VOLUME 113, NUMBER 10
MAY 8, 1991

JOURNAL
OF THE
AMERICAN
CHEMICAL
SOCIETY

Surface Raman Scattering of Self-Assembled Monolayers Formed from 1-Alkanethiols at Ag

Mark A. Bryant and Jeanne E. Pemberton*

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721.
Received August 6, 1990

Abstract: Surface Raman scattering is used to study self-assembled monolayers formed from a series of 1-alkanethiols (1-butanethiol, 1-dodecanethiol, 1-octadecanethiol) at both electrochemically roughened and mechanically polished polycrystalline Ag electrodes. The spectra obtained at both surfaces are similar in all spectral regions. Defect structure in these films is investigated using the relative amounts of trans and gauche conformers in the ν(C–S) and ν(C–C) frequency regions. These monolayer films are most ordered in the cases of 1-butanethiol and 1-octadecanethiol and least ordered in the case of 1-dodecanethiol. This behavior correlates with the ordering observed in the bulk 1-alkanethiols. Surface selection rules are used to determine molecular orientation at Ag.

Introduction

Molecular monolayers and thin films are of interest for many applications including nonlinear optical materials, information storage, biological sensors, protective layers, surface and electrode modification, and protein films.[1] One of the obstacles to widespread application of organic films is the need for further development of surface analysis techniques for the characterization of these films.

Self-assembled monolayer systems offer a versatile method for modifying metal surfaces with molecule-specific thin films. Self-assembling systems reported previously include alkanethiols,[2] carboxylic acids,[3] chlorosilanes,[4] and surfactants.[5] Complete, uniform monolayer films are spontaneously formed with these molecules. For the first three systems, chemisorption of one moiety of the molecule is proposed to be the driving force behind the spontaneous film formation. Various functional groups can be located on the end of the organic molecule opposite the chemisorption site for tailoring the chemical behavior of these films, for example, interaction with solvents.[6]

The adsorption of 1-alkanethiols at Au surfaces has been studied with many analytical methods, including IR spectroscopy,[7] ellipsometry,[8] XPS,[6] electron diffraction,[9] wetting contact angle measurements,[10] and electrochemistry.[11] In general, the conclusions from these studies are that highly ordered, defect-free monolayer films are spontaneously formed at Au surfaces.

IR spectroscopic and ellipsometric results have been interpreted in terms of these self-assembled monolayer films being densely packed in a crystalline arrangement, with the alkane chain in an all-trans conformation.[6] Comparisons of the frequencies in the ν(C–H) region between adsorbed and solid alkanethiols have been used to deduce conformations of the C–C bonds.[6,8] As will be shown in this report, Raman scattering in the ν(C–S), ν(C–C), ν(S–H), and ν(C–H) regions can be used to directly characterize the number and location of gauche conformations in a series of 1-alkanethiol films at Ag.

---

* Author to whom correspondence should be addressed.

[1] Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Raabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932.

[2] Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

[3] Chau, L.-K.; Porter, M. D. *Chem. Phys. Lett.* **1990**, *167*, 198.

[4] Maoz, R.; Sagiv, J. *Langmuir* **1987**, *3*, 1034, 1045.

[5] Diaz, A.; Kaifer, A. E. *J. Electroanal. Chem.* **1988**, *249*, 333.

[6] Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.

[7] Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358.

[8] Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

[9] Strong, L.; Whitesides, G. M. *Langmuir* **1988**, *4*, 546.

[10] Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87.

[11] Finklea, H. O.; Avery, S.; Lynch, M. *Langmuir* **1987**, *3*, 409.

0002-7863/91/1513-3629$02.50/0

Few studies of alkanethiols adsorbed at Ag surfaces have been reported. Ulman studied 1-octadecanethiol at Ag using IR spectroscopy.[12] Joo and co-workers investigated 1-butanethiol,[13] 1-propanethiol, and ethanethiol[14] adsorbed at Ag sols in the ν(C–S) region with surface-enhanced Raman scattering (SERS). Sandroff and co-workers[15] studied 1-hexadecanethiol adsorbed on Ag island films in the ν(C–S) and ν(C–C) regions using SERS. The effect of the surface roughness required for SERS activity on the surface Raman scattering behavior of adsorbed films can be addressed with 1-alkanethiol films. Comparisons between surface spectra from electrochemically roughened and mechanically polished Ag electrodes are presented in this report to investigate the generality of the SERS results and the possible disordering effect of the surface morphology.

