

migration of H(a) formed dissociatively on Ru sites, along defects in the Cu-Ru bimetallic particles, particularly along the interfaces between the two metals.

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A Study of the Orientation and Bonding of Thiophene on Clean Mo(100) Using Angle-Resolved Ultraviolet Photoelectron Spectroscopy

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We have examined the bonding and orientation of thiophene on Mo(100) following chemisorption at 180 K. At these temperatures, thiophene adsorbs predominantly molecularly, and a shift in the binding energy of peaks due to molecular π -orbitals in the photoelectron spectrum suggests that at least part of the bonding of the thiophene molecule to the surface involves these orbitals. Measurements of the variation in intensity of thiophene photoemission peaks as a function of angle of incidence of the radiation suggest that the molecular plane is tilted at $25 \pm 5^\circ$ with respect to the surface normal. These observations suggest a bonding configuration in which thiophene chemisorbs into a fourfold site. This geometry explains the regiospecific hydrogen abstraction seen for thermal decomposition of thiophene on Mo(100) in which the α -hydrogen is preferentially removed.

Introduction

Molybdenum disulfide forms the basis of an active, sulfur-resistant desulfurization catalyst. Such sulfur removal reactions are crucial in the processing of crude oil since many of the catalysts used for the preparation of gasoline and petrochemicals are sensitive to sulfur poisoning, thus requiring prior removal of sulfur-containing compounds. Mo(100) single crystals also appear to be active for the catalytic removal of sulfur, since reactions between thiophene (a commonly used model for a sulfur-containing hydrocarbon) and hydrogen over Mo(100) single crystals reproduce the kinetics and product distribution of a supported MoS₂ catalyst rather well.^{1,2} The pathway by which thiophene decomposes on a single-crystal Mo(100) surface is therefore of some importance for understanding this catalytic process.

Recent thermal desorption studies³ have shown not only that hydrogen is removed from thiophene in a stepwise fashion but also that it is strongly regiospecific. Thus, thermal decomposition of chemisorbed C₄H₂D₂S- α -d₂ shows a sequential removal of hydrogens in the order D-H-H-D which suggests that the decomposition involves a stepwise removal of hydrogen from the 2-, 3-, 4-, and 5-positions. Such a regiospecific hydrogen abstraction has also been observed on nickel surfaces.⁵

Several modes of thiophene chemisorption have been reported on transition-metal surfaces. π -Bonded thiophene has been reported at room temperature on Cu(111).⁶ On Pt(111), Stohr et al. concluded, based on NEXAFS data, that below 230 K thiophene bonds via the sulfur atom, but between 230 and 300 K it rearranges into a π -bonded configuration.⁷ In contrast, Masel concluded that π -bonding occurs below 170 K and that the molecule is tilted between 170 and 325 K.⁸ On Ni(111), Benziger interpreted their infrared data by proposing that thiophene chemisorbs with its ring parallel to the surface below room temperature, followed by polymerization on heating.⁹ The same group also reported C₃ formation following thiophene chemisorption on W(211).¹⁰

We have recently proposed^{3,4} that thiophene chemisorbs molecularly at low temperatures on Mo(100) at high coverages and

then undergoes a preferential α -hydrogen removal at 230 K, the remaining partially dehydrogenated species being bonded to the surface via a C-Mo σ -bond such that the plane of the thiophene molecule is oriented essentially perpendicular to the Mo(100) surface. Subsequent reaction proceeds via abstraction of a hydrogen atom attached to a carbon forming a di- σ -bonded surface species. Here we have investigated the bonding and orientation of thiophene on Mo(100) at 180 K using angle-resolved photoelectron spectroscopy. This temperature is just above that at which condensed thiophene desorbs but still low enough that the chemisorbed thiophene should have undergone minimal decomposition. This conjecture is corroborated experimentally since the photoelectron spectrum of the chemisorbed overlayer correlates well with that of thiophene ice. In addition, we find that the molecular plane of thiophene is tilted at $25 \pm 5^\circ$ with respect to the surface normal and that bonding of the thiophene to the surface involves its π -orbitals. These observations can be reconciled by proposing that the sulfur atom of the thiophene is bonded to the molybdenum atom in a fourfold hollow site (i.e., an exposed atom in the second layer) while the molecule is simultaneously π -bonded to molybdenum atoms in the top layer.

