Adsorption of Sulfur Containing Molecules on Gold: The Effect of Oxidation on Monolayer Formation and Stability Characterized by Experiments and Theory

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Abstract: The formation and stability of self-assembled monolayers (SAMs) of aryl sulfinates and, for the first time, aryl sulfonates are described. The ways in which the molecules interact with the surface and the stability of the resulting SAMs were characterized by surface enhanced Raman (SER) spectroscopy. Aryl sulfinate monolayers can be reversibly oxidized to sulfonate monolayers, but the sulfonate is readily displaced by sulfinate in solution. The relative adsorptivities of aryl sulfur species were found to be $ArSO_3^- << ArSO_2^- < ArS^-$. Through a novel application of perturbation theory, in which the adsorbate−surface Coulombic and charge transfer interactions and the change in the solvation free energy of the adsorbate are taken into account, we have been able to explain this trend. The differences in the adsorptivities of the anions studied here are primarily attributable to differences in the adsorbate−surface charge transfer interactions. These were evaluated by calculating the adsorbate HOMO energies at the ab initio HF/3-21G(d) level. Higher adsorbate HOMO energies are correlated with higher adsorptivities, consistent with established trends in the adsorptivities of soft, basic anions on metal electrodes. Statistical perturbation theory was used to calculate the relative free energies of hydration of the three anions. The sulfonate is most strongly solvated, followed by the sulfinate and thiolate. Thus, the trend in solvation energies is consistent with and probably reinforces the trend in the adsorbate−surface charge transfer interactions. The combination of computational methods used here may prove generally useful for predicting the relative adsorptivities of molecules and ions on metal surfaces.

Introduction

Self-assembled monolayers (SAMs) of thiols and disulfides on silver, copper, and gold surfaces have been studied extensively.[1] These systems are particularly useful as models for interfacial phenomena, including wetting, lubrication, adhesion, and interfacial reactions. Much of the interest in SAMs stems from their ease of preparation, the diverse chemistry that can be built into them, and their apparent stability to oxidation and rinsing. Although the structure and reactivity of SAMs have been analyzed by many techniques, their formation and stability have not been fully characterized. For example, while it is known that adsorption of alkylthiols on gold results in the formation of a gold−sulfur bond with partial covalent character,[1,2] the oxidative stability of that bond has recently come into question. Laser desorption and secondary ion mass spectrometric studies have revealed that hexadecylthiolate and octadecylthiolate monolayers on gold oxidize in air to form sulfonates.[3,4] The sulfonates were detected immediately following self-assembly of the alkylthiolate monolayers, and, while their absolute concentration could not be determined, their relative concentration increased upon prolonged exposure to air and was higher for shorter alkyl chains. In addition to thiol, thiolate, sulfonate and various fragment ion peaks, the mass spectra contained additional features that can be attributed to alkylsulfinates.[3−5] We have recently shown that arylsulfinates readily adsorb on gold surfaces.[5] This led us to investigate the formation and oxidative stability of sulfinate monolayers and the possibility of directly self-assembling sulfonate monolayers.[5]

In this paper, we describe the formation and stability of arylsulfinate and arylsulfonate monolayers on roughened gold electrodes. Using surface-enhanced Raman spectroscopy and electrochemical methods, we have determined experimentally how benzenethiol, sulfinate, and sulfonate bond to gold. By combining *ab initio* calculations with a perturbation theoretical approach, we have been able to explain the relative adsorptivities of these molecules and the resulting monolayer stabilities. Taken together, these results provide the foundation for designing and fabricating mixed monolayers with prescribed composition and durability.

Experimental Section

Materials. The gold electrodes used for the SERS experiments were prepared in the following manner. The rotating disk gold electrode was polished with 5 μm silicon carbide and 1 μm alumina and then roughened in an electrochemical cell containing N_2-purged 0.1 M KCl, a Pt auxiliary electrode, and SCE reference electrode. The roughening

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procedure consisted of 20 oxidation-reduction cycles between −0.6 and +1.2 V at a rate of 0.5 V/s, pausing at −0.6 V for 8 s and at 1.2 V for 1.2 s, and finally holding the potential at −0.6 V for 5 min. The electrode was then rinsed with distilled deionized water. Colloidal gold was prepared by adding 2.7 mL of chilled degassed 3.7 mM aqueous $KAuCl_4$ dropwise to 6 mL of chilled degassed 5.1 mM aqueous $NaBH_4$ with stirring. The colloid was aged 3 days at room temperature prior to use. Benzenethiol, sodium benzenesulfinate, and sodium benzenesulfonate were purchased from Aldrich Chemical Company and used without further purification. Ethanol was 200 proof USP grade and was used without further purification. Water was doubly distilled in glass from potassium permanganate. SAMs were prepared as described in the text.

Raman Spectroscopy. Raman spectra were obtained with a Jobin-Yvon HR 640 single monochromator with a 1200 groove/mm holographic grating, SPEX liquid N_2-cooled CCD detector, and Kaiser supernotch holographic prefilter. The monochromator and data acquisition were controlled by SPEX Prism software on a PC. A Lexel 3500 laser (Ar^+, all lines) pumped a Lexel 479 cw Ti:sapphire laser to provide 25−40 mW of 750 nm radiation, focused to a diameter of *ca.* 400 μm, for the Raman and SER experiments.

***Ab Initio* Calculations.** *Ab initio* restricted Hartree−Fock (RHF) calculations were performed with the Spartan program package (v. 3.0.0, Wavefunction, Inc., Irvine, CA, 1993) on a Silicon Graphics Indigo workstation. Geometry optimizations were performed at the Hartree−Fock (HF) level using the 3-21G(d) basis set with five spherical d orbitals. Electrostatic charges were calculated by Mulliken population analysis at the 6-31G(d) level.

The relative free energies of hydration between benzenesulfonate, benzenesulfinate, and benzenethiolate were computed using statistical perturbation theory as implemented in the BOSS program version 3.4.[6] Both mutations were performed gradually over a series of six Monte Carlo simulations with double-wide sampling,[7] which provided 12 incremental free energy changes. All simulations used periodic boundary conditions, Metropolis and preferential sampling, and the isothermal isobaric ensemble at 25 °C and 1 atm.[8] The systems consisted of the solute plus 504 TIP4P water molecules[9] in a cubic box ca. 25 Å on a side.

