Since the atomic radii of Pt (1.39 Å) and Re (1.37 Å) are very close, the result that fcc Re has a unit cell dimension close to that of Pt is not unusual. A more fundamental question is whether it is reasonable to expect Re to be present in fcc form. It is interesting to note that high pressure X-ray experiments have recently been reported to show that hcp Re is stable up to 2.16 Mbar;¹⁰ i.e., there is no evidence to show the transformation of hcp Re to fcc by pressure. The most direct evidence for the presence of fcc Re comes from an epitaxy growth study. By studying the growth of Re on the Pt(100) face, Godbey et al.²¹ conclude that the epitaxially grown Re is indeed in the fcc form. Another example is the observation of epitaxial films of metastable hcp Ir (bulk Ir is fcc) grown on Re by Cunningham and Flynn.²² Although the relative stabilities of fcc and hcp structures is a separate subject itself for study, it is believed that the difference in energy for these two structures is small.

It is understandable that our proposed structural model only intends to address the main feature observed in the Pt-Re samples. Using the powder samples, we deal with an average structure and have not addressed such issues as miscibility and strain effects. In this work, such effects cannot be clearly separated out from

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those related to crystallite size and disorder.

VI. Summary

We demonstrate the capabilities of anomalous X-ray diffraction with synchrotron radiation in the study of the structure of bimetallic catalysts. Using Pt-Re catalysts with a SiO₂ support, the presence of Re in the fcc form, a new structural form for Re, was revealed. We propose that this form of Re is grown on Pt by an epitaxial effect.

The feasibility of studying metal catalysts with crystallite sizes as low as 10 Å using current synchrotron sources is particularly encouraging. High-brilliance synchrotron sources of the next generation would allow the study to extend to catalysts of even higher dispersion. In such cases, combined use of EXAFS and anomalous X-ray diffraction would be a powerful approach in dealing with the complexity of catalyst structure and other heterogeneous structures in general. Also, the X-ray technique can readily be applied for in situ studies.

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Axial and Azimuthal Angle Determination with Surface-Enhanced Raman Spectroscopy: Thiophenol on Copper, Silver, and Gold Metal Surfaces

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Raman spectra of noble-metal phenylthiolates and the corresponding surface-enhanced Raman (SER) spectra of the surface species on copper, silver, and gold are reported. Periodic trends were found in both the bulk Raman spectra of the phenylthiolates and the SER spectra. Intensities of the Raman spectra approach that of liquid thiophenol as the metal changes from copper to silver to gold. The SER spectra were used to obtain orientations of the thiophenol species at the noble-metal surfaces. Orientations were determined through the electric field enhancement of vibrations normal to the metal surface. The model developed in this paper allows one to determine both the azimuthal and axial angles of $C_{2\nu}$ molecules at surfaces. This is possible by performing the SERS measurement in media of differing indexes of refraction. For silver and gold we found the axial angle θ = 85 and 76°, respectively. The azimuthal angle Φ was found to vary from 32 to 0° from silver to gold. The SER spectra of copper were too weak for accurate angle determinations with a surrounding media other than air. However, the SER spectrum observed on copper in air does indicate a near-perpendicular orientation.

Introduction

The orientation of molecules at surfaces is important for the understanding of metal-adsorbate binding and the reactivity of adsorbed species. Examples of optical methods for orientation determination consist of SHG measurements,¹ ellipsometry,² IR reflectance,³ and SERS.⁴⁻⁶ Orientation in SERS is found due to the preferential enhancement of vibration modes which are perpendicular to the surface. Creighton first derived a procedure for qualitative orientation analysis on spherical particles.⁴ Moskovits expanded the analysis to both smooth and roughened SERS active substrates.⁵ Recently, Moskovits et al. have made a qualitative study of the orientations of substituted benzenes on silver in ultrahigh vacuum.⁶ A similar study has been carried out

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by Gao et al.⁷ Walls and Bohn have made determinations on SERS active substrates which are coated with thin SiO₂ films.⁸ Their method involved orientation determination through depo-

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larization measurements. The conclusion from this work was that the changes in Raman depolarization at surfaces were too small to allow accurate determination of orientations. In this paper we will describe a method which uses the intensity ratios of SERS bands which contain components of the α_{xz} , α_{zz} , and α_{yy} polarization vectors relative to equivalent Raman bands in the bulk material. Alone these measurements are not able to accurately provide orientations. However, when spectra are obtained in solvents with differing indexes of refraction, both the axial and azimuthal angles of the phenyl ring of thiophenol relative to the surface could be determined.

