Self-Assembled Monolayers of Ferrocenylazobenzenes on Au(111)/Mica Films: Surface-Enhanced Raman Scattering Response vs Surface Morphology

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Surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS) results are reported for self-assembled monolayers (SAMs) of 4-(4-mercaptobutyl)-4'-ferrocenylazobenzene, compound 1, on Au/mica and Pt/mica thin films. Two different Au/mica surfaces, designated Au(rough)/mica and Au(111)/mica, have been characterized by atomic force microscopy (AFM) to define their respective surface morphologies. Cyclic voltammetry of SAMs of 1 on Au(rough)/mica, Au(111)/mica, and Pt/mica was used to directly measure the surface coverage of 1. A quantitative determination of the contributions to the measured surface Raman intensity from adsorbate-localized resonance Raman and substrate-derived electromagnetic enhancement effects is made. The surprising conclusion is that Au(111)/mica surfaces of the type traditionally used for preparing and studying SAMs are “SERS-active” without the need for additional roughening or treatment with a “SERS-active” overlayer.

Introduction

Surface-enhanced Raman spectroscopy (SERS) and surface-enhanced resonance Raman spectroscopy (SERRS) are widely used and extremely sensitive techniques for obtaining vibrational spectra of adsorbates at roughened Ag, Cu, and Au surfaces. Recent review articles provide a comprehensive overview of fundamental studies on SERS enhancement mechanism(s) as well as applications of SERS/SERRS to a variety of problems in electrochemistry, surface science, materials science, and biochemistry.1–5

The hallmarks of SERS/SERRS are their sensitivity to and selectivity for molecules adsorbed at solid/liquid, solid/gas, and solid/ultrahigh vacuum (UHV) interfaces. SERS readily yields high quality, adsorbate general, vibrational spectra with signal-to-noise (S/N) ratios typically between 10:1 and 1000:1 for fractional surface coverage between 0.01 and 1.0 monolayer. When implemented in a spatially-resolved (SR) mode with a ca. 2 µm laser spot size, SERS possesses an extraordinary mass sensitivity ranging from 20 amol to 20 zmol.6–8 This unparalleled sensitivity for SERS is currently believed to arise from the simultaneous operation of two distinct enhancement mechanisms that amplify the intensity of surface Raman scattering. These mechanisms are (1) a long range, classical electromagnetic (EM) effect that contributes a surface enhancement factor, EFEM \( \geq 10^{10} \) and (2) a short range “chemical” (CHEM) effect that contributes EF CHEM \( \geq 10^{1} \)–\( 10^{2} \). Schatz9–12 has discussed the EM mechanism and its dependence on large scale roughness while Otto11,13 has similarly discussed the CHEM mechanism and its dependence on atomic scale roughness. When SERS is implemented, the laser excitation wavelength, \( \lambda_{ex} \), overlaps the electronic absorption spectrum of the adsorbate and yields an additional resonance Raman enhancement factor EF RRM \( \geq 10^{1} \)–\( 10^{2} \) through excitation of adsorbate localized, electronic transitions.1–5

As spectroscopic probes of surface chemistry and dynamics, SERS/SERRS have both strengths and weaknesses relative to other interfacial vibrational spectroscopies.14 It is widely believed that one such weakness of SERS/SERRS is the requirement that a “SERS-active” metal surface must be either inherently “rough”, such as that found in aggregated metal colloids or vacuum-deposited metal island films, or intentionally roughened by either an electrochemical oxidation–reduction cycle or deposition of a film over a preroughened substrate.14 Exact what length scale of surface roughness is required for SERS is not yet precisely defined. The optimum contribution of the EM mechanism to the overall EF is predicted to occur for large scale roughness in the 10–100 nm range.9–12 The CHEM mechanism, on the other hand, invokes a specific role for atomic scale roughness in the form of labile adatoms and/or adatom clusters.1,13

The necessity for using naturally rough surfaces or for roughening the surface to obtain the large enhancement

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in signal has rendered SERS inapplicable to the study of the vibrational spectroscopy of adsorbates on well-defined single-crystal surfaces. Consequently, surface infrared–absorption spectroscopy (IRRAS),16–18 infrared–visible surface sum frequency generation (SFG) spectroscopy,19 and unenhanced surface Raman spectroscopy (USRS)20 have emerged as the techniques of choice for such applications.