The intrasolute interactions were excluded, while solvent−solvent interactions were spherically truncated at an O−O separation of 10 Å with quadratic feathering over the last 0.5 Å. A solute−solvent interaction was included with the same feathering if the distance between the oxygen of TIP4P and any non-hydrogen atom in the solute was less than 10 Å.

Each simulation consisted of 1.1×10^6 configurations of equilibration followed by 4.0×10^6 configurations of averaging. The solute and solvent molecules were independently translated and rotated at random such that an overall acceptance rate of ca. 40% was obtained for new configurations. No intramolecular degrees of freedom were included in these simulations, i.e., the geometries of the solvent and solute molecules were kept constant.

The structures of the solutes were obtained via full 3-21G(d) optimizations using Gaussian 92.[10,11] The charges were derived from CHELPG calculations at the HF level using the 6-31G(d) basis set within Gaussian 92.[10] Lennard-Jones interactions were described using standard OPLS potential functions.[12−14]

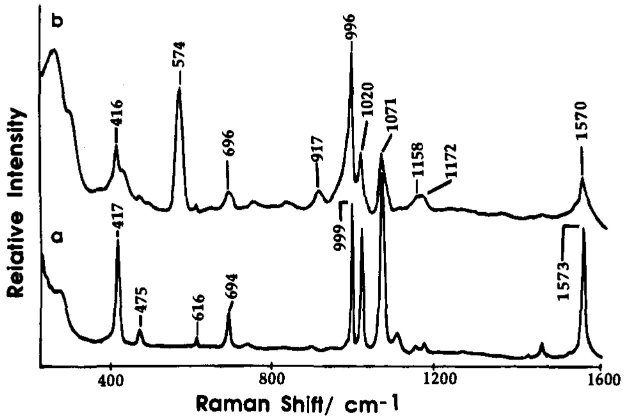

Figure 1. Surface enhanced Raman spectra of monolayers of (a) benzenethiolate and (b) benzenesulfinate on roughened gold electrodes.

Results and Discussion

Arylsulfinate and Sulfonate Monolayer Formation and Stability. Monolayers of alkyl and aryl thiols are typically prepared by immersing a gold substrate into a solution of the adsorbate. Our benzenethiol monolayer was prepared by immersing a roughened gold electrode in a 1 mM ethanolic solution of benzenethiol for 30 min, followed by rinsing with ethanol and drying in air.[5,15−17] The surface-enhanced Raman spectrum, shown in Figure 1a, shows that benzenethiol, like alkylthiols, adsorbs on gold through the sulfur atom with cleavage of the S−H bond.[15−20] The spectrum obtained after immersing the gold electrode overnight in the thiol tincture was identical to that obtained after only a 30 min immersion, showing that adsorption and possibly restructuring of the benzenethiol monolayer occur rapidly and faster than for monolayers of long chain alkyl thiols.[21] A detailed analysis of this spectrum and its vibrational assignments are presented elsewhere.[17,18,22] Evidence that benzenethiol adsorbs through the sulfur atom includes our inability to detect the δ CSH bending (917 cm^{-1}) and the ν SH stretching (2560 cm^{-1}) vibrations, and the shifting of the ($\nu_{7a} + \nu$ CS) mode from 699 to 692 cm^{-1} upon adsorption. Because both the ν SH and ν SS stretching modes have intrinsically high Raman cross sections, we would expect to observe them if thiol or disulfide were present on the surface. In order to determine the detection limit for adsorbed disulfides in the SERS experiment, the Raman and SER spectra of diphenyl disulfide (not shown) were analyzed. We found that in a typical SERS experiment, i.e., without unusual effort to maximize the signal-to-noise ratio, the disulfide stretching vibration would be detected if disulfide were present as ≥5−10% of the total coverage. In this analysis, it was assumed that the S−S bond in the adsorbed disulfide was parallel to the surface, causing the bond stretch to exhibit

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the lowest relative enhancement (ca. 10-fold lower than modes involving a change in polarizability normal to the surface). The disulfide spectra and complete details of the analysis are given in the supporting information. Thus the SER spectrum in Figure 1a provides strong evidence that at least benzenethiol adsorbs as the thiolate, not as the disulfide, in contradiction to the recent inference that disulfides form at the interface.[23] (Whether the differences are related do differences in substrate morphology is not yet known.) Most experimental work on alkylthiol SAMs has provided at least indirect evidence that the adsorbed species is the thiolate,[24-27] so adsorption of benzenethiol as the thiolate is consistent with those results.

Exposing the benzenethiolate monolayer to air for 10 days causes no change in the spectrum, indicating that no oxidation occurs,[5] in marked contrast to the behavior of the alkylthiolates characterized by mass spectrometry.[3,4] Apparently, UV irradiation is necessary to oxidize adsorbed benzenethiols *in situ* to the corresponding sulfinates and sulfonates.[28] Our results, along with those of Huang and Hemminger,[28] suggest that aromatic thiolate monolayers are less prone to oxidation than are alkylthiolate monolayers. Although this assertion involves comparing behavior on different types of surfaces (ours rough, others' smooth[3,4,28]), we believe that it is valid because oxidation would be expected to occur *more* readily on surfaces such as ours that contain a large number of defects. Furthermore, our monolayer, being supported by a heterogeneous substrate, must itself contain defects through which oxygen could penetrate. Thus, the lack of oxidation on rough surfaces is a fairly stringent test of monolayer stability.

We next examined the stability of the benzenethiolate monolayer to electrochemical oxidation. The monolayer-coated electrode was placed in an electrochemical cell containing 0.1 M KCl. The potential was ramped as high as +800 mV vs SCE, but the spectrum remained essentially unchanged, indicating that neither desorption nor oxidation occurred. As described in detail elsewhere,[17,18] the overall intensity of the SER spectrum decreases substantially between +800 and +1000 mV. This has been interpreted as resulting from desorption of the adsorbate, which occurs concomitantly with oxidation of the gold surface at about +900 mV. Whether the benzenethiol is also oxidized at this potential, in a manner similar to the oxidation of alkyl thiols to the corresponding sulfinic acids,[29] was not determined in our experiments. In any case, these results show that a benzenesulfinate or sulfonate monolayer cannot be formed by direct electrochemical oxidation of the benzenethiolate monolayer *in situ*, at least under these conditions.

