electrode with Luggin capillary, and an argon in- and outlet port, consisting of a septum with two syringe needles. The working electrode was either a glassy carbon disk of 6-mm diameter, carefully polished before use, or a carbon rod of 7-mm height and 8-mm diameter, employed in the mediated electrolyses. A disk of 6-mm diameter of amalgamated gold was used as a mercury working electrode. It was prepared by galvanostatic electrolysis of an aqueous solution of 0.1 M $Hg(NO_3)_2$ with the gold electrode as cathode and a platinum anode. A current of 10 mA was applied to the cell for 2 min, and the electrode was subsequently washed with dry DMF before use. The cell was immersed in a water bath to keep it at 20 °C.

The electrolyses were carried out with a Wenking potentiostat 68 FR 0.5 from Bank Elektronik. The charge was counted by a calibrated direct current integrator. The working potential was controlled with a Fluke digital multimeter.

Procedures of Electrolyses. All operations were carried out after removal of dioxygen by argon or nitrogen bubbling.

1. Direct electrolyses at glassy carbon or amalgamated gold: the empty cell was heated and degassed with argon for 15 min. Each of the cell compartments was then filled with 7 mL of the degassed 0.1 M solution of Bu_4NBF_4 in DMF, and the background current was determined. After addition of 0.4 mmol of the substrate and 44.6 mg of *n*-decane, used as internal standard, the catholyte was vigorously stirred for 15 min. Before starting the electrolysis a 0.1-mL probe of the catholyte was taken to determine the concentration of the starting compound at the beginning. The electrolyses were stopped when no starting material could be detected by GC analysis.

2. Indirect electrolyses with 1,4-diacetylbenzene as mediator: the procedure was the same as for the direct electrolyses with one exception—before addition of the dibromoalkane and the internal standard 0.4 mmol of the mediator was dissolved in the DMF solution, and the background current of the catalyst was determined.

3. Indirect electrolyses with metalloporphyrin mediators: 0.01 mmol of the mediator was dissolved in 5 mL of the degassed 0.1 M Bu_4NBF_4/DMF solution under argon with vigorous stirring. This solution was transferred into the cathode compartment of the degassed cell. The emptied flask was rinsed two times with 1 mL of the solvent, which were also transferred into the cathode compartment. The anode compartment was filled with 8 mL of the electrolyte solution and a cyclic voltammogram was taken to control the absence of oxygen. Then 0.4 mmol of the substrate and 44.6 mg of *n*-decane were added and after taking the first sample the electrolysis was started. It was stopped when the current had decreased to 1-3%.

Analysis. To remove DMF and the supporting electrolyte the electrolysis probes were filtered through a Pasteur pipette half-filled with flash silica gel (Merck). Five milliliters of *n*-pentane were taken as eluent. The resulting solutions were analyzed by GC by using a quarz capillary column (FS-SE54-CB 0.25 μ, 50-m length). *n*-Decane was employed as internal standard to determine the yield of the olefins and the dibromoalkanes. The different compounds were identified by comparison of their retention times and their MS spectra with those of authentic samples.

Differential Pulse Polarography. Instrumentation. Differential pulse polarography was performed with the Bruker Polarograph E310 in combination with the Metrohm polarographic equipment E354. The recording of the polarograms was done on a Hewlett-Packard XY-writer 7044A in a Metrohm cell (EA876). It was equipped with a platinum foil counter electrode of 1 cm^2, a saturated calomel reference electrode with Luggin capillary, and a nitrogen in- and outlet.

Procedures. Twenty milliliters of a degassed 4×10^{-4} M solution of the dibromoalkane in 0.1 MBu_4NBF_4/DMF were examined under the following conditions: drop time, 1 s; sweep rate, 5 mV/s; differential pulse amplitude, 50 mV; room temperature.

Cyclic Voltammetry. The instrumentation, cell, electrodes, and procedures were the same as previously described.[12a]

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(59) Marple, L. W. *Anal. Chem.* **1967**, *39*, 844.

Surface Raman Scattering of Methanol, 1-Propanol, 1-Pentanol, and 1-Butanethiol on in Situ and Emersed Silver Electrodes

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Abstract: Surface Raman scattering is used to study the adsorption of several straight-chain alcohols (methanol, 1-propanol, 1-pentanol) and a straight-chain alkanethiol (1-butanethiol) at Ag electrodes. Surface-enhanced Raman scattering (SERS) studies are carried out on both in situ and emersed roughened electrodes. Normal surface Raman scattering is performed on mechanically polished, mirrored polycrystalline electrodes that have been emersed from solution. It is generally observed that the Raman scattering results, in terms of the orientation and bonding for the alcohols and the thiol, are similar on rough and mirrored electrodes. This observation suggests that SERS probes the average surface molecules in these cases and not only those existing at chemically distinct surface sites. The utility of emersed electrode approaches for molecular characterization of the electrochemical interface is demonstrated for these systems. The interfacial molecular structure for these in situ organic species appears to be maintained upon emersion.

Introduction

Considerable recent effort has been focused on elucidating the factors that impact the efficiency of electron transfer between a metal electrode and a solution-confined redox species. Toward this end, a detailed description of the molecular characteristics of the interface that develops upon immersion of a metal electrode into an electrolyte solution has been sought. A variety of spectroscopic methods have been applied to the investigation of this problem. Of these, Raman scattering has been demonstrated to be a particularly attractive probe of these systems due to the sensitivity of molecular vibrations to chemical environment.

One Raman spectroscopic approach for the investigation of these interfaces that has received intensive study is surface-enhanced Raman scattering (SERS). As a result of the ca. 10^4 to

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10^6 enhancement realized for molecules in the vicinity of appropriately prepared electrodes, SERS has interfacial sensitivity unparalleled by other in situ vibrational spectroscopic probes. Moreover, the nature of the enhancement confers a selectivity to the interfacial region in these systems that is not easily achieved with other approaches.