An extremely interesting and important area of current research in interfacial science, to which SERS/SERRS techniques would seem to be inapplicable, is that of self-assembled monolayers (SAMs).21 Interest in SAMs and other organized molecular assemblies (viz., Langmuir–Blodgett films) has greatly intensified in recent years. SAMs provide relevant model systems for a variety of important scientific and technological problems including adhesion,21 biological interfaces21 and membranes,21 electron transfer,22 microstructure and molecule-based device fabrication,23 and wetting.21 Knowledge of the structure–function relationships in these monolayers will play an important role in developing an atomic level picture of several complex phenomena. Indeed, it has been shown that the monolayer structure in SAMs of ferrocenyl-azobenzenealkanethiols can be used to control electron transfer processes between the electrode surface and the azobenzene or ferroene redox centers within the film.24

The most thoroughly studied and best characterized SAM system is that of n-alkanethiols on Au(111) surfaces. Detailed surface structural information on n-alkanethiol/Au(111) SAMs has been obtained from scanning tunneling microscopy (STM),25 atomic force microscopy (AFM),26 helium diffraction,26 and X-ray diffraction.26 Information on polymethylene chain structure, molecular orientation, Au–S surface bond formation, and the dynamics of chemical processes occurring on or within SAMs has been obtained from IRRAS,21 SFG,27 and SERS/SERRS.28–31 Except for the SERS/SERRS studies, both Au(111) bulk single crystals and Au(111) thin films on mica have been used in the structural and vibrational studies. The Au films preferred for use in the study of SAMs have predominantly (111) orientation and large, atomically flat surface domains. They are formed by epitaxial growth of helium diffraction,26 and X-ray diffraction.26 Information obtained from scanning tunneling microscopy,25 atomic force microscopy (AFM),26

Not being able to use SERS to directly study SAMs on substrates traditionally used to prepare them (viz., Au(111)/mica)26 has been viewed as a severe limitation of the method. In this paper, we will demonstrate that it is, in fact, possible to use SERS or SERRS to directly acquire chemical structure and dynamical information from SAMs on Au(111)/mica substrates. Furthermore, we will show that, through the use of a near-infrared laser excitation wavelength, the SERS response of the Au(111)/mica substrate is very strong indeed, yielding high S/N vibrational spectra without perturbing the substrate structure from its natural state. Although a linear alkanethiol might seem like a logical choice of an adsorbate molecule for this study, we chose 4-(4-mercaptobutyl)-4'-ferrocenylazo-benzene,24 compound 1 (Scheme 1), because it has several distinct advantages: (i) it is known to form densely packed monolayer films on Au substrates;24 (ii) its azobenzene chromophore is a large cross-section Raman-active tag with characteristic modes in the region between 1200 and 1600 cm⁻¹,35,36 (iii) its ferrocenyl group is an electrochemical tag for coulometric determination of surface coverage. On the basis of the AFM work described herein and published STM/AFM studies of Au(111)/mica25 which show this material to be essentially an island film with large, atomically flat tops, as well as our detailed theoretical37–39 and experimental40 knowledge of the dependence of the EM contribution to EF on particle size and λₚ, we hypothesized that a weak ~10⁻⁶ EM contribution to the SERS EF should exist. The presence of EF_EM ~ 10⁻⁹

10⁸ could be readily verified by using a CCD detector and SAM precursor 1, which would ensure adequate S/N.

The verification of this hypothesis has several important implications for SERS/SERRS as techniques and for their application to SAM/Au(111)/mica systems. With regard to SERS/SERRS as techniques, verification could open the door to a much wider range of applications. In the specific case of SAM/Au(111)/mica systems, verification would bring the following unique capabilities of SERS/SERRS to bear on an important class of experimental systems: (i) an unparalleled combination of interfacial sensitivity and selectivity; (ii) experimental simplicity; (iii) detection of vibrational frequencies that are Raman-active only; and (iv) easy access to low-frequency vibrations in the 5–500 cm⁻¹ range where one can directly observe the surface chemisorption bond.