There is considerable interest in the mechanism by which organodisulfide, sulfide, and thiols adsorb to noble-metal surfaces. This class of molecules has found applications in tribology due to their unique antiwear properties.⁹ More recently, they have become popular as anchors for constructing self-assembled organic layers on gold.¹⁰ Their ability to order on gold surfaces has been attributed to Au-SR bond strengths which are weak enough to allow lateral surface diffusion, yet strong enough to prevent desorption under ambient conditions. Since much of the work has been on noble-metal surfaces and the symmetric disulfide stretches are not IR active, many of the spectroscopic studies have used SERS as the spectroscopic tool.¹¹⁻¹⁴ The first reported SERS study of thiols and disulfides on a surface was by Sandroff and Herschbach.¹¹ They found that the surface products of thiophenol and phenyl disulfide on silver were identical. Sobocinski et al. have studied alkylthiols at electrode surfaces using SERS and have made comparisons between the surface interactions of alcohols and thiols.¹² Another study of interest is that by Joo et al. which indicates a photochemical cleavage of one of the C-S bonds in organosulfides on silver colloids.¹³ While some studies indicating the existence of surface-enhanced photochemistry have been reported, it has been shown that photochemistry on noble metals is unlikely due to the rapid energy transfer which occurs between metal and adsorbate.15

In our study we found that the mechanism on roughened noble-metal surfaces in air is not photochemical. However, our studies with colloids do confirm the results of photochemistry on colloids and roughened surfaces in aqueous salt solutions.

Experimental Section

The sulfides and disulfides were purchased from Aldrich and used without further purification. The silver substrates were prepared by vapor deposition of silver onto calcium fluoride roughened slides. This substrate has been shown to produce enhancements of 1.7×10^5 for pyridine.¹⁶ Microscope slides were cleaned with a concentrated ammonia solution and cleaned with a Harrick 30-W rf plasma cleaner for 10 min. An Edwards vacuum coating unit operating at 10⁻⁶ mbar pressure was used for the vacuum depositions. The roughened substrate was prepared by first depositing a 600-nm-thick layer of calcium fluoride followed by 50 nm of silver. The depositions were carried out from a resistively heated molybdenum boat. The silver (Aldrich) was 99.9% pure, and the calcium fluoride (Aesar) was optical grade. The film thickness and deposition rate were monitored with a quartz crystal microbalance. The silver was deposited at the rate of 0.2 nm/s. Gold (G.F. Goldsmith) substrates were prepared using the above method from 99.999% pure gold.

The sample was dissolved in acetone and was spun coat onto the substrates. The concentration of the thiol, sulfide, and disulfide

was 0.01 M, and a 50- μ L aliquot was used for the spin coating. Immersion was also tested as a viable application procedure. The spectral features were identical with spun coat samples. However, the quality of the spectra was not as good as with spin coating.

The copper substrates were prepared from 99.999% pure, 0.025-mm copper foil (Aldrich). These substrates were roughened by etching in 12% HNO₃ for 4 min under vigorous stirring. This procedure is similar to that developed by Miller et al.¹⁷ and recently by Carron et al.¹⁸ The metallic copper samples were prepared by etching the copper with nitric acid, washing with distilled water, immediate immersion in a 0.01 M acetone solution of the molecule of interest which had been warmed to 50 °C, and a final washing of acetone to remove any adsorbed reagent.