We then attempted to form a benzenesulfinate monolayer directly. Figure 1b shows the SER spectrum of a benzenesulfinate monolayer formed by immersing the rough gold electrode for 1 h in a solution containing 1 mM sodium benzenesulfinate in degassed deionized water, followed by rinsing with water and air drying. This preparation is hereafter referred to as "*ex situ*" adsorption. The key feature that distinguishes the SER spectrum of the benzenesulfinate monolayer on gold from the Raman spectrum of the aqueous salt, and from the SER spectrum of benzenethiol, is the $-SO_2^-$ bending vibration at 574 cm^{-1}.[30] This mode is scarcely apparent in the Raman spectrum but is intense in the SER spectrum. The ν_s SO_2^- vibration at 958 cm^{-1} in the solution spectrum shifts to 917 cm^{-1} in the SER spectrum, while the ν_{as} SO_2^- vibration shifts from 1087 cm^{-1} in solution to a shoulder on the high frequency side of the 1071 cm^{-1} band in the SER spectrum.[30,31] The ν C−S vibration is at 696 cm^{-1} the Raman spectrum of benzenesulfinate and does not shift when the anion adsorbs on gold. The lack of a shift of ν C−S, combined with the large red-shift of ν_s SO_2^-, are characteristic of *O*-sulfinate coordination.[30,31] This is typical of phenylsulfinate coordination to soft metals such as mercury and thallium. In those complexes, ν_{as} SO_2^- shifts to higher frequency when coordination is unidentate, because the equivalence of the oxygens is removed.[30,31] The downshift observed here would therefore indicate bidentate *O*-coordination.

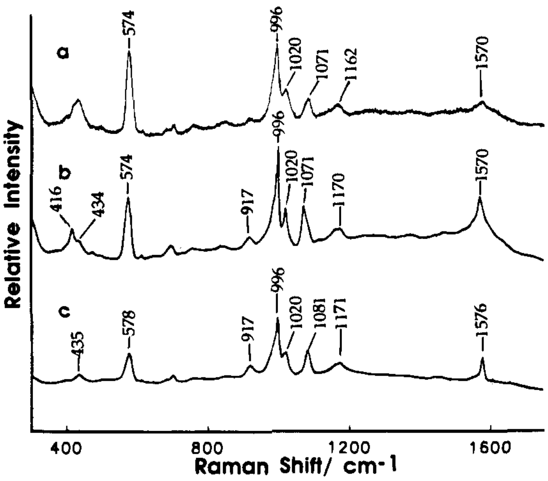

Figure 2. SER spectra of benzenesulfinate on gold: (a) adsorbed from a 1 mM solution in 0.1 M KCl onto a roughened gold electrode held at +100 mV vs SCE; (b) adsorbed onto a roughened gold electrode immersed in 1 mM sodium benzenesulfinate in water for 1 h, followed by rinsing with water; and (c) adsorbed onto colloidal gold from a 1 mM solution.

The sulfinate monolayer prepared by the *ex situ* method was stable in air for at least 10 days and could not be easily rinsed off with water or ethanol. When the fresh, dry monolayer was immersed in an electrochemical cell containing 0.1 M KCl and a potential of less than 0 mV vs SCE was applied, however, the monolayer desorbed with a half-life of ~10 min.

A benzenesulfinate monolayer can also be prepared by placing the roughened gold electrode in an electrochemical cell containing 1 mM analyte in 0.1 M KCl and applying a potential of +100 mV. The SER spectrum of this "*in situ*" monolayer is shown in Figure 2a. The *ex situ* spectrum is shown again in Figure 2b for comparison. The SER spectrum of benzenesulfinate on aqueous colloidal gold is shown in Figure 2c. The fact that the sulfinate adsorbs spontaneously on colloidal gold is not surprising, as the effective potential at the colloid surface is between +300 and +400 mV vs SCE.[32,33] Note that in the

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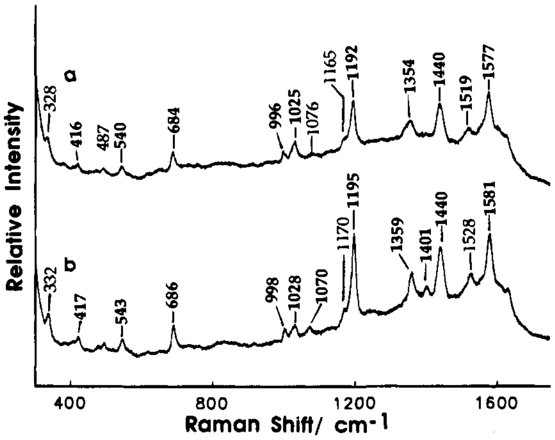

Figure 3. SER spectra of benzenesulfonate on roughened gold electrodes: (a) benzenesulfinate monolayer prepared *ex situ* (see text) and then oxidized at +500 mV vs SCE in an electrochemical cell containing 0.1 M KCl and (b) benzenesulfonate adsorbed at +500 mV vs SCE from a 1 mM solution in 0.1 M KCl.

"*in situ*" and colloid experiments, the analyte concentration in solution is too low for Raman scattering to be observed; the signal arises entirely from adsorbed molecules. The three SER spectra of benzenesulfinate shown in Figure 2 are quite similar in their peak positions and relative intensities, indicating that similar average adsorbate orientations and surface interactions obtain under the different conditions of monolayer formation.

The SERS intensity was used as a qualitative measure of surface coverage. An *ex situ* adlayer was prepared by immersing the electrode for 3 h in 3 mM benzenesulfinate. The electrode was dried in air without rinsing, and a SER spectrum was obtained. The electrode was then rinsed with water, and a second spectrum was obtained whose overall intensity was the same as in the first spectrum, within experimental error. Because benzenesulfinate is quite water soluble, this result indicates that less than or equal to a monolayer adsorbed spontaneously. The exact surface coverage and degree of ordering of the benzenesulfinate monolayers are not known. Contact angle measurements on the *ex situ*-prepared monolayer show that the outer surface of the monolayer is nonpolar (water beads up, while hexane wets the surface very well) and that the molecules are closely packed.[5]

Benzenesulfonate monolayers are much more difficult to prepare than benzenesulfinate and benzenethiolate monolayers. A benzenesulfonate monolayer cannot be formed by the *ex situ* procedure described above. Even after soaking a gold electrode overnight in 1 mM sodium benzenesulfonate in water, followed by rinsing and drying, no SER signal is detectable, nor is there any change in the wettability of the surface, indicating that little, if any, adsorption of the sulfonate has occurred.[5] Similarly, *p*-toluenesulfonic acid does not adsorb on the gold electrode from toluene.

