumping rate ω_R among sites 1, 2, and 3 or sites 4, 5, and 6, and the inversion takes place with another jumping rate ω_I between sites 1 and 5, sites 1 and 6, sites 2 and 4, sites, 2 and 6, sites 3 and 4, or sites 3 and 5. The transition matrix D is given in eq 18.

$$D = \frac{1}{2} \times \begin{bmatrix} 2(\omega_R + \omega_I) & -\omega_R & -\omega_R & 0 & -\omega_I & -\omega_I \\ -\omega_R & 2(\omega_R + \omega_I) & -\omega_R & -\omega_I & 0 & -\omega_I \\ -\omega_R & -\omega_R & 2(\omega_R + \omega_I) & -\omega_I & -\omega_I & 0 \\ 0 & -\omega_I & -\omega_I & 2(\omega_R + \omega_I) & -\omega_R & -\omega_R \\ -\omega_I & 0 & -\omega_I & -\omega_R & 2(\omega_R + \omega_I) & -\omega_R \\ -\omega_I & -\omega_I & 0 & -\omega_R & -\omega_R & 2(\omega_R + \omega_I) \end{bmatrix} \quad (18)$$

This matrix can be diagonalized by

$$U = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \times \frac{1}{\sqrt{3}} \begin{bmatrix} 1 & 1 & 1 \\ 1 & \epsilon & \epsilon^* \\ 1 & \epsilon^* & \epsilon \end{bmatrix} \quad (19)$$

where \times means a direct product. The nonzero eigenvalues of Λ are

$$\begin{aligned} \Lambda_{22} = \Lambda_{33} &= 3(\omega_R + \omega_I)/2 = \tau_1^{-1} & \Lambda_{44} &= 2\omega_I = \tau_2^{-1} \\ \Lambda_{55} = \Lambda_{66} &= (3\omega_R + \omega_I)/2 = \tau_3^{-1} \end{aligned} \quad (20)$$

A_l for the normal mode l is given by eq 16 with $P_i^0 = P_j^0 = 1/6$.

After evaluation of the A_l values, one obtains the contribution of the intraamino protons to the relaxation time

$$\left(\frac{1}{T_1} \right)_{\text{intra}} = \frac{2}{15} \frac{9}{40} \gamma^4 \hbar^2 R_{\text{HH}}^{-6} B(\tau_1) \quad (21)$$

where 2/15 is a factor for the spin diffusion and R_{HH} is the distance between the amino protons. The contribution from the proton pairs between the amino protons and the peri hydrogen atoms is given by

$$\left(\frac{1}{T_1} \right)_{\text{inter}} = \frac{4}{5} \frac{9}{4} \gamma^4 \hbar^2 \sum_{l=1,3} A_l B(\tau_l) \quad (22)$$

where A_2 vanishes and 4/5 is a factor for the spin diffusion.

Registry No. 1, 73597-16-7; 2, 793-41-9; 3, 793-39-5; 9-acetoxypentriptycene, 97733-14-7; 9-acetoxyanthracene, 1499-12-3; benzyne, 462-80-6; 9-nitrotricyptene, 797-67-1.

Fundamental Studies of the Chemisorption of Organosulfur Compounds on Au(111). Implications for Molecular Self-Assembly on Gold Surfaces

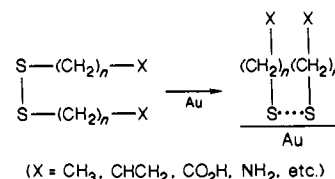
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Abstract: Studies of the adsorption of methanethiol and dimethyl disulfide on an Au(111) surface under UHV conditions are described. Both adsorbates bind strongly, with the bonding of the disulfide being greatly favored. It is found that, under these conditions, the disulfide bond is dissociated to give a stable surface thiolate. Adsorption of methanethiol does not involve cleavage of the S-H bond. The implications of these results for solution adsorption experiments and the thermodynamics characterizing monolayer formation are discussed.

The adsorption of organosulfur compounds on gold surfaces represents a chemisorption system with unique and important properties. In an earlier communication,¹ a general description of the chemisorption of organic disulfides (RSSR') from solution on clean, evaporated gold films was presented. Given the inertness of gold toward the chemisorption of most polar organic functionalities, we were surprised to find that all of the disulfides we examined formed very strong chemisorption bonds. We also observed that when an appropriate molecular structure in the adsorbate molecule is used, it is possible to prepare structurally and chemically complex organic surfaces with well-defined microscopic characteristics. Further, it was found that this technique is completely general, in that these molecular self-assembly processes (also called spontaneous organization) are disposed equally well toward the construction of both high- and low-surface free energy monolayer films.¹⁻⁶ We note that it is the preparation

Scheme I



of high-surface free energy organic materials which most distinguishes this chemisorption system from other, well-documented films obtained by molecular self-assembly.⁷⁻⁹

(1) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481-4483.
(2) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1986**, *2*, 266-281.
Holmes-Farley, S. R.; Reamy, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725-740.

(3) Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107. Li, T. T.-T.; Liu, H. Y.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 1233-1239.
(4) Nuzzo, R. G.; Fusco, F. M.; Allara, D. L., submitted for publication in *J. Am. Chem. Soc.*
(5) Whitesides, G. M.; Troughton, B., personal communication.
(6) Porter, M. D.; Allara, D. L.; Chidsey, C., submitted for publication in *J. Am. Chem. Soc.*
(7) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92-98. Netzer, L.; Sagiv, J. *J. Am. Chem. Soc.* **1983**, *105*, 674-683 and references cited therein.

The general process described above is depicted for a specific structural class of organic disulfide in Scheme I. As is suggested by the scheme, and shown experimentally in numerous systems,^{1,4-6} the assembled organic phases are of high density, approaching or equalling that of the bulk material. In fact, many of these two-dimensional films closely resemble a one-layer crystalline phase.^{4,5}

During the conduct of these studies, it became clear that the properties described above for disulfides also attend to the chemisorption of other organosulfur compounds. The chemisorption of alkylthiols (RSH)^{5,6} or dialkyl sulfides (RSR')⁵ yields oriented structures similar to those described above, with those derived from alkylthiols being almost indistinguishable from that obtained from disulfide chemisorption.⁶ The present study addresses one central feature of this broader chemisorption reactivity, namely, the nature of the interaction of organosulfur compounds with gold. In the discussion which follows, the differing reactivity of an Au(111) surface toward dimethyl disulfide (Me₂S₂) and methanethiol (MeSH) under UHV conditions is described. Our findings, based on data obtained from X-ray photoelectron (XPS) and Auger electron (AES) spectroscopies, temperature-programmed desorption (TPD), and high-resolution electron energy loss spectroscopy (EELS), suggest that dimethyl disulfide chemisorbs dissociatively while methanethiol adsorbs molecularly on the Au(111) surface under these conditions. The heat of adsorption of Me₂S₂ obtained from temperature-programmed desorption is large and is significantly greater than that of methanethiol on this same surface. The implications of these results for solution adsorption experiments and the thermodynamics characterizing monolayer formation are discussed.