**Experimental Section**

**Materials.** Au (99.99%, 0.50 mm diameter), NaClO₄, NaOH, and NaH₂PO₄ were purchased from Aldrich Chemical Co. Pt wire (99.95%, 0.25 mm diameter) was purchased from D.F. Goldsmith, Evanston, IL. Red muscovite mica was purchased from Asheville Mica, Newport News, VA. W boat sources and point source loop filaments were purchased from R. D. Mathis, Long Beach, CA. Compound 1 and SAMs of compound 1 were prepared by literature methods. Tetrahydrofuran was dried using a point source loop filament in a Japan Electron Optics Laboratory Model JEE-4C thermal evaporator. Base pressure of the system was 4 × 10⁻⁸ Torr.

**SAM Preparation and Electrochemical Experiments.** In a typical experiment, monolayer films were prepared by soaking freshly prepared Au or Pt substrates in a saturated cyclohexane solution of I for 24 h, followed by copious rinsing with THF. Surface coverages were measured electrochemically in H₂O/0.2 M NaClO₄ with a Pine AFMREDE4 biopotentiostat with a Kipp and Zonen BD90 X-Y recorder. Surface roughness factors, Rₚₛ, were determined by the method of Janata. H₂O was deoxygenated by bubbling with prepurified grade N₂ for 30 min before all electrochemical experiments.

**Surface and Bulk Raman Spectroscopy.** A Spectra Physics Model 124B HeNe laser was used for λ = 632.8 nm, and λ = 575.2 nm was obtained from a Spectra Physics Model 3900 Ti:Al₂O₃ laser pumped by a Spectra Physics Model 171-18 Ar⁺ laser. The SERS/SERRS spectra were obtained on an ACTON VM-505 single grating monochromator equipped with a Photometrics PM-512 CCD detector. Holographic edge filters (Physical Optics Co.) were used at both wavelengths for rejection of λ₁ós. For typical surface Raman experiments, the angle of incidence of the laser excitation source was ~45° with respect to the surface normal, and Raman scattered light was collected parallel to the surface normal with f/1 optics.

In those surface Raman experiments pertaining to the measurement of EFs, the laser source was line-focused to 2 mm × 0.1 mm, illuminating a maximum geometric surface area A_geom = 0.01 cm² × 0.01 cm = 0.00002 cm². Similarly, in the corresponding bulk Raman experiments required for EF measurement, the sample was contained in a glass tube with a 0.8 mm × 0.8 mm square cross section. The laser source was then line-focused to 2 mm × 0.1 mm, illuminating a maximum volume V_vol = 0.003 cm³ × 0.05 cm × 0.01 cm = 1.5 × 10⁻⁷ cm³.

**AFM Measurements.** Images were recorded using a NanoScope II microscope equipped with a 0.7 μm scan head (Digital Instruments). All images were acquired in air with SiN₃ cantilevers (force constant 0.58 N/m) having pyramidal tips with 70° cone angles and 20–40 nm effective radii of curvature (Rₑ). Large scan size images were acquired in height mode with the force equal to 20–60 nN and a scan rate of 1.34 lines s⁻¹ while the atomically resolved image was acquired in force mode at a scan rate of 78 lines s⁻¹. Each image is 400 × 400 pixels, and all reported images are unfiltered.

**Results and Discussion**

**Au/Mica Films.** The surface morphology of Au thin films deposited on freshly cleaved mica substrates is extremely sensitive to all the details of sample preparation, including the parameters d_m, rₐ, T_s, and chamber pressure. Although a series of substrates with a range of surface morphologies was examined, in this manuscript we focus only on the two extreme cases, which are referred to as Au(111)/mica and Au(rough)/mica to designate their relative surface morphologies. The surface features of these Au films were controlled by regulating T_s and rₐ (Table 1). In general, higher T and slower rₐ resulted in smoother Au films with larger (111) domains.

**Atomic Force Microscopy.** AFM was used to examine the surface morphology of both Au(rough)/mica and Au(111)/mica substrates on the nanometer scale and Au(111)/mica on the atomic scale (Figure 1 A–D). All AFM images are given in a top-view presentation with the lighter areas denoting higher regions and the darker areas representing lower regions. The AFM image of Au(rough)/mica, Figure 1A, shows a surface morphology exhibiting a broad distribution of spheroidal particles with diameters in the 50–100 nm range. Higher resolution images consistently failed to reveal an ordered array of...