Nevertheless, it is possible to prepare aryl sulfonate monolayers by applying a positive potential to the gold surface immersed in the sulfonate solution. Figure 3 shows SER spectra of benzenesulfonate monolayers prepared two ways: (1) by *in situ* oxidation of a pre-formed benzenesulfinate monolayer at +500 mV vs SCE (Figure 3a) and (2) by adsorption from a 6 mM sodium benzenesulfinate solution in 0.1 M KCl with an applied potential at the electrode of +500 mV (Figure 3b). The important features that distinguish these spectra from those of benzenesulfinate and benzenethiol are the asymmetric (ν_{as}) SO_3^- vibration at 1195 cm^{-1}, and the δ_s SO_3^-+δ_{ring} vibration at about 543 cm^{-1}. The latter is downshifted from its position in the spectrum of solid benzenesulfonate (567 cm^{-1}), evidence that the sulfonate group interacts with the metal surface.[34] Although there are slight differences in the positions of the SER bands, overall, the two spectra in Figure 3 are comparable. (The slightly better signal-to-noise ratio in the Figure 3b spectrum is probably due to better sample alignment in the spectrometer.) When the sulfonate-coated electrode prepared by either method is emersed, the sulfonate monolayer can easily be rinsed off with water, in marked contrast to the more strongly adhering sulfinate and thiol(ate) monolayers.

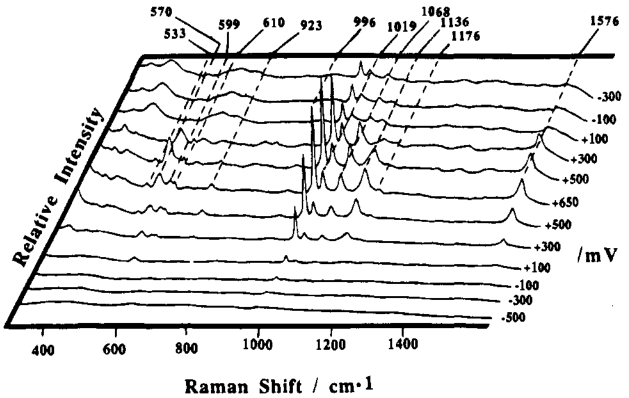

Figure 4. Potential-dependent SER spectra of benzenesulfinate, obtained in the order bottom-to-top.

Because the sulfonate is easily rinsed off by water, it was not possible to perform contact angle measurements to evaluate the quality of the monolayer. Information is available from recent capacitance measurements of benzenesulfonate monolayers on gold [210], however. Although capacitance measurements can be subject to large errors, they reveal that a monolayer does form at the aqueous electrolyte-gold interface when a positive potential is applied. At the highest surface coverage, the molecular footprint is 36 Å^2 per molecule.[35] This area is less than the 56 Å^2 calculated by Skoluda and Dutkiewicz for complete monolayer coverage with the molecule in a flat orientation and was interpreted by them as evidence that the arylsulfonate molecules adsorb in a perpendicular or tilted orientation.[35,36] This would be consistent with the *O*-sulfonate coordination deduced here from the SER spectra.

The SER spectrum of the benzenesulfinate monolayer prepared by the *in situ* method is potential dependent, as shown in Figure 4. It was noted above that adsorption of the sulfinate from solution begins at an applied potential of about +100 mV vs SCE. In Figure 4, it can be seen that new bands appear as the potential is shifted to +500 mV. The overall maximum in spectral intensity is reached after the potential has been stepped to +650 mV and then back to +500 or +300 mV. The higher intensity at positive potentials is probably due to an increase in surface coverage. In the presence of excess sulfinate (~2 mM in the electrolyte solution), the intensity changes and frequency shifts that occur as the potential is raised from −500 to +650 mV are reversible upon returning the potential to more negative values. This indicates that the interfacial processes (adsorption, desorption, redox reactions) are reversible and that the electrode does not become fouled or passivated by redox products.

The bands in the spectra in Figure 4 can be classified into three groups: those whose position is independent of the applied potential, those that shift with applied potential, and new bands that are present only at the most positive potentials. The positionally invariant bands include the ring modes at 612−

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614, 995–996, and 1019–1020 cm^{-1}. The 598–600 cm^{-1} SER band does not shift, but it increases in intensity. This is due either to an increase in the intensity of the δ SO_2^- mode or to the growth of contributions from δ_{as} SO_3^-, which would be down-shifted from 610 cm^{-1} in the Raman spectrum. Bands that red shift at more positive potentials include the δ SO_2^- vibration at 573 cm^{-1} in the +100 mV spectrum and the ring mode at 1072 cm^{-1} in the same spectrum. The ring modes at ~1170 and ~1576 cm^{-1} in the +300 mV spectrum each develop a shoulder on their high frequency side at more positive potentials. These new features are assigned to the strongest vibrations of benzenesulfonate, formed by oxidation of the adsorbed sulfinate. Specifically, in the sulfonate spectra in Figure 3, the strong ν_{as} SO_3^- band is at 1192–1195 cm^{-1}; it appears at the high frequency side of the 1165–1170 cm^{-1} band in the sulfinate spectra at positive potentials. The ring mode at 1577–1581 in the sulfonate spectra (Figure 3) grows in as a shoulder that overlaps the 1576 cm^{-1} band in the sulfinate spectra (Figure 4).

Clearer evidence for the interfacial formation of benzenesulfonate is the appearance of four new vibrations at potentials approaching +500 mV, which persist at more positive potentials but disappear when the potential is stepped back down to +300 or +100 mV. The assignments for these vibrations are based on those for solid sodium benzenesulfonate by Uno et al.[34] In some cases, the normal modes are very complex, and we note only the specific contributions of the sulfonate group and ring motions to the potential energy distribution.[34] The band at 530–534 cm^{-1} involves δ_s SO_3^- + δ ring, shifted from 567 cm^{-1} in solution. The 712–714 cm^{-1} mode is assigned to a ν CS + δ ring mode (at 735 cm^{-1} in the Raman spectrum). The new band at 921–924 cm^{-1} may correspond to the γCH + tor mode found at 921 cm^{-1} in the IR spectrum of the solid. Lastly, the 1136 cm^{-1} band arises from the ν CS + ν CC + ν_s SO_3^- vibration, corresponding to the 1136 cm^{-1} band in the Raman spectrum of the solid.