The Raman spectra were obtained using a Jobin-Yvon Mole 1000 double monochromator, an RCA 31034 PMT, and Ortec photon counting electronics. Laser excitation was provided with a Spectra Physics 2025 Kr⁺ ion laser. A backscattering geometry was used for all samples, and a cylindrical lens was used to focus the laser in order to decrease the power density at the sample. The SERS sample was spun at 1800 Hz to avoid any possible damage due to laser-induced heating. A 647-nm filter was used to remove the plasma lines.

Bulk Raman spectra were obtained on metal thiolates prepared in the laboratory. Silver phenylthiolate (AgSPh) was prepared by mixing an excess of thiophenol in water with AgNO₃.¹³ The resulting precipitate was washed with methanol. Gold phenylthiolate was synthesized through the reduction of $HAu^{III} Cl_4$ in the presence of thiophenol.¹⁹ The resulting precipitate was washed with methanol to remove the phenyl disulfide which results from oxidation of thiophenol by Au(III). Copper phenylthiolate was synthesized by the addition of thiophenol to a aqueous solution of CuCl₂. Again, the product was washed with methanol to remove phenyl disulfide.

Results and Discussion

SER spectra of thiophenol, phenyl sulfide, and phenyl disulfide were obtained on copper, silver, and gold surfaces. In all cases the surface product was identical regardless of the starting material. This indicates that the metals are capable of breaking the thiol, sulfide, and disulfide bond. The surface spectra also closely resembled the bulk Raman spectra of the metal phenylthiolates. Silver and copper phenylthiolates can be synthesized through the reaction of thiophenol with the monovalent metal ions. Copper(I) phenylthiolate could be synthesized from Cu(II) starting materials through the reduction of Cu(II) with excess thiophenol. Gold phenylthiolate was more difficult due to the insolubility of Au(I)compounds. We prepared gold phenylthiolate through the reduction of Au(III) with excess thiophenol.¹⁹

Orientation Determination. The orientation of molecules at metal surfaces has been implied through the propensity toward enhancement of vibrational modes perpendicular to the surface. This propensity arises from the boundary condition which requires the electrostatic displacement, D, normal to the surface to be continuous across the interface:20

$$D_{\perp,\text{in}} = \epsilon_{\text{Ag}} E_{r=a}; \quad D_{\perp,\text{out}} = \epsilon_{\text{surroundings}} E_{r=a}$$
(1)

The parallel component is simply

$$E_{\parallel,\text{in},r=a} = E_{\parallel,\text{out},r=a} \tag{2}$$

The dielectric of the coating, metal-SPh in this case, is ignored and $\epsilon_{surroundings}$ is assumed to be 1.00. This leads to a preferential enhancement of the perpendicular electric field by a factor of ϵ .

We will combine two experimental approaches to indicate the orientation of the molecules at the surface. The first experimental

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method was developed by Creighton and has been applied to several systems.⁴ This method assumes the surface is composed of spheres. The resonance condition for a sphere is

$$E_{\perp} = \epsilon / (\epsilon + 2) \tag{3}$$

$$E_{\parallel} = 1/(\epsilon + 2) \tag{4}$$

where we have made use of eq 1. The intensity depends on the square of the electric field. If z is taken as the direction perpendicular to the surface and x, y are parallel, then this leads to a preferential enhancement of 4 in modes which contain a tensor component perpendicular to the surface relative to normal coordinates which do not contain a z component if the molecule is oriented perpendicular to the surface. A maximum relative enhancement is 16:1 for total symmetric modes which contain only the α_{zz} component relative to modes which contain only the α_{xy} polarizability vector. One important point which we will address in this work is the extension of this approach to particles other than spheres. The resonant condition for spheres is $\epsilon = -2$. For silver this occurs for laser excitation near 380 nm. Experiments with Ar⁺ or Kr⁺ excitation require $\epsilon < -2$, and therefore, eqs 3 and 4 are no longer valid.