The orientation of long-chain 1-alkanethiols at Au has been calculated on the basis of IR spectroscopic data.[6,8] Porter and co-workers propose that the alkane chain is tilted 20 to 30° with respect to the surface normal.[8] Nuzzo and co-workers propose the tilt to be 40° with a rotation of 50° about the chain axis.[6] Ulman estimates the chain tilt for octadecanethiol at Ag to be less than that found for octadecanethiol at Au.[12] Surface Raman selection rules are used here to infer the orientation of the C–S, C–C, and C–H bonds with respect to the Ag surface.

Experimental Section

Spectroscopic Conditions and Instrumentation. Excitation was provided by the 514.5-nm line of a Coherent Radiation Innova 90-5 Ar^+ laser. The laser power incident upon the samples was typically 50 mW for the smooth and roughened Ag electrodes and 200 mW for liquids. The laser beam was focused to a spot of diameter ca. 50 μm. Spectra of all adsorbed molecules were obtained with incident light polarized parallel with respect to the plane of incidence. Spectra of bulk alkanethiols were acquired with the liquid in a sealed NMR tube. Solid alkanethiol spectra were acquired by cooling the capillary and sample with liquid nitrogen and obtaining spectra with series of 10-s integrations to prevent laser warming. Integration times were typically 10 min for surface spectra, 5 min for liquid spectra, and 3 min for solid spectra.

Scattered radiation was collected with a Minolta *f*/1.2 camera lens (50-mm focal length) and focused onto the entrance slits of a Spex 1877 Triplemate. The gratings in the filter stage were 600 grooves/mm, and the grating used in the spectrograph stage was 1200 grooves/mm. Slit widths were typically 0.25 mm/2.8 mm/0.25 mm. Approximately 50 to 75% of the circular image at the entrance slit passed into the spectrometer. Detection was accomplished with a Photometrics PM512 front-side-illuminated charge coupled device (CCD) cooled with liquid nitrogen between −95 and −120 °C. The CCD images were processed with a Photometrics RDS200 system equipped with a custom version of SpectraCalc.

Electrochemical Conditions and Instrumentation. The working electrode consisted of a polycrystalline Ag disk (99.9% Johnson Matthey) which was mechanically polished to a mirror finish using 0.05-μm alumina, rinsed with doubly or triply distilled, deionized water (TDI), and then sonicated for 2 min in TDI water to remove any trapped alumina. A Pt wire served as the auxiliary electrode. Electrode potentials were controlled with an IBM Model EC/225 voltammetric analyzer. Linear potential ramps were performed using a simple triangle wave format. Total charge passed was monitored with a Princeton Applied Research Model 379 digital coulometer.

Materials. 1-Butanethiol (99+%), 1-dodecanethiol (98%), and 1-octadecanethiol (98%) were purchased from Aldrich. Ethanol (absolute) was purchased from Midwest Grain Products. KCl was purchased from Fisher Scientific. Aqueous 1-butanethiolate solutions were made by combining one part 1-butanethiol with nine parts 5 M NaOH. NaOH pellets were purchased from Baker. $Pb(NO_3)_2$ was purchased from MCB. All were used as received.

Electrochemical Roughening and Emersion Procedures. Spectra from films at roughened Ag electrodes were obtained by electrochemically roughening the surface before immersion in an ethanol/alkanethiol solution. Linear potential sweep oxidation–reduction cycles (ORCs) were applied to Ag electrodes in the presence of 0.1 M KCl aqueous solution. The initial potential was −0.20 V versus a Ag/AgCl reference electrode, and the potential sweep was reversed at ca. +0.20 at a scan rate of 10 mV/s, resulting in ca. 40 mC/cm^2 of anodic charge being passed. The electrodes were then removed from solution at open circuit potential, rinsed with 100% ethanol, and then exposed to the alkanethiol solution. Smooth electrodes were prepared by mechanical polishing with alumina (0.05 μm) and rinsing with 100% ethanol before exposure to the alkanethiol solution.

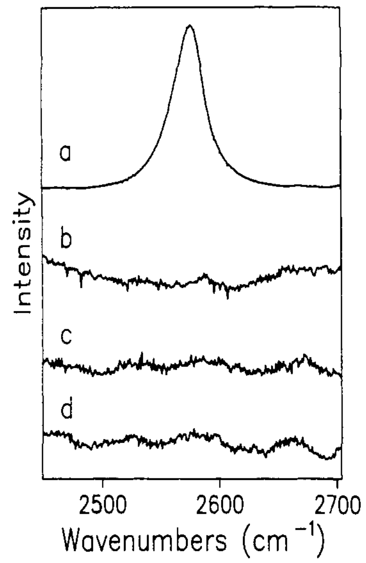

Figure 1. Raman spectra in ν(S–H) region of (a) bulk liquid butanethiol, (b) aqueous butanethiolate, (c) butanethiol adsorbed at smooth Ag, (d) butanethiol adsorbed at rough Ag. Integration times for (a) 1 min, (b) 1 min, (c) 5 min, (d) 1 min; incident laser power, 200 mW.