Experimental Section

Experiments were performed in two UHV chambers with base pressures $< 5 \times 10^{-11}$ torr. One was a diffusion and titanium sublimation pumped system equipped with four-grid low-energy electron diffraction optics (Varian), a single-pass cylindrical mirror analyzer (Phi) for Auger electron spectroscopy (AES), a quadrupole mass spectrometer (Vacuum Generators) for TPD studies, and a high-resolution electron energy loss (EELS) spectrometer. The angle and energy of the incident electron beam were held fixed at 60° and 4.5 eV, respectively, and only electrons scattered within $\sim 1.5^\circ$ of the specular direction were collected. Elastic scattering from a clean gold surface was weak, with typically $< 5 \times 10^4$ counts s⁻¹ in the peak maximum, with a full width at half-maximum (fwhm) between 40 and 50 cm⁻¹. This intensity decreased somewhat after either thiol or disulfide adsorption. TPD experiments employed an initial gas exposure at temperatures $\leq -150^\circ\text{C}$ and a linear heating rate of $\sim 4.0^\circ\text{C s}^{-1}$.

The XPS experiments were run in a second ion pumped UHV chamber containing a modified Kratos X-SAM 800 X-ray photoelectron spectrometer. The hemispherical electron energy analyzer was operated in a fixed analyzer transmission mode with an instrumental resolution of ~ 1.1 eV. A Mg K α X-ray source was used throughout. All core levels have been referenced to the Au 4f_{7/2} core level (binding energy = 84.0 eV). AES and mass spectroscopic analysis could also be performed in this system. Both UHV chambers contained ion sputtering guns for sample cleaning and effusive molecular beam sources for gas dosing.

Au(111) single crystals (>99.99% pure) were oriented ($\pm 1/2^\circ$), cut, and polished by standard metallographic techniques. The samples were cleaned by repeated cycles of either argon or neon ion bombardment (500–1000 eV, 10 μA) at 650 °C followed by annealing under vacuum at 650 °C. Sample cleanliness was carefully monitored by both AES and XPS. The sample could be cooled to -150°C with liquid nitrogen for low-temperature adsorption studies.

Methanethiol (CH₃SH) was obtained from Alfa-Ventron. Analysis of the contents of this cylinder by mass spectroscopy indicated that the head gas was extensively contaminated with nitrogen. Repeated purge cycles were used to remove this impurity. Dimethyl disulfide (CH₃SS-CH₃) was obtained from Aldrich and was distilled under argon prior to use. Freeze-pump-thaw cycles were used to remove dissolved gasses. Methanethiol-d₃ (CD₃SH) was obtained from Merck Sharp & Dohme

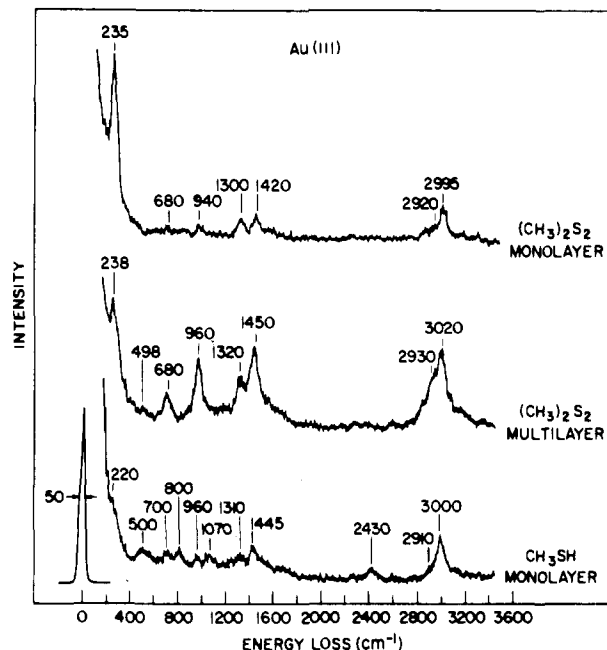


Figure 1. High-resolution EELS spectra of a monolayer of methanethiol (lower trace), a multilayer of dimethyl disulfide (middle trace), and a monolayer of dimethyl disulfide (upper trace) adsorbed on Au(111). The adsorption conditions are indicated in the text. Vibrational mode assignments are summarized in Tables I and II.

Stable Isotopes (Montreal). The entire sample (~ 5.0 g) was converted to the perdeuterated disulfide by the procedure of McAllan et al.¹⁰ with aqueous H₂O₂ as the oxidant. *Caution:* It was noted that this reaction mixture failed to give a definitive indication of excess peroxide with iodide-starch test paper. After the addition of concentrated aqueous NaCl, the product was extracted with methylene chloride, the solvent was removed, and the product was isolated by fractional distillation. The isolated product was further scrubbed and dried with neutral anhydrous alumina. The isolated yield was $\sim 50\%$.

Results

The chemisorption of methanethiol and dimethyl disulfide on a clean Au(111) single-crystal surface under UHV conditions does not lead to the formation of the same adsorbed species. In the discussion which follows, we detail the data which lead to this conclusion and discuss the nature of the relevant surface bonding for these two adsorbates and the energetics and thermodynamics associated with each. For simplicity, each adsorbate is treated separately and, where appropriate, references to solution adsorption experiments are made.

Adsorption of Methanethiol on Au(111). Exposure of an Au(111) surface to methanethiol at -150°C leads to the formation of a stable monolayer (chemisorbed) or multilayer (physisorbed) depending on the exact exposure employed. In the chamber containing the electron energy loss spectrometer (doses were somewhat higher in the XPS system), saturation of the surface occurred at exposures of ~ 2 langmuir (1 langmuir = 10^{-6} torr s). Figure 1 shows high-resolution EELS data (lower trace) for a saturated monolayer of methanethiol at -150°C . The weak intensity of this spectrum,¹¹ reflecting in part the weak elastic scattering from the gold crystal, precludes a definitive assignment of all of the modes observed. Table I lists the loss frequencies seen and, for comparison purposes, details infrared data for methanethiol in the gas phase¹² along with the relevant mode

(10) McAllan, D. T.; Cullum, T. V.; Dean, R. A.; Fidler, F. A. *J. Am. Chem. Soc.* **1951**, *73*, 3627–3631.

(11) (a) Weak scattering was also seen for the case of methanethiol chemisorption on Cu(100). (b) See: Sexton, B. A.; Nyberg, G. L. *Surf. Sci.* **1986**, *165*, 251–267.

(12) Thompson, H. W.; Skerrett, N. P. *Trans. Faraday Soc.* **1940**, *36*, 812–817. May, I. W.; Pace, E. L. *Spectrochim. Acta, Part A* **1968**, *24A*, 1605–1615.

(8) Bowden, F. P.; Tabor, D. *The Friction and Lubrication of Solids*; Oxford University Press: London, 1968; Part II, Chapter 19 and references cited therein. Timmons, C. O.; Zisman, W. A. *J. Phys. Chem.* **1965**, *69*, 984–990. Gaines, G. L. *J. Colloid Interface Sci.* **1960**, *15*, 321–339.

(9) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45–52 and references cited therein.