The general formula, which includes ellipsoidal particles, for the electromagnetic contribution to SERS is²¹

$$E_{\perp} = \epsilon / (1 + A(\epsilon - 1))$$
 (5)

$$E_{\parallel} = 1/(1 + A(\epsilon - 1)) \tag{6}$$

A is a geometric factor and is equivalent to^{22}

$$A = \frac{1 - e^2}{e^2} \left[-1 + \frac{1}{2e} \ln \frac{1 + e}{1 - e} \right]$$
(7)

$$e^2 = 1 - (b^2/a^2) \tag{8}$$

where a and b are the major and minor axes of the ellipsoid, respectively. The resonance condition shifts toward the red as ϵ becomes more negative. This can have drastic effects on the orientation analysis. For copper, silver, and gold at 647 nm ϵ is about -12.2, -18.4, and -11.5, respectively.²³ This means that the ratio of modes with a single perpendicular component will be enhanced 338:1 over purely parallel modes if the molecule is oriented perpendicular to a silver surface.

We have made an assumption in using eqs 5 and 6 for the determination of orientation. The assumption is that Raman scattering from molecules adsorbed to small particles which may exhibit a large imaginary dielectric constant is not significant.²⁴ This is justified since the large imaginary part will dampen the SERS effect, and therefore, small particles will not contribute significantly to the signals which we observed. Large particles also exhibit a dampening of the SERS effect. The dampening is due to radiation damping²⁵ and dynamic depolarization.² Carron et al. have shown that these effects can be described through a modification of the A term in eqs 5 and 6.²⁷ However, they should not affect our results since the A term will cancel when we take the ratio of eq 5 to eq 6 to determine the value of E_{\perp} relative to E_{\parallel} . Since the A term cancels when the ratio of eq 5 to eq 6 is taken, particle eccentricity should not affect our orientation determination.

We have extended the orientation analysis not only to find the tilt, axial angle, of the molecular z axis but also to include the



Figure 1. Definition of the axial and azimuthal angles. The axial angle θ is the angle between the C_2 axis and the surface. The azimuthal angle Φ is the angle of rotation about the C_2 axis of the phenyl ring. In the text θ is equal to 0 when the molecule is oriented perpendicular to the surface. Φ is 0 when the plane of the ring is parallel to the surface.



Figure 2. Changes in the value of R as a function of Θ for various values of Φ for $\epsilon = 16$. When Φ is less than 45°, R goes to $1/\epsilon^2$ as Θ goes to 90°. When Φ is greater than 45°, R goes to ϵ^2 as Θ goes to 90°. Our method of angle determinations fails when Φ is 45°. This indeterminacy could be alleviated by using an a_1 mode which contains an α_{xx} component. Note that the y axis has two regions: it goes from 0 to 1.33 for $\Phi < 45^{\circ}$ and from 1.33 to 256 for $\Phi > 45^{\circ}$.

possible azimuthal rotation of the molecule about the molecular z axis. See Figure 1 for our angle definitions. Our analysis and experiments will be for molecules with C_{2v} symmetry. In general, a₂ modes are very weak in aromatic ring systems. This is due to the relatively small polarization changes which occur when the ring bends out of its plane. We are able to observe a b_1 mode. b_1 modes contain the α_{xz} polarizability vector. The b_2 modes are composed of the α_{yz} vector. Unfortunately, b_2 modes are weak in the bulk spectra and SER spectra of phenylthiolates. This precludes accurate determinations of orientations at surfaces. a_1 modes are very strong in the Raman spectra of aromatic compounds. The a1 modes are difficult to analyze for orientation since they are composed of a linear combination of α_{xx} , α_{yy} , and α_{zz} . The solution to solving orientations is to use the totally symmetric a₁ stretch mode of the phenyl ring. Simple geometric arguments show that if this molecule is oriented with the ring perpendicular to the surface, then the intensity ratio of a_1/b_1 must be $(1.155)^2$, where a_1 only indicates the ring breathing stretch. Equations 4 and 5 indicate that the intensity ratio should be $1/\epsilon^2$ for parallel orientation. A more complete analysis shows that

$$R = \frac{I_{a_1}}{I_{b_1}} = \left[\frac{\sin(\Theta)\cos(\Phi) + \epsilon\sin(\Theta)\sin(\Phi) + 1.155\cos(\Theta)}{\sin(\Theta)\sin(\Phi) + \epsilon\sin(\Theta)\cos(\Phi) + \cos(\Theta)}\right]^2 (9)$$