Despite the fact that these surfaces are designated as smooth, it must be recognized that they are not as smooth as single-crystal surfaces. Mechanical polishing produces a gently corrugated surface whose roughness is confined to a size dictated by the size of the alumina particles. These surfaces have been previously shown in this laboratory to be very weakly enhancing by a factor of ca. 100 relative to a surface that does not support any enhancement through electromagnetic enhancement of the corrugated surface.[16] It is unlikely that chemically distinct sites of the type thought to be important in SERS on electrochemically roughened surfaces exist on these mechanically polished surfaces. It is known that these sites are extremely labile; therefore, even if a small number of such sites were formed during the mechanical polishing procedure, it is unlikely that they would survive the subsequent rinsing and transfer steps before the self-assembled films are formed. Questions regarding monolayer film quality on these mechanically polished, polycrystalline surfaces were addressed by comparison of spectra obtained on these surfaces to those prepared on evaporated Ag films on Si substrates.[17] The similarity between the spectra from these two types of Ag surfaces suggests that the films formed on the mechanically polished surfaces are of the same quality as those formed on evaporated Ag surfaces.

Smooth and roughened surfaces were immersed in 1 to 20 mM alkanethiol solutions in 100% ethanol for 15 to 24 h to allow the self-assembled monolayers to form. These surfaces were then rinsed again with 100% ethanol and allowed to air dry.

Results and Discussion

Formation of Alkanethiol Self-Assembled Monolayer Films. 1-Alkanethiols are proposed to form monolayers at Au by chemisorption of the S head group to the metal substrate.[10] The mechanism, shown in eq 1, involves cleavage of the S–H bond

$$RSH + Au^0_n \xrightarrow[-H_2O?]{-H_2?} RS^-Au^+ + Au^0_{n-1} \qquad (1)$$

with concomitant oxidation of a Au atom to form a S–Au bond. The lost H may be released as H_2 or combine with trace oxidants in solution such as O_2 to form H_2O. A similar reaction scheme can be envisioned on Ag in which a Ag–S bond is formed.

---

[12] Ulman, A. *J. Mater. Ed.* **1989**, *11*, 205.

[13] Joo, T. H.; Kim, K.; Kim, M. S. *J. Mol. Struct.* **1987**, *158*, 265.

[14] Joo, T. H.; Kim, K.; Kim, M. S. *J. Phys. Chem.* **1986**, *90*, 5816.

[15] Sandroff, C. J.; Garoff, S.; Leung, K. P. *Chem. Phys. Lett.* **1983**, *96*, 547.

[16] Sobocinski, R. L.; Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 6177.

[17] Self-assembled monolayer films on Ag evaporated onto smooth Si substrates were graciously provided by Dr. Marc D. Porter.

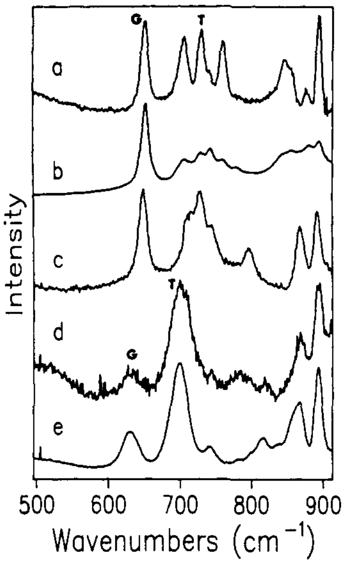

Figure 2. Raman spectra in ν(C–S) region in (a) bulk solid butanethiol, (b) bulk liquid butanethiol, (c) aqueous butanethiolate, (d) butanethiol adsorbed at smooth Ag, (e) butanethiol adsorbed at rough Ag.