Experimental Section

These experiments were performed on beamline U14A at the National Synchrotron Light Source at Brookhaven National Laboratory. The monochromator and beamline have been described in detail elsewhere.¹¹

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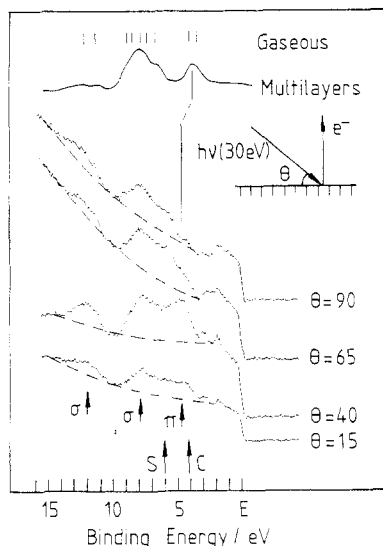


Figure 1. Angle-resolved photoelectron spectra of a Mo(100) surface exposed to 5 langmuirs of thiophene at 180 K taken at normal emission as a function of incidence angle with 30-eV photons. Shown for comparison are the positions of the peaks in a photoelectron spectrum of gas-phase thiophene and multilayers of thiophene. Both of these spectra have been rigidly shifted to coincide with the overlayer spectrum. The positions of peaks due to atomic sulfur and carbon are indicated by arrows.

The stainless-steel bakeable ultrahigh-vacuum (UHV) chamber used for these experiments operated at a base pressure of 1×10^{-10} Torr following bakeout. It was equipped with a cylindrical mirror analyzer (CMA) which was primarily used for Auger analysis of the molybdenum sample to establish surface cleanliness. The chamber also contained a rotatable hemispherical analyzer which was used to obtain the angle-resolved photoelectron spectra presented in this paper. The total instrument resolution (i.e., the combined ultraviolet line width and analyzer resolution) was ~ 0.2 eV.

The Mo(100) crystal, mounted via tantalum rods to a rotatable manipulator, could be resistively heated to ~ 2000 K and cooled to ~ 120 K by thermal contact to a liquid nitrogen reservoir. The sample was cleaned by using a standard protocol, i.e., by heating briefly to 2000 K in vacuo (to remove sulfur) and then at ~ 1700 K in 2×10^{-7} Torr of oxygen (to remove carbon). The sample was adjudged clean when no Auger signals due to any surface contaminants (primarily oxygen and carbon) were observed after annealing at 2000 K.

Thiophene was purified by repeated bulb-to-bulb distillations and stored in glass until used. No impurities were detected mass spectroscopically.

Results

The clean Mo(100) surface was exposed to 5 langmuirs of thiophene (uncorrected for ion gauge sensitivity) at a sample temperature of 180 K. This temperature is just above the multilayer desorption temperature so that only a chemisorbed monolayer of thiophene is formed under these conditions.

An initial series of experiments were performed in order to establish the optimum photon energy with which to obtain the photoelectron spectra. It was found that 40-eV photons produced spectra that optimized the overlayer photoemission intensity compared to emission from the substrate. However, the spectral resolution with 30-eV photons was significantly better, so that experiments were performed using both 30- and 40-eV photons.

Figure 1 shows a series of angle-resolved photoelectron spectra obtained by using 30-eV photons taken as a function of incidence angle while detecting only electrons emitted normal to the surface. θ is the light incidence angle measured with respect to the surface and therefore also is the angle of the electric field with respect to the surface normal (see Figure 6). An estimated inelastic base line is drawn in the spectra to emphasize the overlayer-induced