Despite the enormous advantages of sensitivity and selectivity associated with SERS, a number of significant limitations to this approach do exist. Foremost among these is the fact that intense SERS signals can only be observed on a discrete set of metal surfaces that have been appropriately roughened. In electrochemical systems, this roughening is usually carried out through a procedure known as an oxidation–reduction cycle (ORC), which consists of anodization of the electrode surface with a subsequent reduction. Although the exact distribution of surface roughness generated by these procedures is not quantitatively known, it is generally agreed that both microscopic (significantly larger than molecular dimensions) and submicroscopic (on the order of molecular dimensions) roughness features are produced during the ORC procedure. On Ag surfaces, the submicroscopic features are known to be relatively labile and have been proposed to exist as tetramers of Ag atoms possessing a single positive charge.[1] Such sites would most likely be chemically distinct from others on the surface from the standpoint of adsorbate interactions. The potential existence of chemically unique SERS-active surface sites has stimulated much debate over the generality of the vibrational information obtained in these studies. To date, this issue has not been adequately addressed experimentally. Several studies have been reported in which the SERS results for simple anions adsorbed at roughened electrodes were compared with the corresponding in situ IR behavior on mirrored electrodes.[2-5] The similarity of the Raman scattering and IR absorption for the anions was interpreted to indicate that SERS provides information on the average surface species. The generality of this conclusion and its extension to more complex molecules has not yet been evaluated.

In order to circumvent the problems associated with the requisite surface roughness for SERS, several other Raman spectroscopic approaches for the investigation of the interfacial region in electrochemical systems can be envisioned. First, normal (unenhanced) Raman spectroscopy of surface adsorbates on smooth electrodes could be performed in situ. These experiments are extraordinarily difficult due to both poor sensitivity and poor interfacial selectivity. To date, only one such study has been reported in the literature,[6] although further work in this area is in progress.[7]

An alternate approach for the investigation of interfacial structure on smooth electrodes is the use of emersed electrodes, those that have been exposed to an electrochemical environment and removed carefully from the electrolyte solution. Previous work has suggested that the electrochemical double layer can be removed intact from solution.[8-12] With the notable exception of recent HREELS studies on strongly adsorbed organic molecules performed by Hubbard and co-workers,[13-15] most previous work has focused on the ionic structure of the emersed interface and not on the molecular structure of the interfacial solvent.

The presence of interfacial solvent molecules on emersed electrode surfaces has been somewhat controversial. It is generally agreed that water does not remain on the electrode surface after emersion and subsequent introduction into an ultrahigh vacuum environment.[10,11] However, the behavior of interfacial solvent molecules upon emersion into environments at higher pressures is uncertain. Furthermore, in the event that the interfacial solvent molecules do remain attached to the electrode after emersion, virtually nothing is known about their molecular orientation and how it compares to that existing in situ.

Thus, the goals of the work reported here were 2-fold. First, it was of interest to establish the relationship between the SERS behavior of interfacial molecules on roughened electrode surfaces and their corresponding surface Raman scattering behavior on mirrored electrode surfaces. Second, we sought to investigate the utility of emersed electrode techniques for the molecular characterization of electrochemical interfaces by comparing interfacial structure of in situ and emersed interfaces. Toward this end, we have investigated the surface Raman scattering behavior of a series of alcohols and one alkanethiol adsorbed at electrochemically roughened and mechanically polished, mirrored polycrystalline electrode surfaces both in situ and emersed from solution. These results have important implications regarding the general utility of SERS for such systems and the validity of emersed electrode models of in situ interfaces.

Experimental Section

Spectroscopic Conditions and Instrumentation. Excitation was provided by the 488.0- and 514.5-nm lines of a Coherent Radiation Innova 90-5 Ar^+ laser or the 600-nm line from a Coherent Radiation 599 tunable dye laser containing Rhodamine 6G dye. For the alkanethiol work, the laser power incident on the samples was between 100 and 250 mW except where noted. The spectra from alcohols were obtained with an incident laser power of 200 mW. In all experiments, the laser was focused to a 50 μm diameter spot. Spectra were obtained with incident light polarized parallel with respect to the plane of incidence. Liquid spectra were collected in the same optical configuration. Bulk liquid spectra of the alcohols were acquired by sampling a drop of the liquid clinging to the electrode. A spectrum of the bulk 1-butanethiol was acquired with the liquid in a sealed capillary.

Scattered radiation was collected with a 50 mm diameter $f/2.0$ (Pentax) or $f/1.4$ camera lens (Nikon) and focused onto the entrance slits of a Spex 1877 Triplemate. Approximately 20% of the circular image at the entrance slit passed into the spectrometer. The grating in the filter stage was 600 gr/mm, and the gratings used at the spectrograph stage were 1200 gr/mm. Slit widths were 0.5 mm/4 mm/0.5 mm for the alcohols and 0.25 mm/2.6 mm/0.25 mm for the alkanethiols except where noted. Detection was accomplished with a liquid N_2 cooled Photometrics PM512, frontside illuminated charge coupled device (CCD). Integration times for the acquisition of each spectrum are noted in the figure captions. Spectra were acquired with CCD temperatures between −95 and −124 °C.

Electrochemical Conditions and Instrumentation. The working electrode consisted of polycrystalline Ag or Au disks (99.9% Johnson Matthey) that were mechanically polished to a mirror finish with 0.3-μm alumina (alcohol studies) or 0.05-μm alumina (alkanethiol studies), rinsed with triply distilled, deionized water (TDI), and then sonicated for 2 min in TDI to remove any trapped alumina. A Pt wire served as the auxiliary electrode. Electrode potentials are reported versus SCE or Ag/AgCl reference electrodes as indicated.

Electrode potentials were controlled with an IBM Model EC/225 voltammetric analyzer. Linear potential ramps were performed with use of a simple triangle wave format. Total charge passed was monitored with an EG&G Princeton Applied Research Model 379 digital coulometer.

Materials. Methanol was purchased as high purity solvent grade from Burdick and Jackson and contained 0.011% water. 1-Propanol was also purchased from Burdick and Jackson as a high purity solvent with 0.012% water. 1-Pentanol was purchased from Fisher Scientific

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(1) Roy, D.; Furtak, T. E. *Phys. Rev. B* **1986**, *34*, 5111.

(2) Corrigan, D. S.; Foley, J. K.; Gao, P.; Pons, S.; Weaver, M. J. *Langmuir* **1985**, *1*, 616.

(3) Corrigan, D. S.; Gao, P.; Leung, L.-W.; Weaver, M. J. *Langmuir* **1986**, *2*, 744.

(4) Kunimatsu, K.; Seki, H.; Golden, W. G. *Chem. Phys. Lett.* **1984**, *108*, 195.

(5) Kunimatsu, K.; Seki, H.; Golden, W. G.; Gordon, J. G.; Philpott, M. R. *Surface Sci.* **1985**, *158*, 596.