Table I. Vibrational Mode Assignments of Methanethiol^a

| | gas phase ^b | adsorbed on Au(111) |
|---------------------------------------|------------------------|---------------------|
| <i>a'</i> | | |
| ν_1 , CH ₃ d-stretch | 3015 | 3000 ^c |
| ν_2 , CH ₃ s-stretch | 2948 | 2910 ^d |
| ν_2 , SH stretch | 2605 | 2430 |
| ν_4 , CH ₃ d-deform | 1453 | 1445 ^e |
| ν_5 , CH ₃ s-deform | 1332 | 1310 |
| ν_6 , CH ₃ rock | 1072 | 1070 |
| ν_7 , SH bend | 802 | 800 |
| ν_8 , CS stretch | 710 | 700 |
| <i>a''</i> | | |
| ν_9 , CH ₃ d-stretch | 3012 | 3000 ^c |
| ν_{10} , CH ₃ d-deform | 1444 | 1445 ^c |
| ν_{11} , CH ₃ rock | 956 | 960 |
| Au-S stretch | | 220 ^c |

^aAll frequencies in cm⁻¹. ^bReference 12. ^cMay be of either *a'* or *a''* symmetry. ^dUnresolved shoulder. ^eShoulder on tailing elastic peak.

assignments. Several features of the data in Table I deserve specific mention. First, modes of both *a'* and *a''* symmetry are clearly seen; especially significant in this regard is a large apparent contribution made by the antisymmetric mode in the C-H stretching region ($\nu \approx 3000$ cm⁻¹; the *a'* mode in this region is expected to be weak). This contribution is so large, in fact, that we feel it is unlikely to result solely from impact scattering but must also contain a strong dipolar component. As a result, a simple application of the dipole selection rule¹³ tells us that the main axis of the molecule (as defined by the C-S bond) must be significantly canted (the exact angle cannot be deduced from these data) from the surface normal in order for modes of both symmetry types to be observable. The fact that an S-H stretch is also present (~ 2430 cm⁻¹) further suggests that the adsorption of this molecule on gold does not involve dissociation of the S-H bond. In addition, most vibrational frequencies, with the notable exceptions of the S-H stretch and the mode at 500 cm⁻¹ (the origin of which is unclear), are only slightly perturbed from their gas-phase values indicating little, if any, structural rearrangement of the molecule and implying only a weak chemisorption bond. The significant shift in the S-H stretch may be due to hydrogen bonding in the adsorbed film. Further comment on these data is deferred to the Discussion section.

Figure 2 shows S 2p core level photoemission data for similarly prepared mono- and multilayers of methanethiol on Au(111). Trace A shows data obtained for an ~ 5 langmuir exposure of the surface to the adsorbate gas at -150 °C. A single peak (under these conditions, the 2p core level is an unresolved doublet), showing an unusual asymmetry at lower binding energy, is seen at ~ 163.9 eV. Slowly warming this surface above ~ -125 °C led to the desorption of the multilayer, leaving a monolayer characterized by the S 2p core level spectrum shown in trace B of Figure 2. Note that the line shape observed is complex; a simple and highly qualitative analysis based on the line width of the dominant multilayer peak shows that there are at least two S 2p binding energies present at ~ 164.0 and 162.7 eV. This, however, is not the intrinsic spectrum of methanethiol on this surface. This is clearly demonstrated by the S 2p core level spectrum shown in trace C of Figure 2. The spectrum in C shows a sample prepared as above but in which no multilayer data was acquired; the spectrum was scanned rapidly to minimize its exposure to the X-ray flux. Note that in comparing the spectra in B and C, the relative intensity of the higher binding energy peak is increased relative to that of the lower binding energy peak in the latter sample (there is less asymmetry at lower binding energy). Continued exposure to Mg K α radiation resulted in a significant decrease in this ratio. The complex character of these spectra is most clearly revealed by examination of the spectra shown in traces D and E of Figure 2. In D, we show the spectrum that was obtained from a multilayer sample which had been exposed

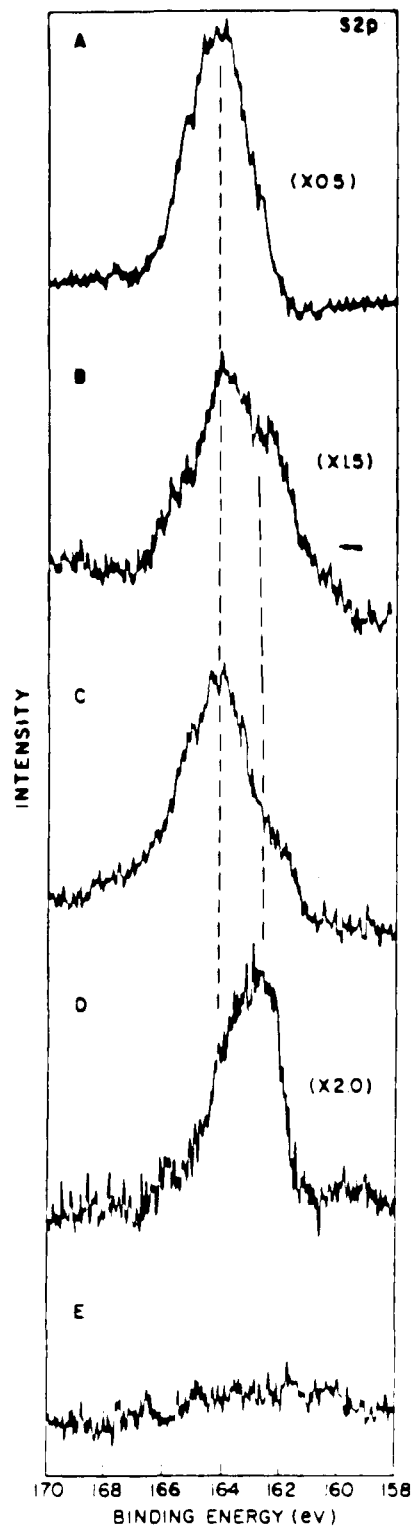


Figure 2. XPS data showing the S 2p core levels for (A) a multilayer of methanethiol adsorbed at -150 °C, (B) the chemisorbed product remaining after desorption of the multilayer at -125 °C, (C) a monolayer prepared in a manner similar to B except with no data being collected on the multilayer precursor, (D) a monolayer similar to the X-ray exposure history of B except showing the stable adsorbate state which remains bound to the surface at ambient temperature, and (E) a surface which results from a multilayer receiving no X-ray exposure, after warming to ambient temperature.

to the X-ray source at -150 °C and then warmed to ~ 20 °C. Note that a single peak of reasonably simple line shape is seen at ~ 162.7 eV, the value inferred from the asymmetry described above. In E, a comparable sample, but with no history of X-ray exposure at the lower temperature, shows no evidence of bound sulfur and hence that the thiol is not retained on the surface at

(13) Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic: New York, 1982.