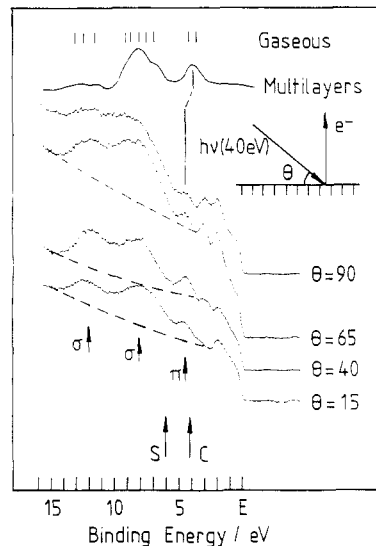


Figure 2. Angle-resolved photoemission spectra taken with 40-eV photons of Mo(100) following exposure to 5 langmuirs of thiophene at 180 K. Spectra of gas phase and multilayers of thiophene are shown for comparison. The positions of peaks due to atomic sulfur and carbon are indicated by arrows at the bottom of the spectrum.

peaks. Shown for comparison are the peak positions from a gas-phase photoelectron spectrum of thiophene^{12,13} and the photoelectron spectrum of thiophene ice taken under similar conditions of spectrometer resolution.⁴ Both the overlayer-induced peaks and those due to multilayers of thiophene exhibit similar peak widths. The agreement between the spectra of multilayers of thiophene, gas-phase thiophene, and chemisorbed thiophene is extremely good. All three spectra exhibit a broad peak at ~ 12 -eV binding energy (BE) and another broad peak with a low-energy shoulder at ~ 8 -eV BE. These peaks are designated σ in Figure 1. The peak assignments will be discussed in greater detail below. The peak designated π , with a binding energy of ~ 4.6 eV in the overlayer spectrum, is shifted to higher binding energy than in the corresponding gas-phase and multilayer spectra by ~ 1 eV.

A similar set of angle-resolved photoelectron spectra were taken by using 40-eV photons and are shown in Figure 2. The spectra exhibit similar σ -peaks at 12- and 8-eV BE, and the π -peak at 4.5 eV is again shifted from the gas-phase and multilayer values by ~ 1 eV. The resolution of these spectra is slightly worse than when 30-eV photons are used (Figure 1), and the lower binding energy shoulder on the 8-eV BE σ -peak is no longer in evidence. The π -peak at 4.5-eV binding energy is however more clearly resolved. The positions at which signals from atomic sulfur and atomic carbon might be expected to appear (taken from ref 4) are shown in Figures 1 and 2.

Discussion

Nature of the Surface Species. The photoelectron spectra of both the chemisorbed monolayer and ice exhibit three main broad peaks, the correspondence between these spectra suggesting that at least a considerable fraction of the thiophene chemisorbs molecularly. Molecular chemisorption has also been reported on Pt(111)^{7,8} and other surfaces,^{6,9,10} but C-S bond scission has been shown to occur even at 100 K on Ni(100).¹⁸ Our previous data indicate that in the case of Mo(100) dissociation at low temperature amounts to about 10% of the total chemisorbed thiophene.^{3,4} The remaining 90% was reported to adsorb molecularly, in agreement with the results presented here.

Since the thiophene molecule remains essentially intact on the surface, peaks can be assigned by direct comparison between gas-phase spectra and the surface species. The gas-phase peak

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TABLE I: Peak Positions and Their Assignments for Thiophene Chemisorbed on Mo(100) at 180 K

BE/eV	assignt	BE/eV	assignt	BE/eV	assignt
12.9	6a ₁	8.5	8a ₁	6.8	1b ₁
12.2	4b ₂	7.8	6b ₂	4.7	2b ₁
11.3	7a ₁	7.3	9a ₁	4.1	1a ₂
8.9	5b ₂				

TABLE II: Peak Assignments for a Monolayer of Thiophene Chemisorbed on Mo(100) at 180 K