(6) Shannon, C.; Campion, A. *J. Phys. Chem.* **1988**, *92*, 1385.

(7) Seki, H. Private communication.

(8) Hansen, W. N. *J. Electrochemical Chem.* **1983**, *150*, 133.

(9) Hansen, G. J.; Hansen, W. N. *J. Electroanal. Chem.* **1983**, *150*, 193.

(10) Neff, H.; Kotz, R. *J. Electroanal. Chem.* **1983**, *151*, 305.

(11) Hubbard, A. T. *Acc. Chem. Res.* **1980**, *13*, 177.

(12) Wagner, F. T.; Ross, P. N. *J. Electroanal. Chem.* **1983**, *150*, 141.

(13) Stern, D. A.; Weller, E.; Salaita, G. N.; Laguren-Davidson, L.; Lu, F.; Batina, N.; Frank, D. G.; Zapien, D. C.; Walton, N.; Hubbard, A. T. *J. Am. Chem. Soc.* **1988**, *110*, 4885.

(14) Batina, N.; Gui, J. Y.; Kahn, B. E.; Lin, C.-H.; Lu, F.; McCargar, J. W.; Salaita, G. N.; Stern, D. A.; Hubbard, A. T.; Mark, H. B.; Zimmer, H. *Langmuir* **1989**, *5*, 588.

(15) Salaita, G. N.; Hubbard, A. T. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; John Wiley and Sons: New York, 1989.

(A394-500) and used as received. LiBr (Aldrich, anhydrous, 99%) was dried at 160 °C under vacuum (0.17 Torr) for 24 h. 1-Butanethiol (99+%) was purchased from Aldrich. Ethanol (absolute) was purchased from Midwest Grain Products. KCl was purchased from Fisher Scientific. All were used as received.

Electrochemical Roughening and Emersion Procedures. Spectra from alcohols at rough Ag electrodes were obtained after an ex situ roughening procedure to avoid surface trapping of the nonaqueous solvent molecules during the ORC. The electrodes for alcohol studies were first subjected to an ORC with use of a linear potential sweep at 5 mV/s in a 0.4 M LiBr aqueous solution. The sweep was typically from −0.40 V versus SCE to +0.05 V and back to −0.40 V. Total anodic charge passed was typically 40 mC/cm^2.

Emersion from the aqueous 0.4 M LiBr solution was carried out at open circuit potential (ca. +0.20 V versus SCE), and the applied potential was then turned off. The emersed interface was rinsed with the alcohol solvent of study and placed into an air-tight cell which was filled with a solution of 0.4 M LiBr in neat alcohol. The electrode was then placed close to the window such that a small portion of it actually touched the quartz window. The surface was sampled at other portions of the electrode surface. This configuration allowed elimination of bulk solvent contributions to the spectra.

Emersion of rough and smooth electrodes from the alcohol/electrolyte/Ag interface was accomplished by opening a port at the bottom of the cell so the solution could slowly drain out. The electrode was then moved a few microns away from the quartz window such that the bulk could be completely drained away. The emersed interface was always sampled within the air-tight spectroelectrochemical cell. This was particularly crucial for methanol and 1-propanol as they have a significant vapor pressure and quickly become desorbed in the ambient atmosphere.

Spectra from 1-butanethiol at roughened Ag electrodes were obtained by electrochemically roughening the surface before immersion in an ethanol/butanethiol solution. Linear potential sweep ORCs were applied to Ag electrodes in the presence of 0.1 M KCl aqueous solution. The initial potential was −0.20 V versus Ag/AgCl and the potental sweep was reversed at ca. +0.20 V at a scan rate of 10 mV/s, resulting in ca. 30 mC/cm^2 of anodic charge passed. The electrodes were then removed from solution at open circuit potential, rinsed with 100% ethanol, and then modified with the 1-butanethiol solution. Smooth Ag and Au electrodes were prepared by mechanical polishing followed by rinsing with 100% ethanol.

Smooth and roughened electrodes were immersed in 1–10 mM 1-butanethiol solutions in 100% ethanol and removed after a minimum of 2 h. Electrodes were then rinsed again with 100% ethanol and allowed to air dry. It was not necessary to put the electrodes in a closed compartment, because the Raman signal was stable over many hours.

Results and Discussion

SERS is a particularly powerful probe of interfacial solvent structure in organic media. Recent examples of SERS studies in such environments include the study of acetonitrile,[16] propylene carbonate,[17] and pyridine[18] at Ag electrodes. The SERS behavior of pyridine and benzene has also been studied in methanol and ethanol solvents.[19] The vibrational complexity of such molecules makes them ideal probes with which to address the issues of interest in these studies. Thus, methanol, 1-propanol, 1-pentanol, and 1-butanethiol were chosen as probe molecules to investigate the generality of the SERS response and the utility of the emersed electrode approach. These molecules possess a range of volatilities and adsorption strengths at Ag, thereby allowing important limitations of the emersed electrode approach to be evaluated.

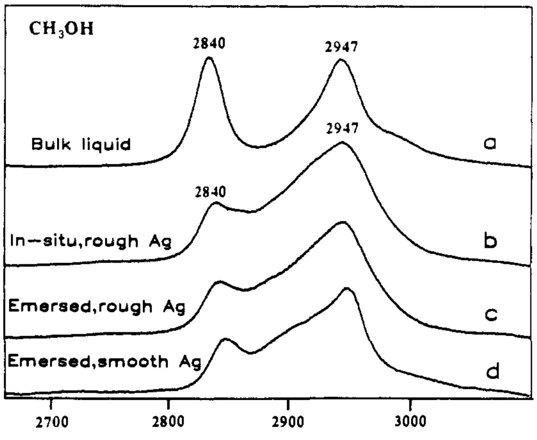

Figure 1. Raman spectra in the ν(C–H) region of (a) bulk liquid methanol, (b) methanol adsorbed to an in situ rough Ag electrode, (c) methanol adsorbed to an emersed rough Ag electrode, and (d) methanol adsorbed to an emersed smooth Ag electrode. Integration times were (a) 50 s, (b) 10 s, (c) 10 s, and (d) 30 min.