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Table 1. Deposition Parameters and Surface Roughness Factors for Au/mica and Pt/mica Films, Surface Coverages for 1, and SERS/SERRS Characteristics of Au/mica and Pt/mica Films Modified with 1.

<table>
<thead>
<tr>
<th></th>
<th>Au(111)/mica</th>
<th>Au(rough)/mica</th>
<th>Pt/mica</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (nm)</td>
<td>100</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>r_A (nm s⁻¹)</td>
<td>0.03</td>
<td>0.3–0.4</td>
<td>N/A</td>
</tr>
<tr>
<td>T_A (°C)</td>
<td>~240</td>
<td>&lt;50</td>
<td>N/A</td>
</tr>
<tr>
<td>surface coverage (mol cm⁻²)</td>
<td>5.0 × 10⁻¹⁰</td>
<td>5.1 × 10⁻¹⁰</td>
<td>4.5 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Rsurf (m²/cm²)</td>
<td>1.35</td>
<td>1.50</td>
<td>N/A</td>
</tr>
</tbody>
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* N/A = not available. |

Figure 1. AFM images and line scans of Au/mica films. Deposition conditions are outlined in Table 1 and scanning parameters are listed in the Experimental Section. (A) 800 x 800 nm image, Au(rough)/mica; (B) 994 x 994 nm image, Au(111)/mica, before surface modification with 1; (C) 994 x 994 nm image, Au(111)/mica, after surface modification with 1 (representative area, not the same as in B); (D) 13.5 x 13.5 nm image, unmodified Au(111)/mica.

Au atoms that could be attributed to a Au(111) face. In contrast, the AFM image of Au(111)/mica shows a surface with large (100–200 nm diameter), flat terraces that account for approximately 80–85% of the geometric surface area and 60–65% of the microscopic surface area (Figure 1B and Table 1, respectively). The microscopic surface area of Au(111)/mica was determined electrochemically by oxidizing representative Au electrodes to form Au₂O₃ with subsequent reduction to reform Au. Integrating the current associated with reduction of the Au₂O₃ layer allowed the microscopic surface area to be determined for each electrode sample. This method is described in detail elsewhere. Significantly, the Au(111)/mica general surface morphology is not drastically altered after modification with 1 (compare Figure 1B and 1C). A higher resolution AFM image of a terrace on Au(111)/mica reveals a hexagonal pattern of bright spots consistent with Au(111) faces with a nearest neighbor Au—Au distance of 2.0 Å (Figure 1D). This Au—Au nearest neighbor distance compares well with literature values reported for other AFM images of Au(111) supported on mica and with single-crystal X-ray diffraction data for Au(111). Larger scan areas of the Au(111)/mica show that the (111) periodicity extends over hundreds of square nanometers.

The surface roughness factor, Rsurf, was determined by dividing the microscopic surface area by the geometric surface area. It is worth noting that although Au(rough)/mica and Au(111)/mica substrates substantially differ in surface morphology, they only slightly differ in microscopic surface area with Rsurf = 1.50 and 1.35, respectively (Table 1).

Electrochemistry. Compound 1 forms densely packed monolayer films on Au(rough)/mica, Au(111)/mica, and Pt/mica. The surface-confined ferrocenylazobenzene species on Au and Pt in H₂O/0.2 M NaClO₄ undergoes a reversible, Fe-centered one-electron oxidation (+0.43 V vs Ag/AgCl) to form a ferrocenium species (Figure 2). Surface coverage values are determined by integrating the current associated with monolayer oxidation and subsequent reduction. Significantly, the surface coverage values obtained from cyclic voltammograms for monolayer films of 1 formed on our Au(111)/mica and Au(rough)/mica substrates are quite comparable, 5.0 × 10⁻¹⁰ mol/cm² and 5.1 × 10⁻¹⁰ mol/cm², respectively (Table 1). Without Rsurf taken into account, the predicted surface coverage for 1 on Au based on its size is 4.5 × 10⁻¹⁰ mol/cm². With Rsurf taken into account, the predicted surface coverage values for 1 become 6.1 × 10⁻¹⁰ mol/cm² on Au(111)/mica and 6.8 × 10⁻¹⁰ mol/cm² on Au(rough)/mica. These surface coverage values are 20–30% higher than those determined experimentally. The reason for this could be the relative sizes of 1 and the microscopic imperfections in the Au(111)/mica and Au(rough)/mica substrates. For Au(rough)/mica, which has a higher density of surface imperfections than Au(111)/mica, its adsorbate surface coverage-to-microscopic surface area ratio would be expected to be comparatively lower than for Au(111)/mica. In addition, films formed on Au(rough)/mica would be expected to be more disordered than those

formed on Au(111)/mica, which would be expected to lead to lower adsorbate surface coverage-to-microscopic surface area ratios.