BE/eV	symmetry	gas-phase BE/eV	peak assignt
12	6a ₁	18.3	σ
	4b ₂	17.6	
	7a ₁	16.6	
8	5b ₂	14.3	π
	8a ₁	13.9	
	6b ₂	13.3	
	9a ₁	12.7	
	1b ₁	12.1	
4.6	2b ₁	9.5	π
	1a ₂	8.9	

positions are shown plotted in Figures 1 and 2. These have been rigidly shifted from their absolute gas-phase binding energies to take account of final-state relaxation effects.⁴ The peak at 12-eV binding energy is assigned to emission from 6a₁, 4b₂, and 7a₁ levels which are all σ -bonding orbitals. The peak at 4-eV binding energy in the multilayer spectrum corresponds to gas-phase 1a₂ and 2b₁ levels, which are shifted by ~ 1 eV due to interaction with the surface. These correspond to ring π -orbitals, suggesting that at least part of the contribution to the surface bonding of thiophene is via its π -orbitals. The broad peak centered at 8 eV consists of a manifold of five overlapping levels, viz., a 9a₁ nonbonding orbital at 7.3-eV BE, a 1b₁ level at 6.8-eV BE, and three σ -orbitals of 5b₂, 8a₁, and 6b₂ symmetry. Since these peaks are not resolved, it is not possible to decide whether any of these levels are further involved with surface bonding. Specifically, it is not possible to tell whether any levels having molecular orbitals with substantial electron density at the sulfur atom are shifted. Peak positions and their assignments are summarized in Table I.

Molecular Orientation. We turn our attention now to determining the orientation of the thiophene molecule with respect to the molybdenum surface using the variation of photoelectron peak intensities with incidence angle. It has been shown in previous publications that it is possible to use angle-resolved photoelectron spectroscopy to determine the angle at which small molecules (e.g., CO and NO) are oriented to the surface.¹⁴⁻¹⁶ In those cases, the variation in electric field along or perpendicular to the internuclear axis was used to generate theoretical curves of the variation of σ -emission intensity as a function of molecular tilt angle.¹⁴ Comparison of the experimental variation in this emission cross section with the theoretical curves yielded tilt angles that agreed well with NEXAFS measurements even in the case where CO is tilted with respect to the surface and therefore has a low symmetry.^{15,16} In the case of thiophene, we apply identical analysis methods to the high-binding-energy σ -peaks centered at 12 eV since they consist of three reasonably well spaced orbitals (see below). The π -orbitals are clearly involved in bonding with the substrate, and so they are likely to be hybridized with the metal d-orbitals. The variation of the intensity of the photoelectron peaks for these levels as a function of light incidence angle therefore is likely *not* to lead to a reasonable value of molecular tilt angle. The molecular orbitals that gives rise to the 12-eV BE σ -peak,

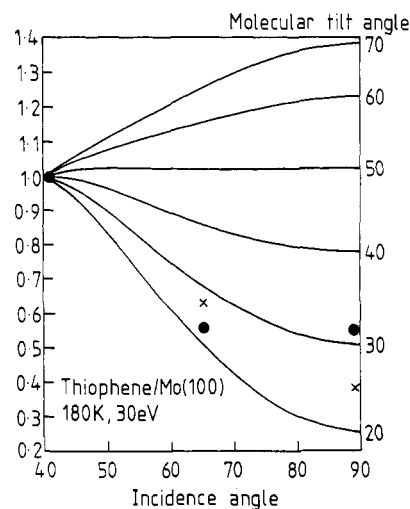


Figure 3. Set of theoretical plots of photoemission intensity (normalized to emission at 40°) from molecular orbitals of a₁ symmetry as a function of incidence angle for various values of molecular tilt angle between 20° and 70° taking account of the substrate refractive index. Shown also plotted are experimental points taken from the data of Figure 1 with 30-eV photons; 6a₁ peak (●), 7a₁ peak (×).

on the other hand, should be almost completely molecular in character, so that they are ideal for geometry determination.