These molecules are studied at electrochemically roughened and mechanically polished, mirrored metal surfaces. Despite the fact that these latter surfaces are designated as "smooth" in Figures 1 through 9, it must be recognized that they are clearly not as smooth as a single-crystal surface. Mechanical polishing with alumina produces a gently corrugated surface whose roughness is confined to a size dictated by the size of the alumina particles. As will be discussed in detail below, these surfaces are actually very weakly enhancing through electromagnetic enhancement on the corrugated surface. It is highly unlikely that a significant number of chemically distinct "active sites" of the type produced by electrochemical roughening exist on these surfaces. Even if a small number were generated during the mechanical polishing procedure, it is implausible that they would be stable during the subsequent sonication and transfer steps. A more detailed description of the quantitative estimate of enhancement realized at these mirrored surfaces is provided below.

Alcohols. The SERS behavior of short-chain alcoholic solvents is relatively uninvestigated, despite their water-like solvent properties and importance as organic fuels. Recent SERS investigations of methanol at Ag electrodes in this laboratory[20] have shown that interfacial methanol molecules are oriented with the C–O bond at a vary large angle (estimated to be ≥60°[21]) with respect to the surface normal. A shift in C–O stretching frequency by ca. 10 cm^{-1} to lower energies upon adsorption is observed, which suggests that methanol interacts with the Ag surface through the oxygen end of the molecule. Finally, the large changes in relative ν(C–H) intensities as a function of electrode potential that were noted suggest that these bands are highly sensitive to changes in solvent orientation. Consequently, the C–H stretching region was the primary focus in the work on the three alcohols reported here.

The two major issues addressed in these studies were the effect of surface roughness on orientation and bonding of the straight-chain alcohols (methanol, 1-propanol, 1-pentanol) at Ag electrodes and the effect of the emersion process on interfacial orientation and bonding of these alcohols at Ag.

Methanol at Ag. Among the straight-chain alcohols discussed here, methanol is somewhat unusual in terms of the strength of the Ag–O interaction. This interaction is detected as a shift of the ν(C–O) vibration by 10 cm^{-1} to lower energy upon adsorption. Alcohols longer than ethanol exhibit no shift in ν(C–O) frequency upon adsorption at Ag electrodes at open circuit potentials.[21] This observation correlates with both the decreasing dielectric constant and the decreasing acidity with increasing chain length of these alcohols. Consequently, only methanol was investigated in both ν(C–O) and ν(C–H) frequency regions.

C–H Stretching Region. The SERS spectrum of methanol in this frequency region acquired at open circuit potential after a double potential step ORC roughening procedure in 0.4 M LiBr is shown in Figure 1b along with the bulk liquid spectrum for this region as Figure 1a. Note the change in relative symmetric and asymmetric C–H intensities upon adsorption as discussed above. In addition, considerable intensity is observed at ca. 2900 cm^{-1} which is proposed to be due to a methyl vibration in Fermi resonance with the overtone of the C–H bending vibration at ca. 1456

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(16) Irish, D. E.; Hill, I. R.; Archambault, P.; Atkinson, G. F. *J. Solution Chem.* **1985**, *14*, 221.

(17) Hill, I. R.; Irish, D. E.; Atkinson, G. F. *Langmuir* **1986**, *2*, 752.

(18) Pemberton, J. E. *Chem. Phys. Lett.* **1985**, *115*, 321.

(19) Kim, J. J.; Shin, G. S. *Chem. Phys. Lett.* **1985**, *118*, 493.

(20) Sobocinski, R. L.; Pemberton, J. E. *Langmuir* **1990**, *6*, 43.

(21) Sobocinski, R. L.; Pemberton, J. E. *J. Electroanal. Chem.* To be submitted.

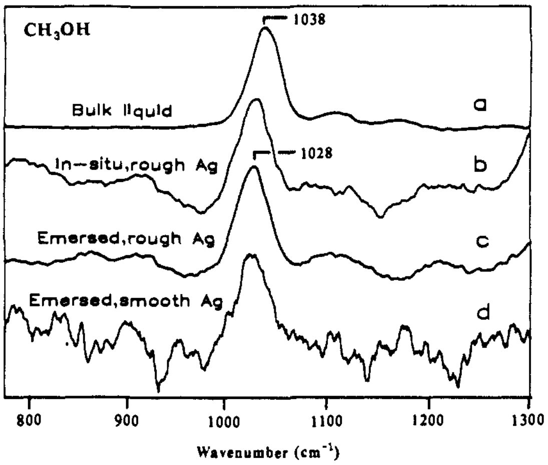

Figure 2. Raman spectra in the ν(C–O) region of (a) bulk liquid methanol, (b) methanol adsorbed to an in situ rough Ag electrode, (c) methanol adsorbed to an emersed rough Ag electrode, and (d) methanol adsorbed to an emersed smooth Ag electrode. Integration times were (a) 10 min, (b) 40 min, (c) 30 min, and (d) 30 min. Spectra were smoothed once with a 9-point Savitsky-Golay smoothing algorithm.

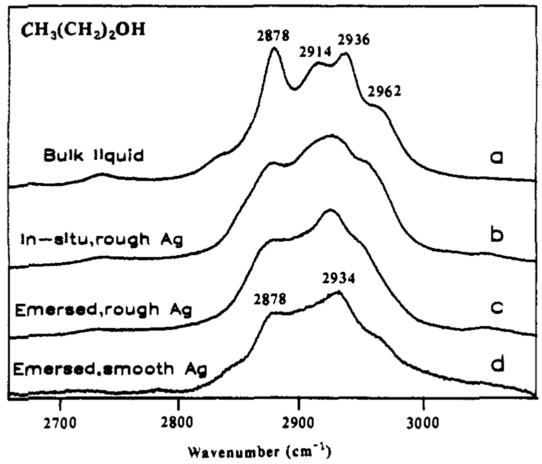

Figure 3. Raman spectra in the ν(C–H) region of (a) bulk liquid 1-propanol, (b) 1-propanol adsorbed to an in situ rough Ag electrode, (c) 1-propanol adsorbed to an emersed rough Ag electrode, and (d) 1-propanol adsorbed to an emersed smooth Ag electrode. Integration times were (a) 40 s, (b) 20 s, (c) 30 s, and (d) 20 min.

cm^{-1}.[22] The band at ca. 2900 cm^{-1} must derive its intensity from the fact that the C–H bending vibration with which it is in Fermi resonance possesses a significant component perpendicular to the surface.