The potential dependence of the "*in situ*" prepared benzenesulfinate monolayer SER spectrum thus shows that the sulfinate–surface interactions are slightly potential dependent and that the sulfonate can be formed and can coexist with the sulfinate on the surface. The latter result is in marked contrast to the results for the "*ex situ*" prepared monolayer shown in Figure 3. In that experiment, benzenesulfinate was only on the surface and not in solution, and we observed reversible potential-dependent shifts in some of the bands, and reversible oxidation to benzenesulfonate occurred near +500 mV. When benzenesulfinate is present in solution as well as in the monolayer (Figure 4), we still see potential-dependent shifts in the benzenesulfinate monolayer spectrum, but the bands that appear upon oxidation to benzenesulfonate are much weaker. The fact that the adsorbed sulfonate bands are much weaker when sulfinate is present in solution (Figure 4) than when it is absent (Figure 3a) reveals that a dynamic equilibrium exists between solution and adsorbed species and that the sulfinate displaces the sulfonate as it forms on the surface. This explanation accounts for the relatively low intensity of the sulfonate bands in the +500 and +650 mV spectra in Figure 4. Furthermore, these experiments indicate that the adsorptivities of benzenesulfinate and benzenesulfonate differ significantly.[37]

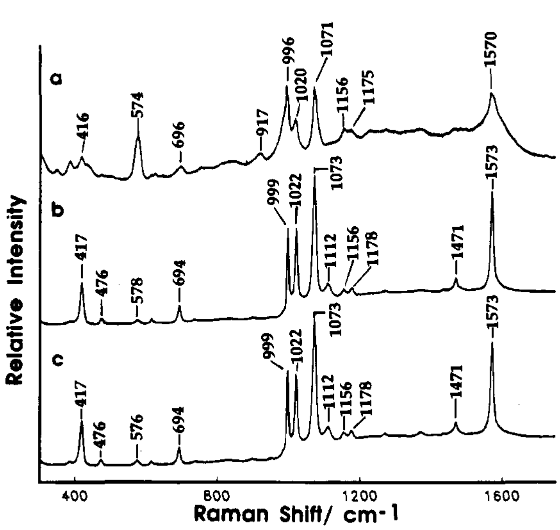

Figure 5. SER spectra of a gold electrode: (a) with a monolayer of benzenesulfinate, prepared *ex situ* as in Figure 2b; (b) the spectrum obtained after immersing (a) in a 1 mM solution of benzenethiol for 10 min, followed by rinsing with ethanol; and (c) the spectrum obtained after immersing (b) in a 1 mM solution of sodium benzenesulfinate in water for 2 h, followed by rinsing with water.

As demonstrated by the results shown in Figure 4, benzenesulfinate in solution displaces benzenesulfonate as it forms at the interface. When a benzenesulfinate monolayer is prepared *ex situ* and then immersed in an ethanol solution containing 1 mM benzenethiol, the sulfinate is completely displaced. This is shown by the SER spectra in Figure 5. Spectrum 5a is of the sulfinate monolayer prior to displacement and 5b the spectrum after displacement, which agrees well with the benzenethiolate spectrum in Figure 1a. The most obvious evidence for displacement is the disappearance of the sulfinate band at 574 cm^{-1} (Figure 5a) after immersion of the sulfinate monolayer in the benzenethiol solution (Figure 5b). Sulfinate bands do not reappear in the spectrum even after the thiol-modified gold electrode is immersed for a prolonged period in a fresh benzenesulfinate solution (Figure 5c). This demonstrates preferential adsorption of benzenethiol over benzenesulfinate. Similar monolayer displacement was observed by Tarlov and Newman, who found that alkylthiols in ethanol displace alkylsulfonates on gold.[3,4]

The relative ease of formation and stability to rinsing of the arylthiolate, sulfinate, and sulfonate monolayers and the results of these displacement experiment reveal two key features of aryl sulfur monolayers. First, they show that the adsorbed species is in dynamic equilibrium with species in solution. This has important consequences for the fabrication of mixed monolayers, in that the surface coverage and monolayer composition will depend on both the solution concentrations and relative adsorptivities of the potential adsorbates. Second, they show that the relative adsorptivities and strength of surface interactions follow the trend: benzenesulfonate << benzenesulfinate < benzenethiolate. This explains why sulfinates and sulfonates are not routinely observed as contaminants when thiolate SAMs are fabricated.[5] If the oxidized species were present as contaminates in the thiol solution and did adsorb, they would quickly be displaced by the more-readily-adsorbing thiol, which is also present at much higher concentration.

Analysis of Adsorbate–Surface Interactions by Perturbation Molecular Orbital Theory. The relative adsorptivities of benzenethiolate, sulfinate, and sulfonate are not simply related to differences in their solubilities or solvent compatibilities, since all of the monolayers were formed from solvents in which the adsorbate was readily soluble. Instead, we can ascribe the different adsorptivities to differences in the adsorption free energies. The adsorption free energy includes the change in the solvation energy of the adsorbate and surface upon adsorp-

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(37) Preliminary results of experiments with colloids indicate that a > 500:1 ratio of sulfonate to sulfinate in solution is required in order to obtain a mixed monolayer that contains detectable sulfonate. Dindot, J., Garrell, R. L. unpublished results, June 1994.

Chart 1

ΔE = energy gained or lost when reactant orbitals overlap

$$\Delta E = -\sum_{ab}(q_a + q_b)\beta_{ab}S_{ab}$$

first order closed shell repulsion (net antibonding)

q_a, q_b	electron densities
β_{ab}	resonance integral
S_{ab}	overlap integral

$$+\sum_{k<l}\frac{Q_k Q_l}{\varepsilon R_{kl}}$$

Coulombic repulsion or attraction

Q_k, Q_l	total charges on reactants
ε	dielectric constant
R_{kl}	distance

$$+\sum_{r}^{\mathrm{occ}}\sum_{s}^{\mathrm{unocc}}-\sum_{s}^{\mathrm{occ}}\sum_{r}^{\mathrm{unocc}}\frac{2(\sum_{ab}c_{ra}c_{sb}\beta_{ab})^2}{E_r - E_s}$$

charge transfer [second order; interaction of filled orbitals with all unfilled orbitals of correct symmetry]

c_{ra}	coefficient of a.o. a in MO r [r's are MOs on one atom, s's on the other]
E_r	MO energy, orbital r
E_s	MO energy, orbital s

$$+\,\Delta E_{\mathrm{solvation}}$$

tion, along with the energy of forming adsorbate–adsorbate and adsorbate–surface interactions.