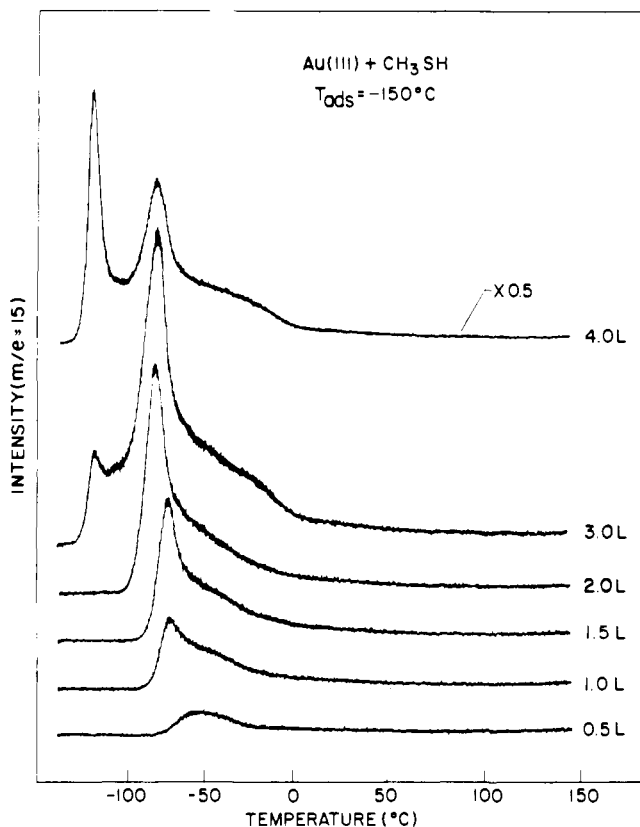


Figure 3. Temperature-programmed desorption spectra of methanethiol from Au(111) as a function of gas dose. The largest cracking fragment of methanethiol (m/e 15) was monitored rather than the parent molecule (m/e 48) to increase the signal-to-noise ratio. The origin of all of the peaks is discussed in the text.

20 °C. On the basis of data and arguments which follow, we assign the higher binding energy peak at ~ 164.0 eV to that of chemisorbed methanethiol. The second peak in this spectrum (seen at ~ 162.7 eV) is due to a decomposition product (presumably from a reduction of the adsorbate by the secondary electron emission). A comparison of the intrinsic S 2p binding energy of chemisorbed methanethiol to that observed for the multilayer shows that there is a small and perhaps negligible shift ($\Delta BE \approx 0.1$ eV) to higher binding energy upon adsorption. Analyses were also made of data taken in the C 1s and Au 4f core level regions, but these data were unexceptional; no shifts or line shape changes were seen for the Au 4f_{7/2} core level compared to the clean surface, and as expected, a single C 1s ($BE \approx 284.9$ eV) peak was seen in the presence of adsorbed thiol.

Additional information about the adsorption of this simple thiol on Au(111) was obtained from TPD studies. Figure 3 shows representative data obtained for a range of exposures of the surface to the adsorbate at -150 °C. Several significant features are apparent. First, the desorption process is *exclusively* molecular; there is no evidence for ions derived from adsorbate decomposition products, and Auger and XPS analyses *show the surface to be clean after desorption*. Second, the lowest temperature peak ($T_m \approx -135$ °C), growing without saturation at exposures greater than ~ 2.0 langmuir, is clearly due to the formation of a multilayer. Third, two discrete peaks for chemisorbed thiol are seen. The first, a relatively broad peak observed at the lowest exposures used, is largely coverage insensitive and is centered at roughly -45 °C. The second peak, observed for exposures greater than ~ 1.0 langmuir, was also insensitive to coverage; the peak maximum was typically centered at ~ -83 °C. The origin of this latter peak is unclear and may, in fact, reflect desorption from a strongly bound second layer, the occupation of a second, weaker binding site, or even the onset of repulsive and/or destabilizing interactions within the monolayer.

In no instance have we observed ordered LEED patterns for any of the exposures/coverages described in Figure 3. In fact,

Table II. Vibrational Mode Assignments for Dimethyl Disulfide^a

| mode ^b | liquid ^c | multi-layer ^d | mono-layer | monolayer/ Cu(100) ^e |
|--------------------------------|---------------------|--------------------------|-------------------|------------------------------------|
| ν_1 , antisym CH stretch | 2986 | 3020 ^f | 2995 ^f | 3020 |
| ν_2 , sym CH stretch | 2914 | 2930 ^f | 2920 ^f | 2930 |
| ν_3 , antisym CH deform | 1424 | 1420 | 1420 | 1450 |
| ν_4 , sym CH deform | 1307 | 1305 | 1300 | 1320 |
| ν_5 , CH ₃ rock | 952 | 950 | 940 | 960 |
| ν_6 , CS stretch | 693 | 690 | 680 | 680 |
| ν_7 , SS stretch | 509 | 498 ^g | | |
| ν_8 , SSC bend | 240 | | | |
| | 270 | 238 ^h | | 300 |
| Au-S | | i | 235 | |

^aAll frequencies in cm^{-1} . ^bSelected general vibrational classes. ^cAveraged values of closely spaced and similar vibrational modes obtained from ref 14. ^d10-langmuir exposure at -150 °C. ^eReference 11b. ^fMaxima of broad asymmetric peak containing both modes. ^gWeak shoulder. ^hAt this exposure (10 langmuir) the observed peak may contain an important contribution from the Au-S mode of the first layer (see text). ⁱMay be obscured by SSC bend in the multilayer.

LEED analysis only resulted in the extensive decomposition of the organic monolayer, leaving a sulfur residue.

Chemisorption of Dimethyl Disulfide. The chemisorption of dimethyl disulfide on an Au(111) surface was studied in a manner comparable to that described above for methanethiol. Dosing the surface at -150 °C led to the formation of stable multilayers for exposures greater than ~ 2.0 langmuir (where monolayer saturation was observed, see below). High-resolution EELS data were obtained for both multilayer (10-langmuir exposure) and monolayer adsorption and are shown in the middle and upper traces of Figure 1, respectively. The spectral data obtained are also summarized in Table II.

Examination of the EELS data for the multilayer shows, as expected, a close correspondence to the vibrational spectrum of the bulk liquid.¹⁴ The monolayer data show some significant differences, however. First, and most important, there is no clear evidence for an S-S stretch (a weak loss seen at ~ 498 cm^{-1} in the multilayer) in the monolayer spectrum. Second, the intensity in the C-H stretching region shows a significant contribution from the antisymmetric mode. As noted earlier, this most reasonably suggests that the C-S bond exhibits a significant cant away from the surface normal. This interpretation is further supported by the observation of significant intensity in both the CH₃ rocking and antisymmetric deformation modes; the dipole selection rule would preclude this if the adsorbate was oriented normal to the surface. A similar canted species has also been reported to result from the dissociative chemisorption of both dimethyl disulfide on Cu(100)^{11b} and methanethiol on Pt(111);¹⁵ the vibrational frequencies observed for this adsorbate on all three surfaces are quite similar (see Table II). The most intense band in the monolayer spectrum is the loss at 235 cm^{-1} . We assign this peak to a gold-sulfur stretch from a surface thiolate (from the data which follow, it is evident that the disulfide bond dissociates on the Au(111) surface).

Examination of the XPS spectra of both multi- and monolayers provided additional insight into the nature of the adsorption of this simple disulfide on gold. Figure 4 shows representative S 2p core level data for a multilayer (upper trace) and monolayer (lower trace) of CH₃SSCH₃ on Au(111). As expected, the observed S 2p binding energy is slightly higher for a multilayer of dimethyl disulfide, 164.8 eV, than that of physisorbed methanethiol, 163.9 eV. This is expected on the basis of a simple judgment of the differences in the formal oxidation state of the two adsorbates. This analogy is not applicable to the chemisorbed species, however. As shown in the figure, chemisorption results in a complex spectral

(14) Frankiss, S. G. *J. Mol. Struct.* **1969**, *3*, 89-101. Hamada, K.; Morishita, H. *Spectrosc. Lett.* **1980**, *13*, 185-197.