The effect of emersion of the rough Ag surface into air at open circuit potential on the spectral response of surface methanol is shown by a comparison of spectra b and c in Figure 1. The similarity of the asymmetric ν(C–H) to symmetric ν(C–H) intensity ratio of these two spectra suggests that the methanol orientation is preserved during the emersion process. However, one subtle difference is observed between the spectra that may be significant. The asymmetric ν(C–H) band observed from the in situ interface is broader than that from the emersed interface. The broadness of this band results from a peak that grows in at ca. 2919 cm^{-1} which does not have a counterpart in the bulk methanol spectrum. This behavior may be the result of a unique chemical environment created in situ by the presence of other methanol molecules in the interface which is absent for the emersed surface.

The effect of surface roughness on the spectral response and orientation of methanol can be assessed from spectra c and d in Figure 1. The spectra from the emersed roughened electrode and the emersed smooth electrode are quite similar, and both are considerably different than that of the bulk liquid. This observation suggests that the methanol molecules probed in the SERS experiment at roughened surfaces are in similar chemical environments and orientations as those detected with Raman scattering at the mirrored surfaces. Subtle differences are observed between roughened and smooth emersed electrode behavior, however. The spectra from smooth electrodes exhibit a better resolved asymmetric ν(C–H) vibration than those from the roughened electrodes. Since these spectra were acquired under conditions of similar spectral bandpass, this observation may suggest that a narrower distribution of methanol environments exists at the smooth Ag electrode.

C–O Stretching Region. Comparison of the in situ and emersed roughened electrode spectra b and c in Figure 2 shows that the extent of Ag–O interaction is retained following the emersion process based on the same frequency decrease of the ν(C–O) vibration. Similar results are obtained for the emersed mirrored Ag electrodes as shown by spectrum d in Figure 2. In total, the results indicate that methanol bonding and orientation at smooth Ag electrodes mimics the methanol bonding and orientation at rough Ag electrodes and that the in situ bonding is preserved after emersion.

1-Propanol at Ag. Unlike methanol, 1-propanol does not appear to have a Ag–O interaction strong enough to perturb the C–O stretching frequency. This vibration from surface-confined 1-propanol is observed at 1060 cm^{-1}, relatively unshifted from the solution band. Preliminary results from this laboratory suggest that 1-propanol is oriented on Ag with the C–O and C–C bond axes at a large angle with respect to the surface normal.[21] This conclusion is based on the relative ν(C–C), ν(C–O), and ν(C–H) intensities of surface-confined species as compared to those observed in the bulk. A more detailed discussion of the surface orientation of these molecules is forthcoming.[21]

C–H Stretching Region. Following the ORC roughening procedure in 0.4 M LiBr, SERS spectra of interfacial 1-propanol can be readily observed at open circuit potential as shown for both in situ and emersed Ag/0.4 M LiBr/1-propanol interfaces in Figure 3. The important vibrational features observed in this region are the symmetric and asymmetric methyl ν(C–H) vibrations at 2878 and 2962 cm^{-1}, respectively, the asymmetric methylene ν(C–H) vibration at 2900 cm^{-1}, and the ν(C–H) Fermi resonance bands (coupling with the overtone of the C–H bending vibration at 1467 cm^{-1}) at 2914 and 2936 cm^{-1}.[22] This latter band is the most intense in the surface spectrum due to the fact that it results from Fermi resonance with a vibrational mode that has a large component perpendicular to the surface.

Upon adsorption, the intensity of the symmetric ν(C–H) from the methyl group (2878 cm^{-1}) decreases relative to the asymmetric methyl ν(C–H) (2962 cm^{-1}). This further supports a preferred orientation in which the symmetric methyl dipole of the molecule is at a large angle with respect to the surface normal, hence experiencing a smaller electric field. Such an orientation would be realized if the C–C chain axis were at a large angle with respect to the surface normal as stated above.

The effect of emersion into air at open circuit potential can be determined by a comparison of in situ and emersed spectra in the C–H stretching region in spectra b and c in Figure 3. Like methanol, the relative C–H intensities from interfacial 1-propanol remain similar after emersion. Consequently, one concludes that the molecular orientation of 1-propanol is generally preserved during the emersion process.

Figure 3 shows that similar subtleties observed for the methanol/Ag system are also observed in the spectra from the 1-propanol/Ag interface. For example, the in situ interface produces an asymmetric ν(C–H) band which is broader than that of the emersed interface. These data support the idea that bulk 1-propanol species can influence the distribution of interfacial molecules with a given orientation. Furthermore, the methylene vibration at 2914 cm^{-1} decreases in intensity upon emersion indicating some minor rearrangement of the molecule on the surface. A twist of the C–C chain axis possibly accompanied by compaction

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[22] Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145.

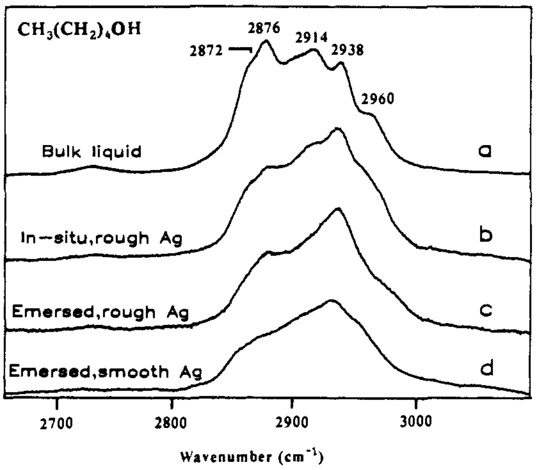

Figure 4. Raman spectra in the ν(C–H) region of (a) bulk liquid 1-pentanol, (b) 1-pentanol adsorbed to an in situ rough Ag electrode, (c) 1-pentanol adsorbed to an emersed rough Ag electrode, and (d) 1-pentanol adsorbed to an emersed smooth Ag electrode. Integration times were (a) 20 s, (b) 3 min, (c) 6 min, and (d) 30 min.

of the layer upon emersion may account for such an intensity decrease. Such an effect may also explain the small decrease in intensity observed for the asymmetric methyl ν(C–H) vibration at 2962 cm^{-1}.

The effect of roughness on the orientation of 1-propanol at Ag is shown in spectra c and d in Figure 3. A comparison of spectra from the roughened and smooth Ag electrodes suggests that the 1-propanol orientation at roughened Ag electrodes generally mimics the orientation at smooth Ag electrodes. However, subtle differences in ν(C–H) bandwidths are observed for 1-propanol between rough and smooth surfaces.