Figure 2 shows a plot of R versus Θ for different values of Φ . The problem which occurs is that for a given value of R several values of θ and Φ exist. This indeterminacy can be overcome

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Figure 3. Raman spectrum of the product of $AgNO_3$ and phenyl disulfide. The laser power was 10 mW, slits were at 5 cm⁻¹, step size was 5 cm⁻¹, and the integration time was 2 s. The 1045- and 1340-cm⁻¹ bands correspond to NO_3^- vibrations.



Figure 4. Raman study of thiophenol on silver. (A) SERS spectrum of thiophenol on silver. This spectrum was obtained with 30 mW of 647-nm laser irradiation, 3-cm^{-1} band-pass, 2-cm^{-1} step size, and 5-s integration. (B) Raman spectrum of bulk AgSPh. This spectrum was obtained with 5 mW of 647-nm laser irradiation, 3-cm^{-1} band-pass, 5-cm^{-1} step size, and 5-s integration time. (C) Raman spectrum of thiophenol. This spectrum was obtained with a depolarizer, 50 mW of 647-nm laser irradiation, 3-cm^{-1} step size, and 2-s integration time.

either by changing the excitation wavelength, thus ϵ , or by changing the dielectric constant of the surrounding media. We have chosen the second approach since resonance Raman effects are predicted due to photochemical degradation that was observed in some cases. The rigorous expression for the ϵ used in the previous equations is $\epsilon_{metal}/\epsilon_{surroundings}$. The new dielectric materials we have chosen are mixed hexanes and cyclohexane. Hexanes and cyclohexane are not expected to adsorb to the surface and perturb the orientation of the phenylthiolate. The mixed hexanes and cyclohexane used in our experiments have a dielectric constant of 1.90 and 2.03, respectively.

Silver. It has been shown in ultrahigh-vacuum experiments that the cleavage of disulfides can occur on zerovalent noble-metal surfaces.²⁸ When phenyl disulfide was added to an aqueous AgNO₃ solution, the product, a precipitate, still contained a disulfide stretch and nitrate stretches. This indicates that the surface species involved in the reactions is Ag(0). The Ag(PhSSPh)NO₃

thiophenol (neat) $\Delta \nu$	thiophenol (SERS) $\Delta \nu$	silver phenylthiolate $\Delta \nu$
	230 (Ag-S)	250 (Ag-S)
278 (b ₁) ^a		335
$414(a_1, a_2)$	420	420
464 (b ₁)	470	480
616 (b ₂)	620	620
$698(a_1)$	695	700
734 (b ₁)	745	740
834 (a ₂)		835
914 (S-H bend)		
988 (b ₁)	985	
$1000 (a_1)$	1000	1000
$1024(a_1)$	1025	1025
1069 (a ₁)	1075	1075
1092 (b ₂)		
1118 (a ₁)	1110	1115
1156 (b ₂)	1160	1160
1180 (a ₁)	1180	1185
1270 (b ₂)		1270
1328 (b ₂)		
$1380 (a_1)$	1375	
1440 (b ₂)	1440	
1478 (a ₁)	1475	1475
1576 (a ₁)	1575	1575
1584 (b ₂)	1600	1600

"Bands assignments are based on refs 13 and 25.