Evidence for this bonding scheme can be seen in the surface Raman spectra of these films. Alkanethiols exhibit a strong ν(S–H) at ca. 2575 cm^{-1} as shown in Figure 1a for neat butanethiol. Upon adsorption to smooth and roughened Ag, evidence for cleavage of the S–H bond is seen by the disappearance of the ν(S–H) band as shown in Figure 1, c and d. The adsorbed molecule is similar to butanethiolate, which is formed upon addition of butanethiol to basic aqueous solutions. Figure 1b shows a spectrum of aqueous butanethiolate in which the ν(S–H) is clearly absent. Dodecanethiol and octadecanethiol exhibit a similar loss of the ν(S–H) band upon adsorption. No unreacted alkanethiol appears to be present in the self-assembled monolayer film based on the lack of ν(S–H) intensity. Additional evidence for the thiolate bonding scheme is noted in the ν(C–S) spectral region as will be discussed further below.

Bonding of the alkanethiol to the Ag substrate through the S atom allows adjacent alkane chains to interact through the van der Waals forces. Minimization of the free energy of the monolayer is the driving force for the ordering of the alkanethiol in a dense packing arrangement.[18] These monolayers at Au substrates have been characterized as having crystalline-like packing.[6] In the following discussion of the vibrational behavior in the ν(C–S), ν(C–C), and ν(C–H) regions, surface Raman spectra will be compared with Raman spectra of both liquid and solid alkanethiols in order to assess the extent of order, and hence crystallinity, in these films. The liquid spectra are indicative of disordered behavior, and the solid spectra correspond to ordered behavior. The vibrational peak frequencies and their assignments for butanethiol, dodecanethiol, and octadecanethiol are given in Tables I through III, respectively. Assignments are based on information in the literature.[13,14,19-25]

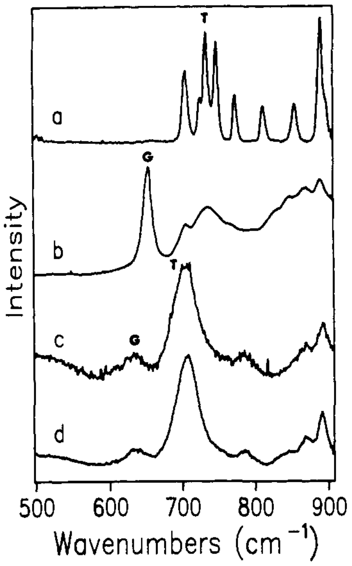

Figure 3. Raman spectra in ν(C–S) region of (a) bulk solid dodecanethiol, (b) bulk liquid dodecanethiol, (b) dodecanethiol adsorbed at smooth Ag (50 mW), (d) dodecanethiol adsorbed at rough Ag.

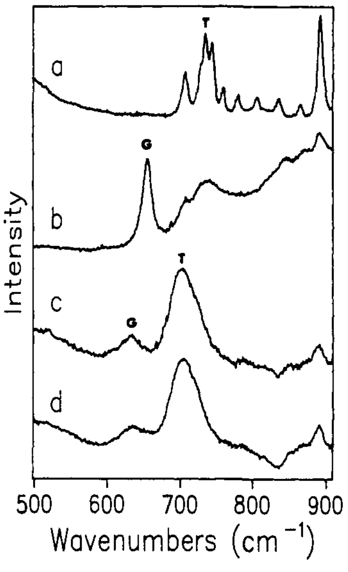

Figure 4. Raman spectra in ν(C–S) region of (a) bulk solid octadecanethiol, (b) bulk liquid octadecanethiol, (c) octadecanethiol adsorbed at smooth Ag, (d) octadecanethiol adsorbed at rough Ag.

C–S Stretching Region. Two ν(C–S) bands are observed for these molecules in the frequency region between 600 and 750 cm^{-1}. These bands correspond to gauche (G) and trans (T) conformations around the two C atoms adjacent to the S atom. Information about the properties of the film can be derived from both the position of these bands and their relative intensities.

As indicated above, bonding of the 1-alkanethiols to Ag is presumed to be through the S head group. Further evidence for this bonding scheme comes from the position of the two ν(C–S) bands when adsorbed at Ag. The behavior of butanethiol at Ag is representative of these systems. The Raman spectra of solid butanethiol, liquid butanethiol, liquid butanethiolate, and butanethiol adsorbed to smooth and roughened Ag surfaces are shown in Figure 2, a through e, respectively. In the solid and liquid butanethiol, Figure 2, a and b, respectively, the G ν(C–S) band is observed at 652 cm^{-1} and the T ν(C–S) is observed at 730 cm^{-1}. These assignments follow those of Joo and co-workers.[13] Upon removal of the thiol proton in solution, these frequencies shift to 650 and 728 cm^{-1} for the G and T bands, respectively, as seen in Figure 2c. Upon adsorption at Ag, the shift toward lower frequencies for these bands is even greater. As shown in Figure 2, d and e, the G band for the surface species is observed at 630 cm^{-1} and that for the T conformer is observed at 700 cm^{-1}. Joo and co-workers confirmed these assignments by comparing the solution spectra of 1-butanethiolate with the SERS spectrum of 1-butanethiol adsorbed at colloidal Ag.[13] The large decrease in

---

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

(19) Torgrimsen, T.; Klaeboe, P. *Acta Chem. Scand.* **1970**, *24*, 1139.