Note that the surface coverage value (4.5 × 10⁻¹⁰ mol/cm²) for 1 on Pt/mica is comparable to the surface coverage values of 1 on Au (Table 1). This observation is important and will play an integral role in interpreting the Raman response for monolayers of 1 on the Au and Pt substrates described herein.

Surface-Enhanced Raman Spectroscopy. In this section we examine the dependence of the surface Raman intensity response (for λex = 632.8 nm and λex = 752.0 nm) as measured by its EF from SAMs of 1 on the Au(rough)/mica and Au(111)/mica substrates characterized above by AFM and surface cyclic voltammetry. These two values of λex were chosen with reference to the UV−vis absorption spectra of compound 1, is typical of molecules with planar, π-aromatic moieties, the solid-state absorption spectrum of compound 1 is broadened and red-shifted with respect to the corresponding solution spectrum due to π−π interactions between adjacent molecules. It is likely that the absorption spectrum of a SAM formed from 1 would be more similar to the solid-state absorption spectrum of 1 than its solution counterpart due to the dense molecular packing in these films.

The Raman spectrum for a monolayer of 1 on Au(rough)/mica excited at λex = 632.8 nm is shown in Figure 4A. Because λex lies within the tail of the electronic absorption band of solid-state 1 (Figure 3A), there may be a significant surface resonance Raman contribution to the overall surface enhancement factor (i.e., SERRS). All of the vibrational bands shown in the 1200−1600 cm⁻¹ region originate from the azobenzene moiety of 1. Surprisingly, a high-intensity surface Raman spectrum is also obtained from a monolayer of 1 on Au(111)/mica excited at λex = 632.8 nm (Figure 4B). This spectrum is also likely to be SERRS in character. Figure 4C shows the surface Raman spectrum obtained from a monolayer of 1 on a Pt/mica substrate. Pt does not support significant EM enhancement when excited in the visible and can, therefore, be considered a “SERS-inactive” substrate. Thus, the vibrational features in Figure 4C are properly termed a surface resonance Raman (SRR) spectrum. A set of surface Raman spectra comparable to those in Figure 4A−C except that λex = 752.0 nm is shown in Figure 4D−F. Since λex = 752.0 nm lies sufficiently far to the red of the electronic absorption band of 1 in either solid or solution forms (Figure 3), little or no SRR contribution to their intensities should exist (viz., EFRR = 1). Therefore, the surface Raman spectra in Figure 4D−F are dominated by the EM enhancement mechanism.

Analysis of EM and RR Enhancement Factors. The primary information content in Figure 4 that we wish to address in this report lies not in the spectroscopic interpretation of the observed vibrational band positions, line widths, etc., but in the analysis of the magnitude of the EM enhancement factor as a function of surface nanostructure. For example, the intensity of the band at 1600 cm⁻¹ for 1 on Au(rough)/mica or Au(111)/mica is given by an expression of the form

\[ T_{\text{surf}}(\lambda_{\text{ex}}) = \frac{N_{\text{surf}} R_{\text{surf}} A_{\text{surf}}}{\Omega} \frac{d\Omega}{d\Omega} P_{\text{surf}} e^{-1/T} \text{EF}_{\text{EM}}(\lambda_{\text{ex}}) \text{EF}_{\text{RR}}(\lambda_{\text{ex}}) \]

where \( T_{\text{surf}}(\lambda_{\text{ex}}) \) is the surface number density in molecules cm⁻², \( R_{\text{surf}} \) and \( A_{\text{surf}} \) are defined in the Experimental Section, and the other symbols have been previously defined. Similarly, the intensity of the band at 1600 cm⁻¹ of bulk solid 1 is given by