Reference to Table II shows that the 12-eV σ -peaks consist of three overlapping levels. The symmetry of the free molecule is C_{2v}, and within the point group the molecular orbitals can be assigned as follows: the 12-eV σ -band contains a 6a₁ peak at 12.9 eV and 4b₂ at 12.2 and a 7a₁ peak at 11.2-eV binding energies, respectively. This assignment was made by using the gas-phase binding energies and rigidly shifting the bands to account for relaxation effects on adsorption. The symmetry of the tilted species is no longer C_{2v}, since in a tilted chemisorption orientation the twofold axis is lost. We may nevertheless use the nomenclature from the C_{2v} point group to label the molecular orbitals. Within the C_{2v} group, a₁ levels transform as z (where z is taken as the principal symmetry axis of the isolated molecule) so that intensity of peaks of a₁ symmetry should vary in a similar manner as a function of incidence angle as σ -orbitals in CO for various tilt angles, and therefore the variation in intensity of these peaks as a function of incidence angle is capable of yielding information on the angle at which the plane of the thiophene molecule tilts with respect to the surface normal. The 4b₂ peak transforms as y and therefore contains different information regarding the tilt angle. Examination of the width of the π -levels in the 30- and 40-eV spectra (Figures 1 and 2) shows that the full width at half-maximum for photoelectron peaks in the overlayer spectrum is ~ 1 eV. Although at this width the 6a₁, 4b₂, and 7a₁ peaks are not resolved, if we may assume that the manifold consists of Lorentzians of ~ 1 -eV width at 18.3-, 17.6-, and 16.6-eV binding energies, then this shows that the contribution to the intensities of the 6a₁ and 7a₁ peaks from the 4b₂ peak is likely to be less than $\sim 10\%$. Thus, a measurement of the height of the envelope at the positions corresponding to the centers of the 6a₁ and 7a₁ peaks (determined from the gas-phase thiophene spectrum) should be a reasonable measure of the relative intensities of these peaks.

In order to accurately determine the molecular tilt angle by angle-resolved photoelectron spectroscopy, it is necessary to take account of the complex refractive index of the molybdenum surface since a portion of the incident light is reflected when the refractive index is not unity.¹⁷ The refractive index of molybdenum is 0.88 + i0.30 at 30 eV and 0.83 + i0.28 at 40 eV. The normal and parallel components of the electric field are calculated via the Fresnel equations¹⁷ as a function of incidence angle, and the component of this field along the molecular axis is averaged over all azimuthal angles for a particular molecular tilt angle in order to generate a set of theoretical curves of photoionization cross section as a function of incidence angle for various tilt angles. Shown plotted in Figure 3 are a set of such theoretical plots of

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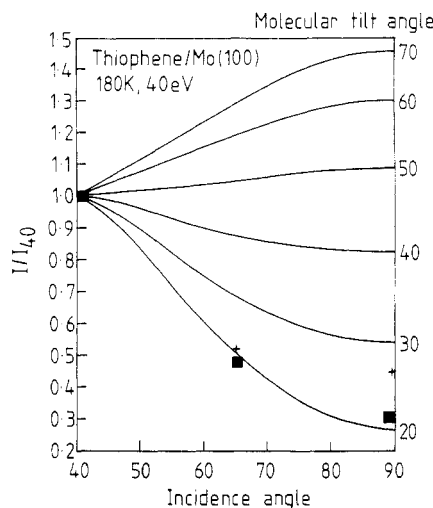


Figure 4. Set of theoretical plot of photoemission intensity (normalized to emission at 40°) from molecular orbitals of a_1 symmetry as a function of incidence angle for various values of molecular tilt angle between 20° and 70° taking account of the substrate refractive index. Shown also plotted are experimental points taken from the data of Figure 2 with 40-eV photons; 6a₁ peak (■), 7a₁ peak (+).

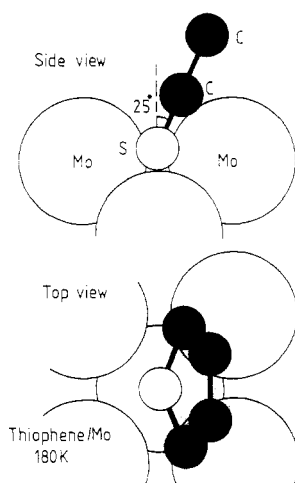


Figure 5. Schematic diagram of the proposed structure of thiophene adsorbed on Mo(100) at 180 K. The top diagram shows a side view of a thiophene molecule adsorbed into the fourfold site on the (100) surface showing two first-layer atoms and one second-layer atom. The bottom diagram shows a top view of the thiophene molecule.