(15) (a) The tilt angle reported for SCH₃ on Pt(111) is $45^\circ \pm 10^\circ$ from the surface normal. (b) Koestner, R. J.; Stöhr, J.; Gland, J. L.; Kollin, E. B.; Sette, F. *Chem. Phys. Lett.* **1985**, *120*, 285-291.

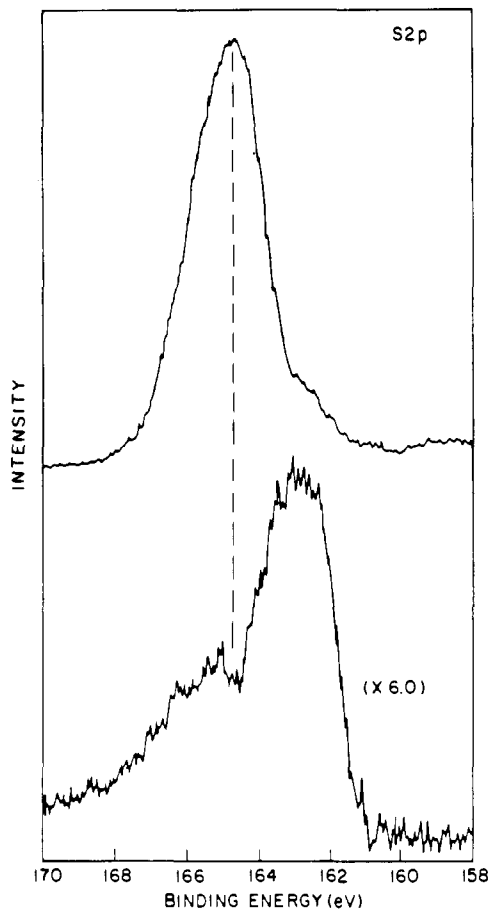


Figure 4. XPS data showing the S 2p core levels for a multilayer of dimethyl disulfide (upper trace) adsorbed on an Au(111) surface at -150°C . The lower trace shows the spectrum which characterizes a stable monolayer at ambient temperature.

pattern involving, predominantly, a *large* shift ($\Delta\text{BE} \approx 2.1\text{ eV}$) to lower binding energy. A considerable, though lesser, contribution is also clearly seen to be present and characterized by a binding energy close to that of the multilayer ($\text{BE} \approx 164.8\text{ eV}$). The observed binding energy of the major peak at 162.7 eV is also seen to be significantly lower than the intrinsic binding energy of chemisorbed methanethiol (seen at $\sim 164.0\text{ eV}$, see above). It is unlikely that this large shift is due, simply, to a core hole screening effect. Rather, we believe that this shift reflects a chemisorbed state which involves dissociation of the S-S bond. It is also significant to note that the binding energy of methanethiol which has been degraded by exposure to the X-ray flux is *identical* with the dominant, stable chemisorbed state of dimethyl disulfide. This strongly suggests that the decomposition noted above arises from a reduction of the sulfhydryl proton by secondary electron emission, liberating hydrogen and yielding a stable surface thiolate.¹⁶ We note that, as in the case of methanethiol adsorption, we were not able to resolve any large perturbations of the Au $4f_{7/2}$ core level binding energy or line shape due to disulfide bonding.

We also attempted to examine the temperature dependence of the appearance of this strong chemisorption state for dimethyl disulfide, but these efforts proved inconclusive; at the lowest temperatures used (-150°C) some strongly chemisorbed disulfide was observed. We also observed that the sticking probability of dimethyl disulfide is reasonably insensitive to temperature; saturation coverages were obtained nearly equally well at -150°C as at room temperature by using a 2.0-langmuir exposure.

Figure 5 shows the results of TPD studies of dimethyl disulfide chemisorption in which the fractional coverage of the adsorbate was varied from ~ 0.1 to saturation. Three significant points

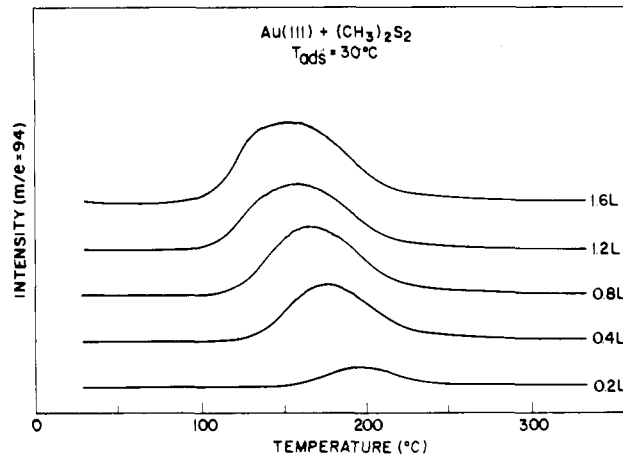


Figure 5. TPD data showing the molecular desorption of dimethyl disulfide from Au(111). The origin of the peak shift and line shape change is discussed in the text.

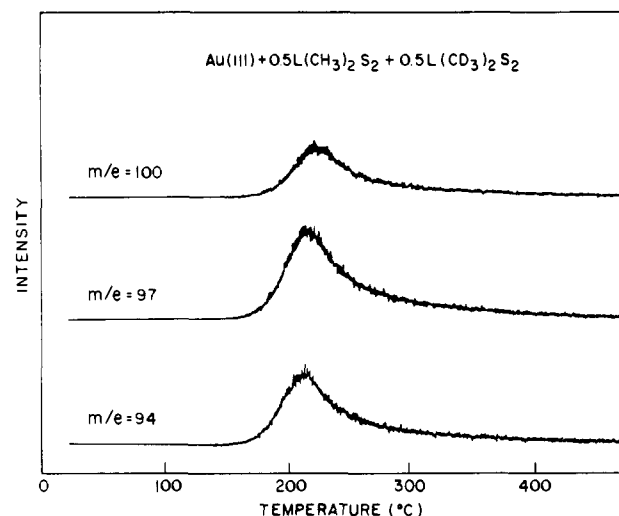


Figure 6. Temperature-programmed desorption spectra of dimethyl disulfide from Au(111) after dosing the surface sequentially with 0.5 L of $(\text{CH}_3)_2\text{S}_2$ and 0.5 L of $(\text{CD}_3)_2\text{S}_2$. Significant isotopic scrambling is observed independent of which isotope was dosed first. The difference in the temperature of the desorption peak maxima between Figures 5 and 6 is due to a slight loosening of the thermocouple leads during the course of the experiments.

emerge from these data. First, the adsorption state is a strongly bound one; the maximum of the highest temperature desorption peak occurs above 170°C over the range of coverages described in the figure. Second, the position of this desorption maximum is strongly coverage dependent. Third, the desorption process is exclusively molecular; there is no evidence for hydrocarbon decomposition products in the desorption spectra, and both XPS and AES confirm that no sulfur is retained on the surface.