\[ I_{\text{bulk}}(\lambda_{\text{ex}}) = \frac{N_{\text{bulk}} R_{\text{bulk}} A_{\text{bulk}}}{\Omega} \frac{d\Omega}{d\Omega} P_{\text{bulk}} e^{-1/T} \text{EF}_{\text{RR}}(\lambda_{\text{ex}}) \]

where \( N_{\text{bulk}} \) is the volume number density of 1, and where \( T_{\text{bulk}} \) and the other symbols are previously defined. The magnitude of EFEM in eq 1 is determined by the details of the surface nanostructure of Au(111)/mica and Au(rough)/mica, whereas the magnitude of EFRR will be the same for the spectra in Figure 4A and 4B. As eqs 1 and 2 are solved for EFRR(λex), the value EFRR cancels to give
where the intensities (intensity units W$^{-1}$ s$^{-1}$) have been corrected for variations in laser power and data acquisition time. Equation 3 consists of two ratios: (1) the surface-to-bulk intensity ratio and (2) the bulk-to-surface ratio of the number of molecules of 1 illuminated in bulk and surface Raman experiments. With Figure 4A as an example, the intensity of the 1600 cm$^{-1}$ band can be compared to the same band of bulk 1 to give a surface-to-bulk intensity ratio of 0.048. The bulk-to-surface ratio of the number of molecules of 1 is 3 x 10$^6$ (Table 1). Using these two ratios in eq 3 leads to EF$_{EM}(632.8 \text{ nm}) = 1.4 \times 10^4$. The results of a similar analysis for the Au(111)/mica sample excited at 632.8 nm and for both the Au(rough)/mica and Au(111)/mica samples excited at 752.0 nm are given in Table 1. The enhancement factors for the other Raman bands shown in Figure 4A,B,D,E are within a factor of 2 of that reported in Table 1.

The value of EF$_{EM}(632.8 \text{ nm})$ was estimated from four intensity measurements: (1) RR intensity of the 1600 cm$^{-1}$ band of bulk solid 1 excited at 632.8 nm; (2) normal Raman (NR) intensity of the 1600 cm$^{-1}$ band of bulk solid 1 excited at 752.0 nm; (3) NR intensity of the standard (viz., diamond crystal 1332 cm$^{-1}$ or bulk liquid pyridine 1592 cm$^{-1}$) excited at 632.8 nm; (4) NR intensity of the standard excited at 752.0 nm. Bulk solid 1 was fabricated as an optically thin sample by dilution with KBr powder to minimize self-absorption effects. From eq 2 applied to these four measurements the following identity can be obtained:

$$EF_{EM}(632.8 \text{ nm}) = \frac{P_{\text{surf}}(\lambda_{ex})^{N_{\text{bulk}}V_{\text{bulk}}}}{P_{\text{bulk}}(\lambda_{ex})^{N_{\text{surf}}R_{\text{surf}}A_{\text{surf}}}}$$

These measurements yield EF$_{EM} = 7.8 \times 10^4$. We take this to be the RR contribution for all SERRS herein (Figure 4A,B). Entries for EF$_{total}(632.8 \text{ nm}) = EF_{EM}(632.8 \text{ nm}) \times EF_{EF}(632.8 \text{ nm})$ are also given in Table 1.