photoemission intensity using 30-eV photons (i.e., for a complex dielectric constant of $0.88 + i0.30$) normalized to emission at $\theta = 40^\circ$ (I/I_{40}) for various molecular tilt angles. Also plotted in this figure are experimental data for the 12-eV peak taken from Figure 1 (i.e., the photoelectron spectra taken at 30 eV). Comparison with the theoretical curves shows that the thiophene z axis is tilted at $25 \pm 5^\circ$ with respect to the surface normal. A similar set of theoretical curves for 40-eV photons is shown in Figure 4, along with the experimental data taken from the photoelectron spectra of Figure 2 (taken at 40 eV). Again, this yields a molecular tilt angle of $25 \pm 5^\circ$ with respect to the surface normal.

In summary, angle-resolved ultraviolet photoelectron spectroscopy experiments, then, lead to the following conclusions: (1) Thiophene chemisorbs predominantly as an intact molecular entity at 180 K. (2) Bonding to the surface is at least partly via π -donation. (3) The molecular axis is tilted at $25 \pm 5^\circ$ with respect to the surface normal.

A schematic representation of a bonding geometry that reconciles these observations is shown in Figure 5, in which the sulfur atom of thiophene bonds at a fourfold hollow site, i.e., to a second-layer molybdenum atom. The molybdenum substrate is

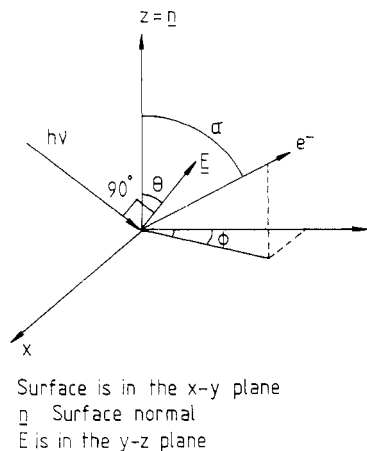


Figure 6. Coordinate system used for the analysis of variation of photoemission intensity as a function of incidence angle for tilted thiophene.

represented as hard spheres whose radius is chosen so that they touch. The thiophene molecule is represented as "balls and sticks". The covalent radius of sulfur is 1.05 Å, and its van der Waals radius is 1.85 Å, which when compared with the minimum diameter of the fourfold hole (1.75 Å) shows that the sulfur atom should be capable of penetrating a reasonable distance into the hole. It should also be emphasized that Figure 5 is only a schematic representation of the postulated geometry since no data exist for admolecule-surface distances. The π -donation takes place via an interaction between the carbons at the α -position and the topmost molybdenum atoms which leads to a stabilization of the thiophene orbitals while simultaneously allowing the molecule to tilt. The angle-resolved UPS data in this paper do not allow the azimuthal angle to be determined, so that it is not known whether the thiophene tilts toward an atop site or a bridge site. However, it is evident that a rotation of the geometry shown in Figure 6 by 45° would lead to a severely sterically hindered configuration.

Finally, the thiophene chemisorption geometry proposed in this paper also has the advantage that it naturally explains the regiospecific hydrogen abstraction. Hydrogen atoms attached to an α -carbon are sufficiently proximate to a surface molybdenum atom that their removal should be fairly facile, whereas the β -hydrogens are remote from the surface, so that removal of these hydrogen atoms to the surface requires a higher activation barrier.

Conclusions

Angle-resolved photoelectron spectroscopy suggests that thiophene mainly adsorbs molecularly onto the Mo(100) surface at 180 K. A shift in energy levels associated with molecular π -orbitals suggests that a component of bonding to the surface is via these π -orbitals. A detailed analysis of the variation of photoemission intensity as a function of photon incidence angle suggests that the molecular plane is tilted at $25 \pm 5^\circ$ to the normal. A bonding configuration is proposed that is consistent with these observations, in which the thiophene molecule chemisorbs into the fourfold site so that the sulfur atom of the thiophene is bonded to the molybdenum atom at the bottom of the fourfold site, while simultaneously being π -bonded to one or more surface molybdenum atoms. This bonding configuration also explains the strongly regiospecific hydrogen abstraction seen for the thermal decomposition of thiophene, the α -hydrogen being sufficiently close to the surface to be removed.

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