Figure 6 shows the results of similar TPD studies in which the initially adsorbed monolayer was prepared by *sequential* half-saturation exposures of the surface to dimethyl disulfide and dimethyl- d_6 disulfide. The molecular desorption products obtained from such monolayers were found to be extensively interchanged (note in Figure 6 the near statistical formation of the trideuterated disulfide ($m/e\ 97$)).¹⁷ At a minimum, these results strongly suggest that during the desorption process, facile dissociation of the S-S bond must be occurring. The large coverage dependence of the position of the desorption maximum is also consistent with a second-order desorption process.¹⁸ The combined weight of the data, however, suggests that this is more than just an inter-

(16) This reaction is seen to occur spontaneously on both Cu(100) and Pt(111). See ref 11b and 15b.

(17) These results are obtained independent of which compound is chemisorbed first.

(18) Redhead, P. A. *Vacuum* 1962, 12, 203-211.

mediate process and that the predominant stable adsorption state of this molecule is, in fact, the dissociated form.

Discussion

The data reported above present some interesting contrasts between the chemistry of simple organic thiols and disulfides on the Au(111) surface. In the discussion which follows, we will attempt to develop these comparisons and establish a clearer structural and thermodynamic understanding of the adsorption of these adsorbates on gold. Where possible, we will suggest how these findings are relevant to both the solution adsorption experiments to be described in forthcoming publications⁴⁻⁶ and the larger issue of monolayers prepared by molecular self-assembly.

The easiest point to establish about the adsorption chemistries described above is that dimethyl disulfide is much more strongly bound to the Au(111) surface than is methanethiol. The TPD data clearly show this to be so. For methanethiol, the data strongly suggest that the adsorbed state involves the bonding of the sulfur atom to gold and that the *S-H bond is not cleaved*. For example, the EELS data in Figure 1 show that an S-H stretch, though hydrogen bonded, is still present, while the XPS data in Figure 2 show that the shift in the S 2p core level in going from the bulk (multilayer) to the chemisorbed state is very small (a large shift would be expected for a chemisorbed thiolate, *vide infra*). Also, only small differences are seen between the vibrational spectra of the gas phase and the adsorbed species. Further, it seems unlikely that any surface hydrogen, arising from S-H bond cleavage, would be retained on the surface (the loss of H₂ being facile at these temperatures). The fact that TPD studies showed only the parent thiol desorbing—we did not see any disulfide and/or decomposition products desorbing—strongly militates against the importance of S-H cleavage in this system *under these conditions*.¹⁹

The chemisorption of dimethyl disulfide is quite different, however. First, in the XPS data (Figure 4) we see, in part, a large shift in the S 2p binding energy in going from the bulk (multilayer) to the chemisorbed state ($\Delta BE \approx 2.1$ eV). Significantly, this shift is to lower binding energy, suggesting either or both a reduction of the sulfur functionality and a screening of the core hole much greater than that evidenced in the case of methanethiol. The EELS data also show a significant difference. Note, in Figure 1, how the monolayer spectrum of the disulfide is dominated by an intense mode at 235 cm⁻¹. If our assignment of this mode as being due to a gold-sulfur stretch is correct, then this suggests a strengthening of this bond relative to that of chemisorbed methanethiol (the same mode appears at a lower frequency for this adsorbate—even so, some caution is required here as the bonding sites for the two adsorbates may be different). The most telling evidence is derived from the TPD results, however. The position of the desorption maximum observed occurs at a much higher temperature than that seen for the two chemisorbed states of methanethiol (≈ 180 °C vs. -45 and -85 °C). This peak position is also found to be strongly coverage dependent, suggesting the occurrence of either a strongly coverage-dependent heat of adsorption or a bimolecular desorption process.¹⁸ We feel, given the extensive isotopic scrambling observed in mixed monolayer studies (Figure 6) and the results of the EELS (Figure 1) and XPS (Figure 4) studies described above, that the simplest interpretation of the data is that the S-S bond is cleaved during disulfide adsorption on the Au(111) surface.

Another point of interest is that the stable adsorption states we detail above for methanethiol and dimethyl disulfide are easily formed. Both adsorbates saturate these states at very low exposures (≤ 2.0 langmuir), and in the case of dimethyl disulfide, we have observed that this process is very insensitive to temperature (a 2.0-langmuir exposure is equally effective at -150 and 20 °C).

Taken together, the points described above allow several important conclusions to be reached. First, the barrier to disulfide

cleavage on Au(111) must be reasonably low. Second, the thermodynamically most stable state of either adsorbate should be that of a chemisorbed thiolate (or at least predominately so), the state observed only for chemisorbed dimethyl disulfide. Third, the barrier to methanethiol entering this state (with the concurrent formation of gaseous H₂) must be sufficiently large so as to make this reaction channel difficult to access in UHV.

In addition, one can make, in principle, a simple interpretation of the TPD data in terms of adsorption-state thermodynamics. In practice, some simplifying assumptions must be made in order to relate the actual *kinetic* data obtained to such desired thermodynamic parameters as the heat of adsorption. The central assumption made in most routine analyses of this sort is that the barrier height (activation energy for desorption) can be related to the measured desorption kinetics by an Arrhenius-like relationship. As such, a rigorous treatment of the data requires the determination of both an activation energy, E_a (which we hope to relate to the heat of adsorption), and a preexponential factor, ν_n . Further, for most simple analyses, it is assumed that the heat of adsorption is coverage independent and that the preexponential term varies only slightly with temperature. Many protocols have been devised which, using these assumptions, allow quantification of the data presented in Figures 3 and 5. For simplicity, the first-order desorption peaks characterizing the two adsorbed states of methanethiol have been interpreted according to methods described by Redhead,¹⁸ assuming a preexponential term of $\sim 1 \times 10^{13}$ s⁻¹ ($\Delta S^\ddagger \approx 0$). Given this assumption of a "normal" preexponential term, we calculate binding energies of ~ 11.6 and 13.9 kcal/mol for the two desorption peaks centered at ~ -83 and -45 °C, respectively. Thus, both these chemisorbed states are characterized by modest heats of adsorption.

Interpretation of the dimethyl disulfide TPD data is somewhat more problematic due to the expected bimolecular character of this desorption process (see above); the preexponential term need not be "normal" (10^{13} s⁻¹), and the observed rate must be corrected for its coverage dependence. A close inspection of the data reveals a further complication: we observed that changing the coverage results in a *large* change in the desorption peak line shape. The peaks at low coverage ($\theta_0 \approx 0.2\theta_s$, where s denotes saturation) are skewed, as expected, toward *higher* temperature; at high coverage they are skewed toward *lower* temperatures. In fact, desorption from the high-coverage state could involve two closely spaced and largely unresolved processes, both of which give peak maxima that are highly dependent on coverage. For this reason we have restricted our analysis to an examination of the simpler line shapes seen at low coverage. While the numbers we obtain vary somewhat depending on the method used,^{18,20} they are generally of the order of 28 kcal/mol, which is a factor of 2 *higher* than that of the monodentate methanethiol; the coverage-independent preexponential factors are also normal (of the order of $\sim 10^{12}$ – 10^{13} s⁻¹).²¹ These results, while very qualitative, further confirm the conclusion that disulfides are strongly bound on Au(111).