The adsorbate–adsorbate interactions are likely to be very similar in monolayers of benzenethiolate, sulfinate, and sulfonate. This is because the molecular volumes are very similar (102, 110, and 115 Å^3, respectively, as estimated by MacroModel with the MM2 force field), and the total molecular charges are identical. Furthermore, we expect the packing in the three types of monolayers will be very similar, because it will be dominated by the phenyl groups. (The thiolate, sulfinate, and sulfonate groups are all smaller than the ring, as can be seen in the HOMO plots comprising Figure 8 and discussed below.) Thus, we expect the steric and dipolar interactions to be comparable in the three systems. A qualitative estimate of the strength of the interactions between adjacent molecules is obtained from the calculations of Jorgensen et al.[38] who showed that the interaction between benzene rings in the optimal tilted-T arrangement is −2.3 kcal/mol in vacuum and only ∼ −1.0 kcal in water. That interaction is comparable to the van der Waals interaction between six-carbon alkane chains.[39] These interactions are weak; even if there are small differences in the adsorbate–adsorbate interactions in the three types of monolayers, they are unlikely to be responsible for the significant differences in anion adsorptivities.

We therefore focus on the adsorbate–surface interactions and the solvation free energy change upon adsorption as the main factors controlling the relative adsorptivities of the three anions. The energetics of the process by which a molecule or ion adsorbs on a surface can be described by perturbation theory or frontier orbital theory. In this approach, when two species interact, the change in the energy of the system, ΔE, is the energy gained or lost when reactant orbitals overlap. This energy change can be partitioned into four contributing terms, as shown in Chart 1.[40]

The pair of reactant orbitals with the most similar energies (smallest value of $E_r - E_s$) will contribute most to ΔE. In each of our experiments, we are concerned with an anion (electron donor), which has a filled highest occupied molecular orbital (HOMO) and its interactions with the metal. The metal can accept electrons into its lowest unoccupied or partially occupied molecular orbital (LUMO or conduction band). A small simplification is implicit in this analysis. Ultimately, it is the molecular *ions* (e.g., benzenethiolate) that bond to the gold atom(s), with more or less covalent bond character. Therefore, we are assuming for simplicity that all of the species that interact with and subsequently bond to the surface are ions. In reality, the thiol may first interact with the surface as the neutral molecule and subsequently lose H^+ or $H^\bullet$.

The first term in the perturbation expression above describes interactions between closed (filled) shells and therefore does not contribute to ΔE for the adsorption reactions. The second term in the equation above describes the Coulombic interactions between the reactants, here the adsorbate and surface, while the third term describes charge transfer (CT) interactions. When $E_r - E_s$ is large, the CT term is small, and ΔE is dominated by the Coulombic term. Such a reaction is considered to be under "charge control." When $E_r - E_s$ is small, the CT term dominates, and the reaction is under "orbital control". The closer the adsorbate HOMO and substrate LUMO orbitals are in energy, the larger the magnitude of the CT term. Barclay and Cajá found that the relative adsorptivities of simple anions on electrode surfaces could be explained in terms of Coulombic and charge-transfer interactions.[41] Anions with higher HOMO energies ("softer" bases) adsorbed more readily on metals such as mercury and gold. They achieved greater stabilization upon adsorption than anions with lower HOMO energies, because of stronger charge-transfer interactions. This is illustrated in Figure 6, adapted from ref 41.

The use of perturbation theory to understand both qualitative and quantitative aspects of adsorbate–surface interactions is not new.[42] To our knowledge, this is the first application of perturbation theory to the problem of adsorption from solution, and the first use of *ab initio* calculations to quantify each type of contribution to the adsorption free energy for a series of adsorbates.

Adsorbate–Surface Coulombic Interactions. The potential of zero charge (pzc) of gold electrodes, and of colloids like the one used here, is negative of the open circuit potential in air, ethanol, or water.[32,33] This means that the effective charge on the gold surfaces in our experiments is positive. In the displacement experiments (e.g., Figure 5), two types of ions compete for sites on the same kind of surface. We can therefore treat the metal as a constant in evaluating the relative strengths of the adsorbate–surface Coulombic interactions. With this simplification, the relevant adsorbate properties for the anions

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[38] Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768.

[39] Harris, J.; Rice, S. A. *J. Chem. Phys.* **1988**, *89*, 5898.

[40] Fleming, I. *Frontier Orbitals and Organic Reactions*; Wiley: New York, 1976.

[41] Barclay, D. J.; Caja, J. *Croat. Chem. Acta* **1971**, *43*, 221.

[42] See, for example: Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH Publishers, Inc.: New York, 1988; pp 107–121.

Table 1. Atomic Charges on the Ring Substituent

	C_6H_5SH	$C_6H_5S^-$		$C_6H_5SO_2^-$		$C_6H_5SO_3^-$	
	Mulliken	Mulliken	CHELPG	Mulliken	CHELPG	Mulliken	CHELPG
S	−0.27	−0.65	−0.88	1.03	−0.01	1.55	1.33
O				−0.84	−0.49	−0.74	−0.73
O				−0.84	−0.49	−0.76	−0.73
O						−0.76	−0.73
total	−0.27	−0.65	−0.88	−0.65	−0.99	−0.71	−1.14

studied here are the total charge on the ring substituent and the charges on each atom that could interact with the surface.