1-Pentanol at Ag. 1-Pentanol appears to interact with Ag electrodes in a fashion similar to that of 1-propanol. First, interfacial 1-pentanol exhibits no detectable Ag–O interaction as evidenced from a C–O vibration at 1058 cm^{-1}, unshifted from the bulk solution vibration. Preliminary results in this laboratory also show that 1-pentanol is oriented in a manner similar to that of 1-propanol in which the C–O and C–C bond axes are at large angles with respect to the surface normal.[21]

C–H Stretching Region. Following the ORC procedure described earlier, SERS spectra of interfacial 1-pentanol can be readily observed at open circuit potential. Spectra from both in situ and emersed Ag/0.4 M LiBr/1-pentanol interfaces are shown in Figure 4. The vibrational bands observed are the symmetric and asymmetric methyl ν(C–H) vibrations at 2876 and 2960 cm^{-1}, respectively, the symmetric and asymmetric methylene ν(C–H) vibrations at 2872 and 2900 cm^{-1}, respectively, and the Fermi resonance bands at 2914 and 2938 cm^{-1}.

Upon adsorption of 1-pentanol, similar changes in the spectral response to those discussed for 1-propanol are observed. Thus, the intensity of the symmetric methyl ν(C–H) vibration (2876 cm^{-1}) decreases relative to the asymmetric methyl ν(C–H) vibration (2960 cm^{-1}) supporting the proposal that 1-pentanol is adsorbed with the symmetric methyl dipole at large angles with respect to the surface normal.

The effect of emersion into air at open circuit potential is shown by comparison of in situ and emersed spectra in the ν(C–H) region in spectra b and c in Figure 4. Like 1-propanol, the relative C–H intensities from interfacial 1-pentanol remain generally the same after emersion. One can therefore conclude that the orientation of 1-pentanol is generally preserved during emersion, similar to the behavior observed for methanol and 1-propanol.

A few minor differences in the results from the in situ and emersed Ag/1-pentanol interface are noted which require discussion. The in situ spectrum in the ν(C–H) region has a prominent peak at 2914 cm^{-1} not observed (or not observable) in the emersed spectra. In addition, the asymmetric methyl ν(C–H) vibration at 2960 cm^{-1} decreases in intensity after emersion. These effects can be explained by a slight reorientation of the surface pentanol molecules, possibly a twist of the C–C chain axis, during emersion analogous to that proposed for propanol.

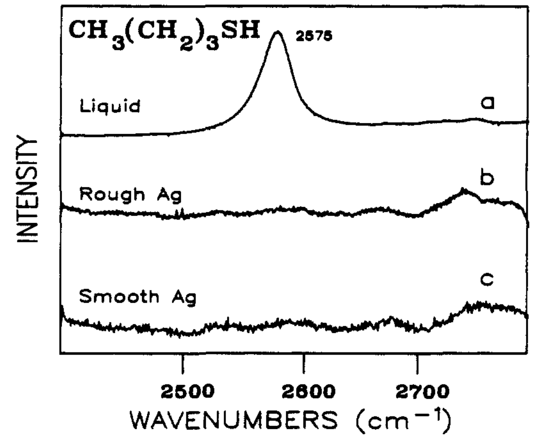

Figure 5. Raman spectra in the ν(S–H) region of (a) liquid 1-butanethiol, (b) 1-butanethiol adsorbed to a rough Ag electrode, and (c) 1-butanethiol adsorbed to a smooth Ag electrode. Integration times were (a) 1 min, (b) 1 min, and (c) 5 min.

The effect of roughness on 1-pentanol orientation is demonstrated by spectra c and d in Figure 4. A comparison of spectra from the emersed smooth and roughened electrodes suggests that 1-pentanol is oriented similarly at these different surfaces.

1-Butanethiol at Ag. Alkanethiols are also suitable molecular probes for studying roughened and smooth surfaces and provide an interesting comparison to the oxygen-analogue alcohol molecules. Several reports for alkanethiols at Au surfaces have shown that these molecules spontaneously self-assemble to form highly ordered monolayers.[23-25] Alkanethiols have been proposed to attach to Au by cleavage of the S–H bond and formation of a Au–S bond. The alkyl chains then organize to form a self-assembled monolayer with a high degree of order. The alkyl chains have been demonstrated to be oriented with a tilt of ca. 30° with respect to the surface normal.[24,25]

These alkanethiols are sensitive probes for comparing the effect of surface roughness on the bonding and ordering of an adsorbed monolayer at an electrode surface. Changes in the sulfur head group, carbon backbone conformations, and orientation of methylene and methyl groups can be determined by observing the appropriate molecular vibrations.

A few SERS studies have been reported for alkanethiols at roughened Ag surfaces. Joo and co-workers conclude that propanethiol adsorbs to Ag in the same manner as described above for Au surfaces.[26] Sandroff and co-workers conclude that hexadecanethiol forms an ordered monolayer at roughened Ag.[27] The study reported here will compare the surface Raman spectra of butanethiol at mirrored, mechanically polished surfaces to that obtained at electrochemically roughened surfaces.

By employing surface selection rules for Raman scattering,[28,29] it is concluded that butanethiol is oriented with a significant vibrational component perpendicular to the Ag surface. Relative to the intensity of the ν(C–H) vibrations, the intensities of the ν(C–S) and ν(C–C) vibrations are stronger in the surface spectra than in the liquid spectrum. Since the C–H bonds are almost orthogonal to the C–S and C–C bonds, it is concluded that the carbon backbone of the alkane chain has a significant component perpendicular to the Ag surface.

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(23) Bain, C. D.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1989**, *5*, 723.

(24) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(25) Ulman, A.; Eilers, J. E.; Tillman, N. *Langmuir* **1989**, *5*, 1147.

(26) Joo, T. H.; Kim, K.; Kim, M. S. *J. Phys. Chem.* **1989**, *90*, 5816.

(27) Sandroff, C. J.; Garoff, S.; Leung, K. P. *Chem. Phys. Lett.* **1983**, *96*, 547.

(28) Creighton, J. A. In *Spectroscopy of Surfaces*; Clark, R. J., Hester, R. E., Eds.; John Wiley and Sons: New York, 1988; Chapter 2.

(29) Moskovits, M. *J. Chem. Phys.* **1982**, *77*, 4408.