We cannot, at present, unambiguously explain why the high-coverage dimethyl disulfide desorption data shown in Figure 5 display additional structure. One interesting possibility is that there may be an equilibrium between the disulfide (intact and bonded through two sulfurs) and the thiolate on the surface. Recall that the XPS data presented in Figure 4 showed that the S 2p core level spectrum of chemisorbed dimethyl disulfide consisted of two discrete peaks: a lesser one centered at or near the binding energy of the bulk (multilayer) adsorbate (164.8 eV) and the other, the major species, at significantly lower binding energy (162.7 eV). We strongly believe that these data describe two chemisorbed states of dimethyl disulfide on this surface at high coverage—one molecular and the other dissociatively chemisorbed.

(20) Chan, C.-M.; Aris, R.; Weinberg, W. H. *Appl. Surf. Sci.* **1978**, *1*, 360–376 and references cited therein.

(21) Using this number, we can also estimate the strength of the gold-sulfur bond as follows: S-S, ~ 62 kcal/mol; 2(Au-S) – 62 = 28, then Au-S ≈ 45 kcal/mol!

(19) A thiolate forms readily on both Cu(100) and Pt(111). Desorption of these species involves a decomposition of the adsorbate, leaving a sulfur residue and liberating gas-phase methane and ethane. See ref 11b and 15b.

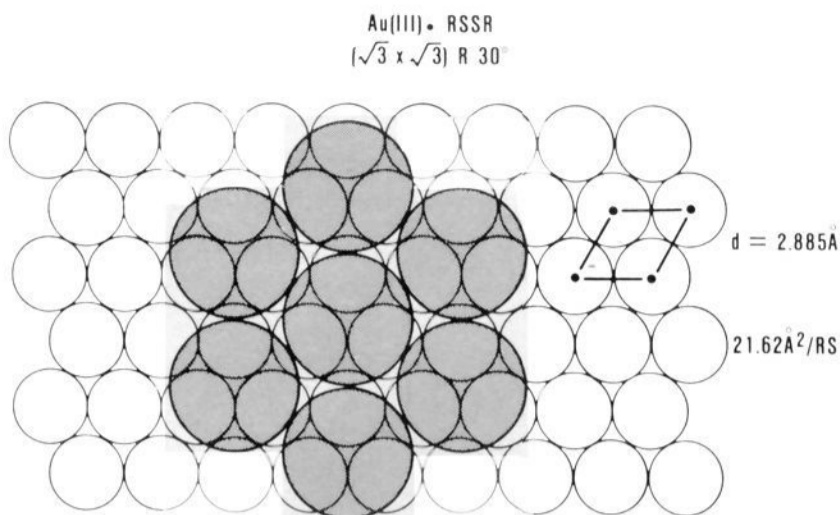


Figure 7. Space-filling projections for spherical (or cylindrical) adsorbates forming a $3^{1/2} \times 3^{1/2} R30^\circ$ hexagonal overlayer and centered on 3-fold hollow sites. The space provided to each by this arrangement, centering one sulfur on three gold atoms, is approximately 21.6 \AA^2 .

The XPS data thus seem to strongly confirm the notions developed independently from TPD data.²²

It is obvious from the preceding discussion that the interaction of the Au(111) surface with dialkyl disulfides is a strong one. Through what type of bonding is this manifested? Part of the answer has been established above. The majority of the species present are expected to be surface thiolates (Au-SR). We also expect, on the basis of an analogy to similar heteroatom-containing organic adsorbates on fcc(111) surfaces, that the preferred binding site is likely to be a 3-fold hollow in order to provide the maximum coordination environment for the *formal* thiolate anion.²³ Figure 7 shows a remarkable feature which attends when one attempts to place these molecules on the Au(111) lattice plane. In the figure, a hexagonal overlayer ($3^{1/2} \times 3^{1/2} R30^\circ$) has been placed on the Au(111) surface. The area per molecule we calculate from this arrangement is $\sim 21.6 \text{ \AA}^2$ (one thiolate adsorbate per three gold surface atoms). Inspection of both space-filling models and the literature on monolayers prepared by Langmuir-Blodgett techniques suggests that normal-chain alkyl thiolates, and perhaps thiols as well, can easily pack at high density with such a spacing on the lattice; to do this the chains would have to show some cant from the surface normal.²⁴ Such a cant for adsorbed methyl thiolate is strongly suggested by the EELS spectra shown in Figure 4. We have, as will be shown shortly, extensively characterized such orientations of long-chain alkyl thiols and disulfides chemisorbed on polycrystalline gold films showing a very strong (111) texture.^{4,6} It is thus an intriguing possibility that closest packed monolayers of organic thiols or disulfides may grow epitaxially on the Au(111) surface. Our own experiments reported here, however, have given us no clear proof that such a circumstance pertains to the UHV environment since LEED studies of both chemisorbed methanethiol and dimethyl disulfide did not show evidence of an ordered overlayer being formed. We did note, however, that both these monolayers were extensively degraded by the electron beam; almost pure sulfur monolayers were generated even after short exposures. For this reason, the presence of ordered domains is not rigorously precluded. Additionally, it is unclear what effect undissociated disulfide would have on adsorbate ordering, as the S-S bond length would not bridge the $3^{1/2}$ distance.

We now turn to a consideration of the relative stabilities of alkylthiol and dialkyl disulfide monolayers on Au(111). The data presented above strongly establish the stability differences which characterize these adsorbates in a *UHV experiment*. Using the

extreme values obtained from TPD data, we conclude that monolayers of this sort derived from disulfides are *much more* stable, so much so, that if we could examine competitive equilibria in UHV, chemisorption of disulfides would be favored by a factor of roughly 10^5 . Is this directly relevant to solution studies? We believe it is but note that this is not rigorously required for the reasons which follow. First, solution-phase experiments do not have the same physical and mechanical limitations as a UHV experiment. Most notably, it is relatively simple to maintain a high flux to the surface, at higher temperatures, when one doses a substrate by immersing it into a reasonably concentrated solution of adsorbate ($\sim 10^{-3} \text{ M}$). The UHV data above strongly suggest that, while energetically favorable, there exists a considerable barrier for thiols to enter the same chemisorption state as disulfides (with the concurrent loss of H_2 or even H_2O , by coupling this redox process to adventitious O_2 present in the solution).²⁵

Second, different *mixed* monolayers might be obtained in solution-phase experiments. The TPD and XPS data presented above for dimethyl disulfide chemisorption show a complicated structure at high coverage. Gold is a reasonably inert surface, and dissociation of the disulfide headgroup does not appear to go to completion with the remaining disulfide binding molecularly. Indeed, such patterns in reactive chemisorption have been observed previously, most notably in the adsorption of simple carboxylic acids on Cu(100);²⁶ roughly half of a monolayer is reduced to form a stable carboxylate while an additional quantity of the undissociated acid coadsorbs molecularly and, in so doing, generates large hydrogen-bonded arrays of "half-acids". If alkylthiols partially cross the barrier to dissociation in a solution experiment, as described above, one then need consider, in any comparison, the stability of mixed monolayers comprised of coadsorbed surface thiolate and thiol (the existence of hydrogen-bonded "half-thiols" is unknown at present).