(20) Yellin, N.; Levin, I. W. *Biochim. Biophys. Acta* **1977**, *468*, 490. Gaver, B. P.; Peticolas, W. L. *Biochim. Biophys. Acta* **1977**, *465*, 260. Spiker, R. C.; Levin, I. W. *Biochim. Biophys. Acta* **1976**, *433*, 457.

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

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

(23) Schachtschneider, J. H.; Snyder, R. G. *Spectrochim. Acta* **1963**, *19*, 117.

(24) MacPhail, R. A.; Snyder, R. G.; Strauss, H. L. *J. Chem. Phys.* **1982**, *77*, 1118.

(25) Hill, I. R.; Levin, I. W. *J. Chem. Phys.* **1979**, *70*, 842.

Table I. Raman Vibrational Assignments and Peak Frequencies for 1-Butanethiol

assignment[a]	solid	liquid	butane-thiolate	adsorbed smooth Ag	adsorbed rough Ag
$\nu(\mathrm{C-S})_\mathrm{G}$	652	653	650	630	630
$\mathrm{CH_2}$ rock	706	707	714		
$\nu(\mathrm{C-S})_\mathrm{T}$	730	729	728	701	699
$\mathrm{CH_2}$ rock	742	743	744	745	742
$\mathrm{CH_2}$ rock	760	760			
		779	798	787	817
CHS def	847	842			
CHS def	857	856			
$\mathrm{CH_3}$ $\mathrm{rock_G}$	877	881	868	869	867
$\mathrm{CH_3}$ $\mathrm{rock_T}$	895	894	893	895	894
	947	951			934
		973	968	971	970
		999	997		1003
	1012	1013	1011	1005	1012
$\nu(\mathrm{C-C})_\mathrm{T}$	1051	1052	1052	1051	1053
$\nu(\mathrm{C-C})_\mathrm{G}$	1064	1063	1066	1069	1067
$\nu(\mathrm{C-C})_\mathrm{T}$	1091	1091	1096	1097	1096
$\nu(\mathrm{C-C})_\mathrm{T}$	1113	1108			1112
					1163
	1208	1202	1196	1186	1184
	1232	1233	1223	1218	1218
	1280	1279	1272		1268
		1293			
$\mathrm{CH_2}$ wag	1298	1303	1297	1297	1292
				1330	1330
$\nu_s(\mathrm{CH_2})$	2842	2848	2847		2837
$\nu_s(\mathrm{CH_2})$	2857	2864	2863	2857	2858
$\nu_s(\mathrm{CH_3})$	2873	2875	2878	2878	2875
$\nu_a(\mathrm{CH_2})$	2900	2905		2899	
$\nu_s(\mathrm{CH_2}$, FR)		2916	2914	2913	2912
$\nu_s(\mathrm{CH_2}$, FR)	2926				
$\nu_s(\mathrm{CH_3}$, FR)	2937	2934	2939	2937	2934
$\nu_a(\mathrm{CH_{3,oop}})$	2956				
$\nu_a(\mathrm{CH_{3,ip}})$	2968	2963	2965	2967	2965

[a] Assignments taken from ref 13, 14, 19–25.