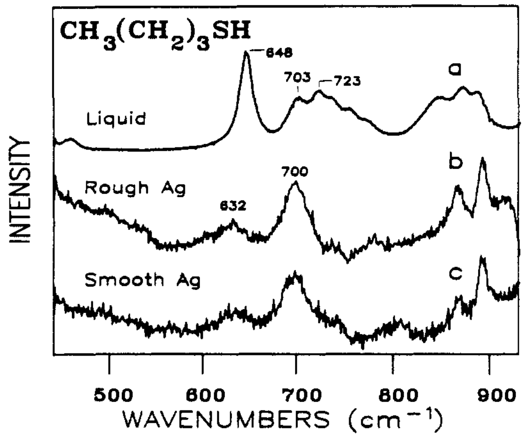

Figure 6. Raman spectra in the ν(C–S) region of (a) liquid 1-butanethiol, (b) 1-butanethiol adsorbed to a rough Ag electrode, and (c) 1-butanethiol adsorbed to a smooth Ag electrode. Integrations times were (a) 1 min, (b) 3 min, and (c) 5 min.

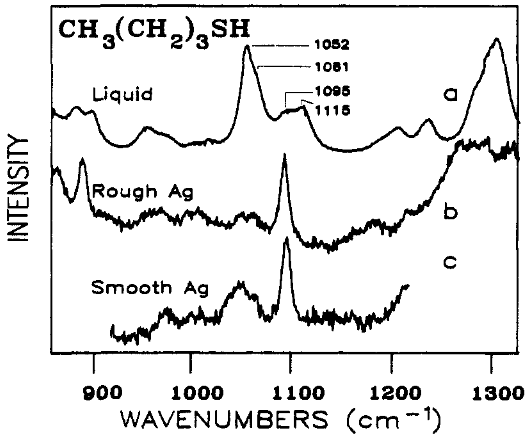

Figure 7. Raman spectra in the ν(C–C) region of (a) liquid 1-butanethiol, (b) 1-butanethiol adsorbed to a rough Ag electrode, and (c) 1-butanethiol adsorbed to a smooth Ag electrode. Integrations times were (a) 1 min, (b) 3 min, and (c) 5 min (slit width: 0.25 mm/2.0 mm/0.25 mm).

S–H Stretching Region. Cleavage of the S–H bond is confirmed by the disappearance of the ν(S–H) vibration at 2575 cm^{-1} in the 1-butanethiol liquid upon adsorption to Ag as shown in Figure 5. In addition, as shown in Figure 6, the ν(C–S) vibrations are shifted lower in frequency, indicating interaction of the Ag with the sulfur atom. The ν(C–C) and ν(C–H) vibrations in Figures 7 and 8 are not shifted in frequency but are only changed in relative intensity. The results of this study and those of the previous SERS studies for alkanethiols suggest that the alkanethiol forms a covalent Ag–S bond, consistent with the behavior of these molecules at Au surfaces.

C–S Stretching Region. Information pertaining to the conformation of the carbon backbone next to the sulfur head group is contained in the ν(C–S) vibration. This stretch is sensitive to the conformation, gauche or trans, of the two adjacent carbon atoms. Two C–S stretches are observed in neat alkanethiols in the region from 600 to 750 cm^{-1} as shown in Figure 6. For neat 1-butanethiol, the stretch assigned to a gauche conformation occurs at 648 cm^{-1}, and the stretch assigned to a trans conformation is at 723 cm^{-1}. These assignments follow those of Joo and coworkers.[26] The peak at 703 cm^{-1} is assigned to a CH$_2$ rocking vibration. The intensity of the gauche ν(C–S) vibration is greater than that of the trans conformation stretch in the neat liquid. Upon adsorption at rough Ag, both stretches for the gauche and trans conformations shift lower in frequency to 632 and 700 cm^{-1}, respectively, as shown in spectra b and c in Figure 6. The intensity for the trans conformation becomes greater than that for the gauche conformation. Thus, the trans conformation appears to be the preferred one for an ordered monolayer of 1-butanethiol, as was previously reported for propanethiol and hexadecanethiol at roughened Ag.[26,27]

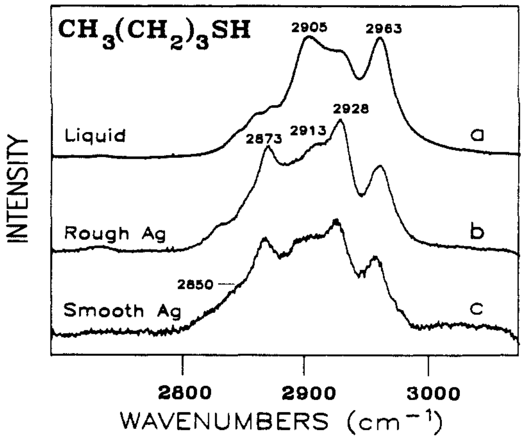

Figure 8. Raman spectra in the ν(C–H) region of (a) liquid 1-butanethiol, (b) 1-butanethiol adsorbed to a rough Ag electrode, and (c) 1-butanethiol adsorbed to a smooth Ag electrode. Integrations times were (a) 1 min, (b) 1 min, and (c) 5 min.

The surface spectrum for butanethiol at smooth Ag in Figure 6c shows similar relative intensities for the gauche and trans ν(C–S) vibrations as observed at roughened Ag. It is concluded that the bonding of the butanethiol to Ag is the same for smooth and rough surfaces. This bonding results in similar conformation and ordering of the butanethiol monolayer in the region of the molecule adjacent to the Ag for both rough and smooth surfaces.

C–C Stretching Region. This frequency region shows the increased ordering along the alkane chain of the molecule of adsorbed 1-butanethiol relative to the liquid 1-butanethiol. Four ν(C–C) vibrations are observed in the region between 1000 and 1200 cm^{-1} that correspond to trans and gauche conformations.[30] The spectra for liquid and adsorbed butanethiol in the ν(C–C) frequency region are shown in Figure 7. In neat 1-butanethiol, the trans stretch at 1052 cm^{-1} dominates the gauche stretch at 1061 cm^{-1}. Two trans vibrations of weaker intensity appear at 1095 and 1115 cm^{-1}. Upon adsorption to rough Ag, the trans ν(C–C) vibration at 1095 cm^{-1} becomes the most intense band. In addition, the gauche ν(C–C) band at 1061 cm^{-1} and the trans ν(C–C) band at 1052 cm^{-1} decrease considerably in intensity. One can conclude from these data that the alkyl chains in the adsorbed monolayer are ordered differently than those of the neat liquid. The predominance of one type of trans band suggests that a significant number of C–C bonds are in a similar environment. One can conclude from this observation that the 1-butanethiol molecules in the monolayer are more ordered than those in the neat liquid in which multiple trans and gauche environments are noted.