The conclusion of this analysis is that for monolayers of 1 on Au(111)/mica excited at 632.8 nm the EM contribution to the total enhancement factor is 6 x 10$^7$, whereas when excited at 752.0 nm, there is no RR contribution, and the EM enhancement factor is 2.4 x 10$^5$. There are no previous measurements of EM enhancement factors on epitaxial Au thin films for comparison. However, some perspective can be given by noting that typical values for EF$_{EM}$ on Ag island film samples are in the range 1 x 10$^4$ to 5 x 10$^5$. The bands in the SERS/SERRS spectra for 1 on Au(111)/mica and Au(rough)/mica are identical in frequency and relative intensity and do not offer significant structural information about the SAM. This is a consequence of the molecule and the Raman frequency region explored in this study; in the spectral region between 1600 and 1200 cm$^{-1}$, Raman spectra for solid 1 and solution 1 (in cyclohexane) do not differ significantly. Although SAM structure is not the primary focus of this manuscript, the excitation behavior for 1 on Pt at 632.8 and 752.0 nm may provide some structural information about the SAM on Pt, and perhaps through extension on Au(111)/mica and Au(rough)/mica. The Raman signal for 1 on Pt at 632.8 nm is significantly more intense than that observed at 752.0 nm (Figure 4C and 4F) and must be a consequence of resonance enhancement. The 632.8 nm line does not overlap the absorption spectrum of solution 1, and, therefore, shows that the absorption spectrum of 1 on Pt is red shifted. This suggests that the azobenzene moieties in the SAM of 1 on Pt are packed closely enough to interact electronically through $\pi-\pi$ interactions, which is also consistent with surface coverage data for 1 on Pt (as well as Au(111)/mica and Au(rough)/mica). The magnitude of this red shift would be expected to be in between that observed for 1 in solution where $\pi-\pi$ interactions would be inconsequential and 1 in the solid state where $\pi-\pi$ interactions would be most significant (Figure 3). In order for the surface absorption spectrum of the SAM to experience a greater red shift than that of solid 1, one would have to assume an unlikely situation where the $\pi-\pi$ interactions in the SAM were stronger than those in the crystalline solid. Future studies will focus on molecules that exhibit spectral frequency-dependent responses that may be linked to SAM structure. Finally, we point out that the observation of surface resonance Raman spectroscopy for 1 on Pt is significant in its own right since this modality of surface Raman spectroscopy is not surface specific as is SERS/SERRS and will not produce different enhancement factors for molecules adsorbed at morphologically distinct sites.

An important caveat to this work needs to be emphasized. Although the majority SERS signal for 1 on Au(111)/mica could be arising from molecules adsorbed on the large, flat Au(111) terraces, which would be of great importance to those interested in studying monolayer films of such substrates, we cannot rule out the possibility that the overall SERS response represents a superposition of contributions from molecules adsorbed at Au(111) terraces, steps, island edges, cavities, etc. Each of these morphologically distinct sites may possess a different electromagnetic enhancement factor. Nevertheless, we have taken the first step in unraveling these different contributions by defining the nanostructure of these "SERS-active" Au(111)/mica surfaces using AFM. Furthermore, it should be noted that it is quite unlikely that any significant contribution is made to these SERS/SERR spectra from molecules adsorbed at the sites of atomic scale roughness thought to be associated with the "chemical" enhancement mechanism of SERS. These sites, which are viewed structurally as adatoms or adatom clusters upon which the SERS-detected molecule adsorbs, are known to be very labile in SERS studies of electrochemically roughened surfaces or cold evaporated films deposited in UHV. The Au(111)/mica surfaces used here would be highly unlikely to support such adatom clusters due to the high temperatures ($T_s = 240 \degree \text{C}$) at which they are grown. Pemberton has also discounted significant contributions from these sites in her surface Raman studies of SAMs.

Conclusions

This study reports the first direct measurement of SERS/SERRS for a self-assembled monolayer on Au(111)/mica. No additional roughening or "SERS-active" metal overcoating was used in this work. Additionally, we have determined that the EM enhancement factors for Au(111)/mica excited at 632.8 and 752.0 nm are in the (2-6) x 10$^4$ range. While these EF$_{EM}$ values are 10$^2$-10$^4$ times smaller than those of electrochemically roughened (EF$_{EM} \sim 10^6$-10$^7$) "SERS-active" surfaces, they do result in high S/N...
vibrational spectra especially when the adsorbate molecule can confer additional RR enhancement and a CCD detector is used.

No attempt has been made in the present work to determine which spatial regions of the Au(111)/mica surface yield the measured signal. Our intent, rather, in this manuscript is to show that valuable vibrational information concerning the chemical nature of the adsorbate molecules may be extracted from SERS experiments on substrates (Au(111)/mica) that are traditionally used to prepare SAMs.

Finally, it is worth noting that, although we find Au films with comparable morphologies may be prepared in a consistent fashion using one set of conditions with a single thermal evaporator, we also find an enormous fluctuation in surface morphology for substrates prepared using comparable experimental conditions with different thermal evaporators. For anyone interested in preparing SAMs on Au substrates, this observation underscores the necessity of examining the substrate morphology at the nanometer and even atomic levels prior to chemical modification.

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