If Coulombic interactions are the main factor determining the relative adsorptivities of benzenesulfinate, sulfonate, and thiolate, we would predict that the anion with the largest negative charge on the atom(s) that could interact with the surface would adsorb most readily. Table 1 gives the atomic charges that have been calculated by Mulliken population analysis and by the CHELPG method, both at the HF level with the 6-31G(d) basis set. While this level of theory cannot be expected to give highly accurate absolute values, the relative values should be reliable. The Mulliken analysis shows that the total charge on the ring substituent is nearly the same for all three anions, while the CHELPG results indicate only small differences; both methods would lead us to expect comparable adsorptivities for the three anions, but this is contrary to experiment. If we consider only the most negatively charged atoms, in the Mulliken analysis, the sulfonate has three oxygen atoms with ~ −0.7 electron charge each, the sulfinate has two oxygen atoms with ~ −0.8 electron charge each, and the thiolate has only the sulfur, with a charge of ~ −0.5. The same trend is predicted by the CHELPG method. Both sets of calculations would lead us to expect relative adsorptivities in the order benzenesulfonate > benzenesulfinate > benzenethiolate, but this is exactly the opposite of what we observe. Thus, adsorbate−surface Coulombic interactions must not be the dominant factor determining the relative adsorptivities of these ions.

Adsorbate−Surface Charge Transfer (CT) Interactions. We now consider whether CT interactions, described by the third term in eq 1, are a factor controlling the relative adsorptivities of these aryl anions. CT interactions are difficult to measure directly, but, because all of our ions are adsorbing on the same surface, we can simply compare the HOMO energies of the ions. Electrons will be donated from the HOMO of the adsorbate to the LUMO of the metal. (For gold, the electron affinity is between 4.78 and 5.32 eV, indicating that the anion is energetically below the neutral.[43,44]) The higher the HOMO energy of the adsorbate, the closer the adsorbate HOMO will be to the LUMO of the metal, the smaller $E_r - E_s$ will be, and the stronger the charge transfer interactions that can result. According to Koopmans' theorem, the HOMO energy is approximately equal to the experimental nonadiabatic ionization potential.[45] Unfortunately, experimental values for the ionization potentials of benzenethiolate, benzenesulfinate, and benzenesulfonate are not available. In their absence, we can compare the anion HOMO energies that have been determined quantum mechanically. The values calculated *ab initio* at the HF/3−21 G(d) level are shown schematically in Figure 7.

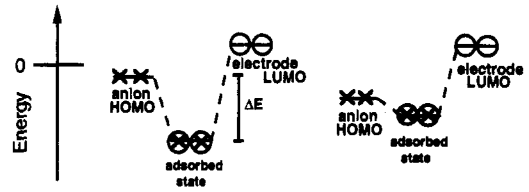

Figure 6. Schematic illustration of the shifts in HOMO and LUMO energies when a molecule adsorbs on a metal surface. Adapted from ref 41.

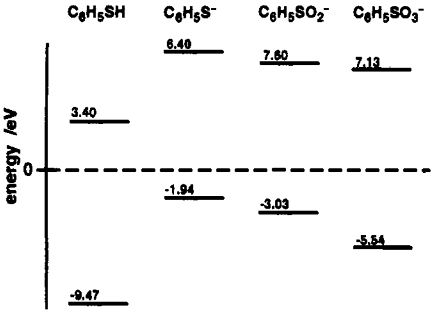

Figure 7. HOMO and LUMO energies (eV) calculated *ab initio* at the HF/3-21G(d) level.

Benzenethiolate has the highest HOMO energy, followed by benzenesulfinate and benzenesulfonate. This would lead us to predict adsorptivities in the order benzenethiolate > benzenesulfinate > benzenesulfonate, which is consistent with the experimental results. As an aside, we note that benzenethiol has an even lower HOMO energy than benzenethiolate. This implies that if both benzenethiol and benzenethiolate were available to adsorb (as would be the case if the monolayer were adsorbed from water, and perhaps ethanol, because of the equilibrium $C_6H_5SH \rightleftharpoons C_6H_5S^- + H^+$), the thiolate would adsorb preferentially.

The electrostatic potential surfaces for the HOMOs of benzenethiolate, benzenesulfinate, and benzenesulfonate are shown in Figure 8. It is clear from these depictions that the HOMOs of the thiolate and sulfinate groups will have significantly larger orbital overlap with metal orbitals than will the HOMO of the sulfonate. The HOMO of the sulfonate is significantly more delocalized onto the benzene ring, which does not interact with the surface. The sulfinate HOMO illustrations also reveal why the molecule should prefer to bond to the surface through the two oxygen atoms, rather than through the sulfur and oxygen atoms. If the coordination to the metal were bidentate, with the ring tilted slightly off normal, maximum overlap of the *p*-orbitals on each oxygen with the metal orbitals would be achieved. Tilting the molecule such that the sulfur orbitals interact with the surface as well would lead to overlap of both the (+) and (−) lobes on each oxygen with the surface, i.e., to an increase in the oxygen−metal anti-bonding contribution. Apparently, an improvement in the sulfur−metal bonding cannot compensate for the weakening of both oxygen−metal interactions. Thus, bidentate coordination through the oxygen is preferred.

Solvation Free Energy Changes. Finally, we consider the contributions from the change in solvation free energy to the relative adsorptivities, described by the $\Delta E_{\text{solvation}}$ term in eq 1. The three anions considered here are very similar in size.

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[43] Trasatti, S. *J. Chem. Soc., Faraday Trans. I* **1972**, *68*, 229.

[44] Huber, E. E. *Appl. Phys. Lett.* **1966**, *8*, 169.

[45] Levine, I. N. *Quantum Chemistry*, 4th ed.; Prentice Hall: Englewood Cliffs, NJ, 1991; p 475.

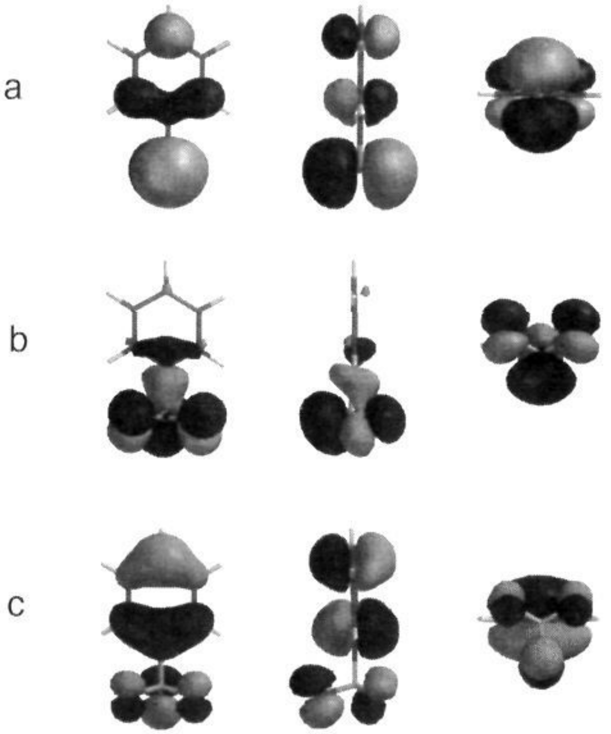

Figure 8. HOMO electrostatic potential surfaces superimposed on the molecular frameworks and shown in front, side, and top views: (a) benzenethiolate; (b) benzenesulfinate; and (c) benzenesulfonate.