TABLE II

TABLE I

	I_x/I_{470}			
	x, cm^{-1}	bulk	SERS	$I_{\rm SERS}/I_{\rm bulk}$
Cu	420	0.54	3.67	6.83
	470	1.00	1.00	1.00
	695	3.54	1.00	0.28
	1000	10.0	9.83	0.98
	1025	2.77	3.33	1.22
	1075	2.54	2.00	0.78
	1575	2.38	1.50	0.63
Ag	420	2.20	6.38	2.90
	470	1.00	1.00	1.00
	695	2.70	1.85	0.68
	1000	10.6	8.54	0.81
	1025	5.60	6.08	1.08
	1075	6.40	7.69	1.20
	1575	7.65	8.08	1.05
Au	420	4.60	4.13	0.90
	470	1.00	1.00	1.00
	695	4.00	1.26	0.32
	1000	52.0	5.41	0.10
	1025	18.4	5.20	0.28
	1075	16.0	8.33	0.52
	1575	14.8	7.60	0.51
thiophenol	414	25.5		
	464	1.00		
	698	31.8		
	1000	214.3		
	1024	47.8		
	1092	15.9		
	1584	15.9		

spectrum is shown in Figure 3. This spectrum contains strong nitrate stretches at 1340 and 1045 cm⁻¹. The disulfide stretch which is at 542 cm^{-1} in the solid state is shifted and split to 515 and 505 cm^{-1} .

Band assignments are made based on ref 29. In the solid state the structure of phenyl disulfide is similar to hydrogen peroxide with an azimuthal angle of 105°.³⁰ The splitting of the disulfide stretch represents the formation of a rigid structure with both trans and cis phenyl groups around the disulfide bond. This product was photoactive and decomposed slowly under 647-nm irradiation.

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TABLE III^a

	Ag	Au
$I_{1000}/I_{470}(\text{bulk})$	10.6	52.0
$I_{1000}/I_{470}(air)$	8.09	6.82
I_{1000}/I_{470} (hexane)	5.18 (85.4, 32) ^b	3.77 (76.0, 0)
I_{1000}/I_{470} (cyclohexane)	4.91 (85.4, 32)	2.71 (75.9, 0)

^a The orientation of thiophenol on silver using the SERS spectrum in air as the reference shows $\theta = 81.3^{\circ}$, $\Phi = 25^{\circ}$. The orientation of thiophenol on gold using the SERS spectrum in air as the reference shows $\theta = 77.0^{\circ}$, $\Phi = 17.2^{\circ}$. The error in the angles for thiophenol on Ag are approximately $\pm 4^{\circ}$ for θ and $\pm 11^{\circ}$ for Φ . The error in the angles for thiophenol on Au are approximately $\pm 1.5^{\circ}$ for θ and $\pm 2^{\circ}$ for Φ . ^b The first value represents θ and the second value Φ (in degrees).

Figure 4 shows the Raman spectra of thiophenol, silver phenylthiolate, and the SER spectrum of the product of thiophenol reacted with a silver substrate. Comparison of thiophenol and the silver phenylthiolate shows that there is a large intensity increase in the band at 1075 cm⁻¹. The low-wavenumber shoulder on the 1600-cm⁻¹ peak has increased in intensity in the metal thiolates. There is also a large intensity increase in the 420-cm⁻¹ vibration. The band assignments are tabulated in Table I. The changes in intensity are tabulated in Table II.

The SER spectrum shows a large enhancement of the 420-cm⁻¹ mode. This is to be expected since this mode is largely composed of the α_{zz} tensor.³¹ Comparison of the SERS spectra of the surface product with the bulk metal thiolates shows several trends. The intensity ratio of the 1000-cm⁻¹ peak relative to the 470-cm⁻¹ peak is about unity. This is predicted for molecules which are perpendicular to the surface.

The orientation of thiophenol was determined by the procedure outlined earlier. We obtained SERS spectra in air, mixed hexanes, cyclohexane. The results are tabulated in Table III. The results are in good agreement with studies of AgSPh, which indicate that the phenyl ring is perpendicular to the layer of silver ions.³² One problem which can occur in SERS based orientation studies is the assumption that the Raman spectrum of the chemisorbed species is equivalent to a bulk spectrum of the organometallic equivalent compound. We were able to check this assumption through the determination of the SERS spectrum in two solvents of differing dielectric constant. This allowed us to make an orientation determination independent of the bulk material. The results from Table III indicate that in this case the assumption is reasonably good. The changes in Φ are related to the relatively free rotation of the phenyl ring on the surface as opposed to the rigid structure found in the bulk.