The spectrum from the smooth surface shows changes in relative intensities of the ν(C–C) vibrations. Compared to the intensity of the gauche ν(C–C) vibration at 1061 cm^{-1}, the intensity of the major trans ν(C–C) band at 1095 cm^{-1} is similar while the intensity of the trans ν(C–C) band at 1052 cm^{-1} is stronger. This change in relative peak intensities may be attributable to a different extent of ordering of the trans conformation C–C bonds along the backbone at smooth versus rough Ag surfaces.

C–H Stretching Region. The region from 2750 to 3050 cm^{-1} contains information about ν(C–H) vibrations from methylene groups along the carbon backbone and the methyl group at the end of the alkane chain. The spectra for this region, shown in Figure 8 for liquid and adsorbed 1-butanethiol, are complex because of the overlap of at least six vibrations. However, the important features are clearly seen in the spectra. These bands have been previously assigned by Snyder and co-workers.[22] The asymmetric ν(CH$_2$) vibration at 2905 cm^{-1} and the asymmetric ν(CH$_3$) vibration at 2963 cm^{-1} are prominent, because the sym-

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(30) Gaber, B. P.; Yager, P.; Peticolas, W. L. *Biophys. J.* **1978**, *21*, 161.

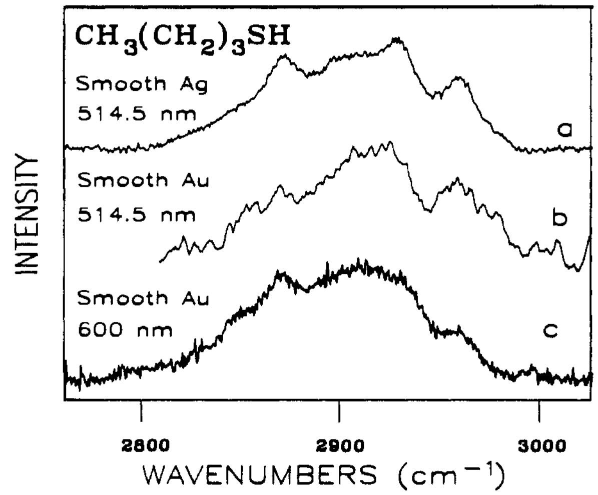

Figure 9. Raman spectra in the ν(C–H) region of (a) 1-butanethiol adsorbed to a smooth Ag electrode with 514.5-nm excitation, (b) 1-butanethiol adsorbed to a smooth Au electrode with 514.5-nm excitation (spectrum smoothed once with a 9-point Savitsky–Golay smoothing algorithm), and (c) 1-butanethiol adsorbed to a smooth Au electrode with 600-nm excitation. Integration times were (a) 5 min, (b) 10 min (1 W power; slit width 0.5 mm/2.6 mm/0.5 mm), and (c) 15 min.

metric, polarized bands of the bulk liquid are greatly decreased in intensity with the incident polarization used in this study.[31] The spectrum of butanethiol at roughened Ag is dramatically different than that of the bulk liquid. The symmetric methyl ν(C–H) vibration at 2873 cm^{-1} and the Fermi resonance symmetric methylene ν(C–H) vibration at 2928 cm^{-1} are the two most intense peaks. These vibrations are intense, because for the 1-butanethiol adsorbed at a tilt with respect to the surface normal, they possess a significant component of their vibrational motion perpendicular to the surface. Another Fermi resonance symmetric methylene vibration can be seen at 2913 cm^{-1}.

The spectrum of 1-butanethiol at smooth Ag is similar to that observed at the rough surface except for the slight increase in the symmetric methylene ν(C–H) intensity at 2850 cm^{-1} and the decrease in intensity of the 2928 cm^{-1} ν(C–H) vibration. The increase of the 2850-cm^{-1} band relative to the 2928-cm^{-1} band has been interpreted to be due to increased ordering of the alkane chains in studies of the liquid-to-solid phase transition in polyethylene chains.[22] Thus, this observation is consistent with a more ordered 1-butanethiol monolayer at mirrored than at rough Ag surfaces.

In summary, it has been shown for three frequency regions that similar spectra can be obtained for a self-assembled monolayer of 1-butanethiol on roughened and smooth Ag surfaces. The only differences in the spectra appear to be due to slightly increased ordering of the monolayer at the smooth surfaces.

Estimation of Surface Enhancement. In order to estimate the magnitude of the enhancement realized at these mechanically polished, mirrored surfaces, an experiment was performed in which the surface Raman spectrum of a monolayer of 1-butanethiol adsorbed on mechanically polished Au was acquired with 514.5-nm excitation. At this excitation wavelength, Au does not support significant electromagnetic enhancement based on its optical properties.[32] A comparison of the ν(C–H) stretching region for 1-butanethiol on mirrored Ag and Au surfaces with 514.5-nm excitation and on Au with 600-nm excitation where Au does support electromagnetic enhancement is shown in Figure 9. A detailed comparison between the signal-to-noise ratios of the spectra on Ag and Au with 514.5-nm excitation yields an estimate for the enhancement on the Ag surface relative to that on the Au surface of ca. 100. It is assumed that all of this enhancement arises from electromagnetic contributions on these mechanically polished surfaces.

Conclusions

Two conclusions can be drawn from the results presented here. First, it has been demonstrated that SERS spectra acquired from a series of alcohols and 1-butanethiol adsorbed at roughened Ag electrodes are essentially identical with those observed on emersed mirrored Ag electrodes. Thus, SERS is apparently probing the average surface species at the Ag electrode in these systems and not only molecules that exist on chemically unique surface sites. This conclusion has important implications for the utility of SERS as a general surface analysis method.

Second, the similarity of the spectra from the emersed electrodes with those acquired on in situ interfaces suggests that the molecular structure of the interface is preserved upon emersion at atmospheric pressure. Thus, electrode emersion appears to be a valid approach for the study of these organic species in the electrochemical interface under the stated conditions.

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Registry No. Methanol, 67-56-1; 1-propanol, 71-23-8; 1-pentanol, 71-41-0; 1-butanethiol, 109-79-5.

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(31) Claassen, H. H.; Selig, H.; Shamir, J. *Appl. Spectrosc.* **1969**, *23*, 8.

(32) Wenning, U.; Pettinger, B.; Wetzel, H. *Chem. Phys. Lett.* **1980**, *70*, 49.