Therefore, we make the approximation that the change in the solvation of the *surface* when each anion adsorbs is about the same. This allows us to approximate the change in solvation energy as the hydration free energy of the anion. Because experimental solvation energies are not available, we have used statistical perturbation theory, as described in the Experimental Section, to calculate the *relative* hydration energies of the three anions. The calculations predict that the sulfonate is better hydrated than the sulfinate by 7.70 ± 0.27 kcal/mol and that the sulfinate better hydrated than the thiolate by 10.72 ± 0.30 kcal/mol, making the sulfonate better hydrated than the thiolate by 18.4 kcal/mol. This trend is consistent with the relative solubilities of benzenethiol, benzenesulfinic acid, and benzenesulfonic acid in water. Because the sulfonate is the most strongly hydrated, it would adsorb least readily. The calculated trend in solvation energies is thus consistent with our experimentally determined relative adsorptivities.

The atomic charges used in the hydration free energy calculations were obtained by the CHELPG method. To test the validity of using CHELPG charges, both G92 (3-21G(d) basis set) and BOSS minimizations were performed on methyl sulfinate and methyl sulfonate interacting with one water molecule. The calculations were qualitatively, if not quantitatively the same; the BOSS calculation favored the sulfinate by 2.7 kcal/mol, and the G92 calculation favored it by 2.5 kcal/mol. A BOSS minimization of the benzene compounds favored the sulfinate by 1.2 kcal/mol. Since each water−oxygen interaction is worth about 15 kcal/mol, this slight difference is not enough to make up for the increase in the number of water−oxygen interaction sites on going from the sulfinate to the sulfonate form and thus lends confidence in the free energies of hydration presented above.

Polarizabilities. An additional, much smaller factor that can influence adsorptivities is polarizability. Pearson found that softer, more polarizable ions generally have higher adsorptivities, particularly on noble metals because of their large size and easily excited valence electrons.[46,47] He associated higher polarizability with a smaller HOMO−LUMO gap. We calculate gaps of 10.34, 10.61, and 12.65 eV for benzenethiolate, benzenesulfinate, and benzenesulfonate, respectively (Figure 7). Thus, the contributions of polarizability to ΔE for the adsorption process would be largest for the thiolate and sulfinate and smallest for the sulfonate. This would reinforce the contributions from charge transfer interactions and solvation free energy changes, which are primarily responsible for the observed trend.

Summary. We therefore conclude that charge-transfer interactions and the change in free energy of solvation upon adsorption are responsible for the relative adsorptivities of benzenethiolate, sulfinate, and sulfonate from water to gold. These conclusions are consistent with qualitative ideas about ion "softness" in solution.[48] In general, the softness of a base, such as a thiolate, is correlated with a low desolvation energy and high HOMO energy. A harder base, such as a sulfonate, is expected to have a higher desolvation energy and lower HOMO energy. The work presented here gives quantitative support to these empirical trends.

We suggested earlier that the overall increase in the intensity of the benzenesulfinate spectrum at positive potentials (Figure 4) may be a consequence of higher surface coverage. This adsorption trend, along the fact that benzenesulfonate can only be induced to adsorb at positive applied potentials, can now be explained in terms of modulating the strength of the adsorbate−surface Coulombic interactions. Coulombic interactions may be too weak for adsorption to occur spontaneously, as in the case of benzenesulfonate when no potential is applied at the surface. Adsorption can be induced, however, by increasing the strength of the Coulombic interactions; this is readily accomplished by applying a more positive potential at the electrode surface. For benzenesulfonate, adsorption occurs at applied potentials >+ 500 mV vs SCE.

Conclusions

The first adsorbed monolayers of sulfinates and sulfonates have been prepared and characterized by SERS, and the relative adsorptivities and reactivities of benzenethiol, sulfinate, and sulfonate have been compared. Our results suggest that aromatic thiolate monolayers are significantly less prone to oxidation than are monolayers of alkyl thiolates. The stability of aryl thiolate and sulfinate monolayers toward oxidation in air and to rinsing by solvents may make them more suitable than alkylthiolates for applications that require handling and prolonged exposure to air. Benzenesulfinate monolayers form spontaneously on gold surfaces, but adsorption can also be induced by applying a positive potential at the surface. By contrast, benzenesulfonate does not adsorb spontaneously, and sulfonate monolayers or submonolayers only form when a positive potential is applied, or when sulfinate monolayers are oxidized *in situ*. The relative adsorptivities of the three compounds on gold are benzenethiolate >> benzenesulfinate > benzenesulfonate. In the first application of perturbation theory and *ab initio* quantum mechanical methods to a problem involving adsorption from solution, this trend has been explained in terms of the relative strength of the adsorbate−surface charge transfer interactions and the relative solvation free energy changes upon adsorption. The results are consistent with previous, more qualitative arguments that rationalize adsorption and adhesion in terms of the adsorbate "hardness" and the surface acidity. The computational methods used here for evaluating the adsorbate−surface

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(46) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(47) Pearson, R. G. *Proc. Natl. Acad. Sci.* U.S.A. **1986**, *83*, 8440.
(48) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.

Coulombic and charge-transfer interactions and the relative solvation energies of the molecules in solution can be widely applied to predict and understand the relative adsorptivities of molecules in solution, the type and relative strength of adsorbate–surface interactions, and the chemical basis for adhesion. The experimental and computational methods developed here provide the fundamental basis for designing and fabricating pure and mixed monolayers with prescribed composition and stability and for understanding the reactivity of adsorbed and self-assembled monolayers.

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Supporting Information Available: Raman spectrum of diphenyl disulfide and SER spectrum of diphenyl disulfide on a roughened gold electrode at −600 mV and analysis of the SERS detection limit for adsorbed disulfide in which the S−S bond is parallel to the surface (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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