The silver phenylthiolate was found to be photoactive even with 647-nm irradiation. The photoreduction of silver was very slow, and with low laser powers (5 mW) it was possible to obtain reproducible spectra. At higher laser powers (30 mW) the spectra changed under laser irradiation. This has been proposed to be due to the formation of SERS active silver clusters. We found the rate of photoreduction increased with increased laser frequency and was slower at 676 nm. No attempts were made to quantify the rate of photoreduction. On our CaF_2 roughened Ag substrates, Ag island films, and HNO3 etched substrates we observed no photoactivity. However, as in the earlier reports of thiophenol on colloids photoactivity was observed. It was also found that our silver substrates in aqueous Cl⁻ solutions were photoactive. Apparently, AgSPh is stable on silver/air surfaces. In the presence of an anion AgSPh can be reduced to Ag(0) and thiophenol. Colloids are produced by the reduction of Ag(I) with $NaBH_4$. The borate byproducts of this reduction represent the anions in the case of colloids.

Gold. Our studies on gold are shown in Figure 5. The Au–S bond was found at 275 cm^{-1} . All other frequencies match those



Figure 5. Raman study of thiophenol on gold. (A) SER spectrum of thiophenol on gold. This spectrum was obtained with 30 mW of 647-nm laser irradiation, 3-cm^{-1} band-pass, 5-cm^{-1} step size, and 10-s integration. (B) Raman spectrum of bulk AuSPh. This spectrum was obtained with 50 mW of 647-nm laser irradiation, 3-cm^{-1} band-pass, 2-cm^{-1} step size, and 2-s integration time. (C) Same as Figure 4C.

observed for AgSPh. It was found that AuSPh was stable under prolonged irradiation at 647 nm. From Table II it can be seen that all modes are decreased in intensity relative to the 470-cm⁻¹ mode. This indicates that gold has an axial angle to the surface which is less than silver. Using eq 9, we find that the axial and azimuthal angles are 76.0 and 0°, respectively. We found excellent correlation to the angles predicted when either hexanes or cyclohexane was used. The orientation determined independent of the bulk spectrum also matched the bulk values very well. This indicates that the surface species closely resembles the structure of Au¹ SPh synthesized from Au(III). The smaller Φ with respect to silver can be attributed to increased steric hindrance with the surface as Θ becomes smaller.

The intensities relative to the 470-cm^{-1} peak in the bulk are larger than those found with silver. We interpret this as an increase in bond polarizability in the phenyl ring due to the decreased charge withdrawal through the Au-S bond. For example, the relative intensity 1000-cm^{-1} band, and most other modes, approaches the value for free thiophenol as the metal is changed from copper to silver to gold. This increase is clearly seen in the Raman spectra of the bulk metal phenylthiolates. The similarity in the Raman spectrum of bulk AuSPh to thiophenol in comparison with its dissimilarities to silver and copper analogues can explain the differences in bonding which lead to self-assembly in thiols on gold. The phenylthiolate species on gold most resembles thiophenol and, therefore, can move laterally on surfaces most easily.

Copper. The Raman spectra associated with our study of thiophenol on copper are shown in Figure 6. The Cu-S stretch was found at 270 cm⁻¹. All other frequencies match those observed for AgSPh. The SER spectra on copper were weak, and we were not able to obtain spectra of copper species in solvents. The ratio of I_{1000}/I_{470} is larger than that of gold and smaller than that of silver. We would expect then that copper is also oriented perpendicular to the surface. No photochemistry was observed with copper phenylthiolates or the surface species.