Table II. Raman Vibrational Assignments and Peak Frequencies for 1-Dodecanethiol

assignment[a]	solid	liquid	adsorbed smooth Ag	adsorbed rough Ag
$\nu(\mathrm{C-S})_\mathrm{G}$	659	654	632	636
$\mathrm{CH_2}$ rock	707	706		
	727			
$\nu(\mathrm{C-S})_\mathrm{T}$	735	737	706	707
	749			
$\mathrm{CH_2}$ rock	775	769	787	789
	813			
	855	848		
		869	870	869
$\mathrm{CH_3}$ $\mathrm{rock_T}$	891	891	894	892
	900			
	945	927	937	933
	980	960		
	993			
	1012			
	1037	1027		
$\nu(\mathrm{C-C})_\mathrm{T}$	1061	1063	1065	1064
$\nu(\mathrm{C-C})_\mathrm{G}$	1083	1078	1081	1081
$\nu(\mathrm{C-C})_\mathrm{T}$	1109			1097
$\nu(\mathrm{C-C})_\mathrm{T}$	1129	1121	1126	1126
	1178	1164		1162
	1191		1191	1189
	1201			
	1218		1216	1215
	1230			
	1245			
	1257			
	1273			
	1281			
$\mathrm{CH_2}$ wag	1295	1302	1299	1300
	1326			1329
$\nu_s(\mathrm{CH_2})$	2848	2851	2853	2852
$\nu_s(\mathrm{CH_2})$	2857	2859		2861
$\nu_s(\mathrm{CH_3})$	2873	2874	2878	2876
$\nu_a(\mathrm{CH_2})$	2882			
$\nu_a(\mathrm{CH_2})$	2891	2897	2900	2903
$\nu_s(\mathrm{CH_2}$,FR)	2911			
$\nu_s(\mathrm{CH_2}$,FR)	2923	2928	2921	2921
$\nu_s(\mathrm{CH_3}$,FR)		2938	2936	2936
$\nu_a(\mathrm{CH_{3,oop}})$	2956			
$\nu_a(\mathrm{CH_{3,ip}})$	2962	2959	2966	2964

[a] Assignments taken from ref 13, 14, 19–25.

energy of these vibrations for the surface molecules is suggestive of substantial withdrawal of electron density from the C–S bond. This picture is consistent with bonding of the S head group to the Ag surface. Similar shifts are observed upon bonding of dodecanethiol and octadecanethiol to Ag as shown in Figures 3 and 4.

The intensity ratio of the T band to the G band is indicative of the degree of ordering within these systems in the vicinity of the C–S bond. As shown in Figure 2, the intensity ratio of the T ν(C–S) band to the G ν(C–S) is larger for solid butanethiol than for liquid butanethiol. The change in the T/G ratio in going from liquid to solid is even larger for the longer chain 1-alkanethiols, dodecanethiol and octadecanethiol, as shown in Figures 3 and 4, respectively. The liquid spectra for dodecanethiol and octadecanethiol, Figure 3b and 4b, are similar to that for butanethiol. However, the spectra for the longer chain *n*-alkanethiols show almost complete disappearance of the G band upon solidification (Figures 3a and 4a). *n*-Alkanethiols[19] and *n*-alkanes[26] in the solid form are found mostly in the all-trans conformation.

For all three alkanethiols adsorbed at Ag, the G ν(C–S) intensity is considerably smaller than the T ν(C–S) intensity, which is similar to the spectral changes seen upon solidification of the liquid alkanethiols. One can conclude from these results that the alkane chain adjacent to the C–S bond, and presumably near the Ag surface, is mostly in the T conformation for all three adsorbed alkanethiols. This conformation corresponds to the crystalline-like packing arrangement seen in the spectra of solid dodecanethiol and octadecanethiol.

The effects of surface roughness on film structure can be assessed by comparison of Figures 3d and 4d with Figures 3c and 4c. Only slight differences between the surface spectra in this region for dodecanethiol and octadecanethiol adsorbed at rough and mirrored Ag are observed. Butanethiol adsorbed at rough surfaces shows a slightly larger G intensity compared to mirrored surfaces (Figure 2e,d). ORC pretreatments of Ag in 0.1 M KCl result in roughness features that range in size from several hundred nanometers to less than 40 nm as determined by scanning electron microscopy.[27] These roughness features as well as those smaller in size, down to clusters of four Ag atoms, are proposed to exist on the surface and be important in the SERS phenomenon.[28] The mirrored surfaces used here are envisioned to be gently corrugated with features on the order of the size of alumina used in polishing (0.05 μm). Similarity between surface spectra for smooth and rough Ag suggests that the same surface species are probed with surface Raman scattering on mirrored surfaces and with SERS on electrochemically roughened surfaces. Similar results have been reported previously for pyridine adsorbed at rough and smooth Ag.[29,30] Additionally, previous results from this laboratory have shown that similar spectra are obtained for methanol, 1-propanol, 1-pentanol, and 1-butanethiol at rough and mirrored Ag surfaces.[16]

These self-assembled monolayers are sensitive to disordering forces.[15] The atomic-scale and large-scale roughness features formed at the Ag surface in the ORC pretreatment might be

---

(26) Maissara, M.; Devaure, J. *J. Raman Spectrosc.* **1987**, *3*, 181.

(27) Tuschel, D. D.; Pemberton, J. E.; Cook, J. E. *Langmuir* **1986**, *2*, 380.