Considerable data have been obtained on the adsorption of alkylthiols and disulfides on polycrystalline gold mirrors by using solution-phase immersion to prepare the samples, and the results suggest that at least some of the notions developed from the UHV data are applicable thereto. Most significant of these was the observation of a distinct chain-length dependence for the molecular self-assembly of alkylthiols; *n*-alkyl chain lengths less than C_{10} consistently produced thin and defect riddled films.⁶ In other chemisorption systems we have argued that such results point to an important aspect of monolayer film stability:²⁵ these films are at equilibrium only in the presence of additional adsorbate. Unless the adsorbate is very strongly bound (via headgroup-substrate chemistry or in combination with more complex lateral interactions), desorption processes will rapidly deplete the film of material. For films that are of very high, perhaps "solid-like", initial densities, the monolayer that results need not simply be "liquid-like". Indeed, such desorption processes *can go to completion*, as we observe for methanethiol, or to some coverage where a coverage-dependent heat of adsorption makes the film stable on a reasonable laboratory time scale. The finding of a chain-length dependence for thiols suggests that, at least under some conditions, desorption processes can be important for this adsorbate. This correlates reasonably with the data we have obtained in UHV.

Why then does the chemistry described in Scheme I—the construction of both polar and nonpolar organic surfaces—work? In simplest terms, the interaction of the gold surface with the sulfur atoms in these classes of adsorbates is strong; the heats of adsorption of other functional groups, such as carboxylic acids or hydroxyls, are considerably lower.²⁷ Gold also appears capable

(22) Coverage-dependent XPS and EELS measurements are consistent with these notions but do not provide definitive proof due to the limited sensitivity of the former technique and the low scattering cross section for the S-S bond in the latter.

(23) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, 1981 and references cited therein.

(24) For leading references, see: Gaines, G. L. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966.

(25) It is important to note that disulfides are a significant contaminant in most alkylthiol preparations. It is extremely problematic to rigorously exclude them in any solution-phase experiment. We also note that in unreported studies of long-chain alkylthiol adsorption from solution, we have observed S 2p binding energies qualitatively very similar to that found here for *dimethyl disulfide*, suggesting a similar adsorption state. The extreme X-ray beam sensitivity we observed above for methanethiol, however, precludes a definitive judgement being drawn only from this XPS data.

(26) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *Langmuir* **1986**, *2*, 412-417.

(27) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G., unpublished results.

of binding these complex adsorbates strongly to very high surface densities, perhaps approaching that of a solid-like organic phase of low dimensionality.

We and others will detail additional properties of this intriguing chemisorption system and show relevant applications to the study of model organic surfaces, interfaces, and their properties in future publications.

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Molecular Structure and Magnetic Properties of a Novel Fe(III) Tetranuclear Complex Containing Oxo, Alkoxo, and Carbonato Bridges

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Abstract: The crystal structure and magnetic properties of a novel antiferromagnetic Fe(III) complex that contains bridging carbonate, oxo, and alkoxo groups are reported. The complex (**1**) crystallizes as brown-green tablets in space group $P\bar{1}$ with $a = 11.712$ (4) Å, $b = 12.914$ (3) Å, $c = 10.987$ (3) Å, $\alpha = 94.03$ (2)°, $\beta = 116.00$ (2)°, $\gamma = 77.70$ (2)°, $Z = 1$, $d_{\text{calcd}} = 1.72$ g/cm³, and $d_{\text{obsd}} = 1.71$ (2) g/cm³. Least-squares refinement of 3126 reflections having $F^2 > 2\sigma$ gave a conventional R factor of 0.085. The structure contains centrosymmetric tetranuclear complexes consisting of two binuclear Fe₂L(O)(CO₃) units where L is the pentaanionic form of [(2-hydroxy-1,3-propanediyl)diimino]tetraacetic acid. The Fe(III) ions within the Fe₂L(O)(CO₃) asymmetric unit have slightly different NO₂ distorted octahedral ligand donor sets in which the O -donors are supplied by two monodentate acetates, a bridging oxide, a bridging alkoxide, and one oxygen atom per Fe from the bridging bidentate carbonates. The bent Fe₂O(oxo) unit (136.4 (3)°) contains the shortest Fe–O bonds (1.828 (4), 1.830 (4) Å) in the structure. These are, however, among the longest reported for an oxo-bridged binuclear Fe(III) unit. The Fe–O bonds arising from the bridging carbonate group are equivalent (1.989 (4), 1.997 (4) Å) within experimental error. The Fe–O(alkoxo) bonds (2.040 (4), 2.066 (4) Å) are nearly equivalent and fall outside the range (1.93–2.01 Å) reported for various hydroxo- or alkoxo-bridged Fe(III) binuclear complexes. One lattice Na⁺ ion, located on a center of symmetry, joins the tetranuclear anions to form infinite chains along [110]. The effective magnetic moment per Fe(III) in **1** varies gradually from 2.42 μ_B at 300 K to 0.36 μ_B at 15 K. Magnetically, the structure is most conveniently viewed as containing μ -oxo, μ -carbonato dimers linked by additional μ -alkoxo bridges. A molecular field model was used to approximate the case where intradimer magnetic coupling (J) of the oxo/carbonato binuclear unit is expected to dominate the relatively weaker interdimer coupling (J') expected from the two long alkoxo bridges. The experimental data were well fit with $J = -63.4$ cm⁻¹, $J' = -11.2$ cm⁻¹, $g = 2.0$, and $\text{TIP} = 800 \times 10^{-6}$ cgsu. The intradimer coupling constant is considerably smaller than the values reported (–90 to –120 cm⁻¹) for oxo-bridged Fe(III) binuclear complexes, and this may be attributed to the somewhat long Fe–O(oxo) bond distances observed in **1**. Structural reasons for this effect are discussed. In contrast, the J' value is typical of that found for hydroxy/alkoxy-bridged Fe(III) dimers.

Polynuclear systems with two or more Fe(III) ions bridged by oxygen donor ligands are pertinent to the inorganic and bioinorganic chemistry of ferric ion. The simplest and most thoroughly studied systems are binuclear complexes in which the Fe(III) ions are bridged by a single oxo or by two hydroxo or alkoxo bridges. The oxo-bridged binuclear complexes exhibit unusual electronic spectroscopic properties² along with appreciable antiferromagnetic exchange interactions which may be described by the $-2JS_1S_2$ exchange Hamiltonian with $S_1 = S_2 = 5/2$, $-J = 90$ to 120 cm⁻¹, and $g = 2.0$. The magnitude of the antiferromagnetic interaction is surprisingly insensitive to the natures of the non-bridging ligands, Fe(III) coordination numbers, and Fe–O–Fe bridging angles.³ The Fe₂(OR)₂⁴⁺ binuclear systems (R = H, alkyl) are far more weakly coupled magnetically ($-J = 10$ to 15 cm⁻¹) and exhibit electronic absorptions which are little changed from those of magnetically isolated Fe(III) monomers.^{3,4}

The oxo-bridged binuclear complexes are by far the most commonly observed of these two types. They seem to constitute a thermodynamic pit for numerous Fe(III)–ligand systems, and their appearance in the literature has continued without interruption since the first structural characterization in 1967.⁵ Studies of binuclear Fe(III) complexes have been stimulated by reports that three metalloprotein systems contain (in their fully oxidized states) binuclear Fe(III) units, all of which seem to be the more common oxo-bridged type. The best characterized of these is the non-heme O₂ transport protein hemerythrin in which the Fe(III) ions additionally are bridged by the carboxylate side chains of glutamate and aspartate protein residues.^{6,7} The non-bridging ligands include five histidine imidazoles and hydroperoxide.^{8,9} Dissociation of

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