Error Analysis. The errors for angle determinations are shown in Table III. The error for silver is $\pm 4^{\circ}$ for θ and $\pm 11^{\circ}$ for Φ . The error for gold is significantly smaller. The error in θ is $\pm 1.5^{\circ}$

⁽³¹⁾ Dollish, F. R.; Fateley, W. G.; Bentley, F. F. Characteristic Raman Frequencies of Organic Compounds; John Wiley & Sons: New York, 1974; p 172.

⁽³²⁾ Dance, I. G.; Fischer, K. J.; Herath Banda, R. M.; Scudder, M. L. Inorg. Chem. 1991, 30, 183. Dance, I. G. Polyhedron 1988, 7, 2205.



Figure 6. Raman study of thiophenol on copper. (A) SER spectrum of phenyl disulfide on copper. This spectrum was obtained with 10 mW of 647-nm laser irradiation, 5-cm^{-1} band-pass, 5-cm^{-1} step size, and 15-s integration. (B) Raman spectrum of bulk CuSPh. This spectrum was obtained with 20 mW of 647-nm laser irradiation, 3-cm^{-1} band-pass, 3-cm^{-1} step size, and 3-s integration time. (C) Same as Figure 4C.

and $\pm 2^{\circ}$ for Φ . These errors are estimated from the noise level associated with the 470-cm⁻¹ band. This peak is much smaller than the 1000-cm⁻¹ peak and, therefore, is the major source of error. The smaller errors associated with gold are due to the much higher signal-to-noise (S/N) spectrum for AuSPh which we obtained. The better S/N for this spectrum is due to the lack of photodegradation and the correspondingly higher laser powers which could be used. The errors observed are on the same order of those found with IR reflection spectroscopy.³ The precision found here is much better than the $\pm 32.5^{\circ}$ found by Walls and Bohn using a depolarization method for angle determinations.⁸

In general, Figure 2 shows that the S/N level of the spectra will be critical as Φ approaches 45°. When Φ is exactly equal

to 45°, the method described fails due to the inability to locate a mode with a known amount of α_{xx} . As Φ approaches 0, the *R* value is critical when Θ is large. On the other hand, as Φ approaches 90°, *R* is critical when Θ is small. When a complete analysis using potential energy diagrams is used, we anticipate more precise determination of angles due to the ability to use two very strong Raman bands.

Conclusion

We have demonstrated a new procedure for the determination of molecular orientation at metal surfaces. This approach gives intuitively reasonable results for phenylthiolates on noble-metal surfaces. Our results indicate that thiophenol, phenyl sulfide, and phenyl disulfide all form metal phenylthiolates with noble-metal surfaces. In air the surface product was not observed to be photoactive under low laser powers and the time scale of several hours. However, in colloids and continuous substrates in the presence of aqueous anions photoactivity was observed.

SERS spectra obtained in mixed hexanes and cyclohexane indicate that the phenylthiolate is oriented nearly perpendicular to the surface. There is a predisposition for thiophenol to tilt more as one changes the metal from copper to silver and to gold. The azimuthal angle, Φ , around the C_2 axis varies between silver and gold. The observation is that the angle Φ approaches 0 as the tilt angle increases. This can be rationalized as increased steric hindrance around the C_2 axis as Θ becomes smaller. The SER spectra on copper were very weak, and accurate measurements in solvents were not obtained. However, relatively large a_1/b_1 ratios indicate that this species is also oriented nearly perpendicular. The ability of this technique to obtain orientations without bulk spectra of the surface species will greatly aid in studies where the surface complex is weak and cannot be synthesized in bulk quantities.

Improvements of this approach are being explored. One very promising approach will be to use potential energy distributions to determine the exact amount of x, y, and z motion in a normal coordinate. This approach would allow one to use other a_1 modes in orientation analysis. In aromatic systems the a_1 modes are very strong, and this would improve our errors in angle determination. The use of a_1 modes with an α_{xx} component would remove the redundancy associated with $\Phi = 45^{\circ}$ in our current use of a_1 modes which do not contain an x component.

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