(28) Furtak, T. E.; Roy, D. *Surf. Sci.* **1985**, *158*, 126.

(29) Schultz, S. G.; Janik-Czachor, M.; Van Duyne, R. P. *Surf. Sci.* **1981**, *104*, 419.

(30) Fleischmann, M.; Graves, P. R.; Robinson, J. *J. Electroanal. Chem.* **1985**, *182*, 73.

Table III. Raman Vibrational Assignments and Peak Frequencies for 1-Octadecanethiol

assignment[a]	solid	warmer solid	liquid	adsorbed smooth Ag	adsorbed rough Ag
$\nu(C\text{–}S)_G$			655	633	634
CH_2 rock	707		707		
	728				
	735				
$\nu(C\text{–}S)_T$	744		739	704	705
	760				
CH_2 rock	781		770	788	
	807				
	836		844		
	866		872		
CH_3 $rock_T$	892	892	892	891	891
					920
				956	958
				991	992
	1025	1029		1026	1026
$\nu(C\text{–}C)_T$	1061	1062	1063	1063	1063
$\nu(C\text{–}C)_G$		1081	1078		
$\nu(C\text{–}C)_T$	1103	1103		1101	1101
$\nu(C\text{–}C)_T$	1129	1130	1123	1128	1129
	1172	1174		1184	1184
				1199	1200
				1218	1218
	1275	1280			
CH_2 wag	1294	1297	1300	1297	1297
$\nu_s(CH_2)$	2848		2850	2848	2849
$\nu_s(CH_2)$	2860				
$\nu_s(CH_3)$	2872		2873	2876	2876
$\nu_a(CH_2)$	2883			2883	2882
$\nu_a(CH_2)$	2903		2892	2906	2905
$\nu_s(CH_2, FR)$	2928		2927		2925
$\nu_s(CH_3,FR)$					
$\nu_a(CH_3)$	2960		2961	2966	2967

[a] Assignments taken from ref 13, 14, 19–25.

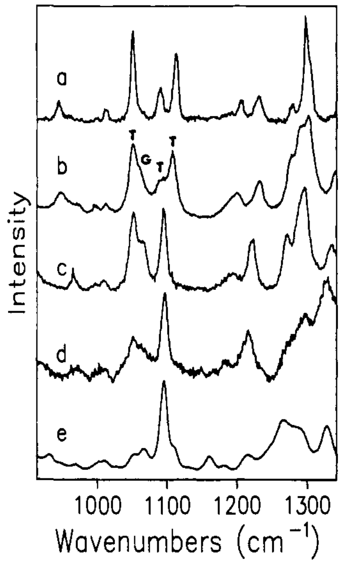

Figure 5. Raman spectra in ν(C–C) region of (a) bulk solid butanethiol, (b) bulk liquid butanethiol, (a) aqueous butanethiolate, (d) butanethiol adsorbed at smooth Ag, (e) butanethiol adsorbed at rough Ag.

expected to result in films with larger numbers of defects or G conformers as compared to mirrored surfaces. However, similarity in the surface spectra for the ν(C–S) region for the longer chain alkanethiols suggests that the roughening pretreatment does not introduce a significantly greater number of defects in the film near the C–S bond at rough Ag as compared to those that exist in the films formed on mirrored polycrystalline Ag.

C–C Stretching Region. Four ν(C–C) vibrations are found in the frequency region between 1030 and 1150 cm^{-1}. As in the case of the C–S bands, T and G bands are observed. Figure 5a shows the spectrum for solid butanethiol. The bands at 1051 and 1113 cm^{-1} are T ν(C–C) bands.[20] Upon melting to the liquid, the spectrum in Figure 5b is observed. The G band at 1063 cm^{-1} increases in intensity, while the 1113-cm^{-1} T band decreases in frequency to 1108 cm^{-1} and decreases in intensity with respect to the 1051-cm^{-1} T band. These changes are indicative of disorder, as found in liquid.[20] A fourth ν(C–C) band at 1091 cm^{-1} has also been assigned as a T band in dipalmitoyl phosphatidylcholine systems.[21] Similar assignments can be made to the four ν(C–C) bands in the spectra of dodecanethiol and octadecanethiol as shown in Figures 6 and 7, respectively. It is not known which types of T conformers give rise to the three different T ν(C–C) bands. These vibrations may be related to T segments that are separated by G conformations in various locations in the chain.[31] Further experiments to clarify the ν(C–C) assignments are being conducted in this laboratory.

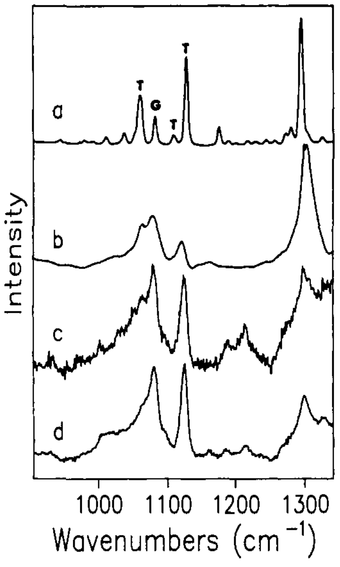

Figure 6. Raman spectra in ν(C–C) region of (a) bulk solid dodecanethiol, (b) bulk liquid dodecanethiol, (c) dodecanethiol adsorbed at smooth Ag, (d) dodecanethiol adsorbed at rough Ag.

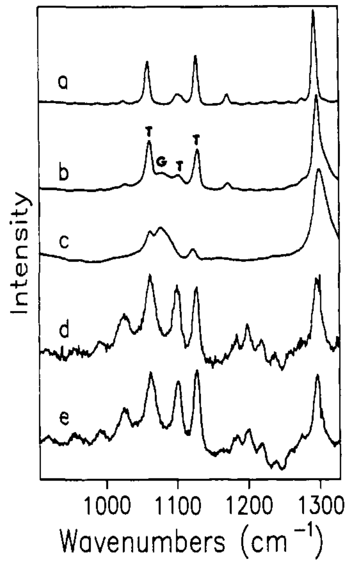

Figure 7. Raman spectra in ν(C–C) region of (a) bulk solid octadecanethiol, (b) bulk solid octadecanethiol, slightly higher temperature, (c) bulk liquid octadecanethiol, (d) octadecanethiol adsorbed at smooth Ag, (e) octadecanethiol adsorbed at rough Ag.

The intensities of these bands are extremely sensitive to both temperature and chain length of the molecule. For example, three bands can be seen in the liquid spectrum for dodecanethiol (Figure 6b). The G band at 1078 cm^{-1} is higher in intensity than the either T band at 1063 or 1121 cm^{-1}, in contrast to liquid butanethiol.

---

[31] Snyder, R. G. *J. Chem. Phys.* **1967**, *47*, 1316.

Upon cooling to a solid (Figure 6a), the G band intensity decreases significantly and the T band at 1109 cm^{-1} is seen. The 1121-cm^{-1} T band shifts to 1129 cm^{-1} and becomes more intense than the 1061-cm^{-1} T band. It is interesting to note that there is still a significant G component in solid dodecanethiol as compared to solid butanethiol in which the G band is only a small shoulder.

No G intensity is observed for solid octadecanethiol (Figure 7a). The T bands at 1061 and 1129 cm^{-1} are approximately equal in intensity. The band at 1103 cm^{-1} is assigned as a T band as well. This assignment can be confirmed by warming the sample by increasing the time of exposure to the incident laser beam. Figure 7b is a spectrum of solid octadecanethiol which has been exposed to a 350-mW laser beam for ca. 60 s. Laser heating of this sample has raised its temperature very slightly such that the 1103-cm^{-1} T band is seen along with a weak G band at 1081 cm^{-1}. Upon total warming to a liquid (Figure 7c), the G band becomes the most intense band and the spectrum resembles that of liquid dodecanethiol.

Several significant changes in the spectra are noted for these molecules upon self-assembly into monolayers on Ag. For butanethiol adsorbed at a mirrored Ag surface (Figure 5d), the strongest band is the T band at 1097 cm^{-1}. This band is probably the same as the 1091-cm^{-1} T band seen in the spectrum of the solid (Figure 5a). The 1112-cm^{-1} T band is seen in the spectrum for butanethiol adsorbed at roughened Ag (Figure 5e). However, in contrast to the neat butanethiol and thiolate spectra, the T and G bands at 1051 and 1069 cm^{-1} for adsorbed butanethiol have greatly decreased in intensity. Similar conclusions are reached after consideration of data in the ν(C–S) region. The alkane chain appears to be predominantly in a T conformation resulting in a crystalline-like, ordered monolayer. The small G intensity observed may correspond to the G conformers seen in the ν(C–S) region.

For dodecanethiol adsorbed at smooth Ag (Figure 6c), the extent of ordering appears to be somewhat different. While the strongest band is the 1126-cm^{-1} T ν(C–C) band, nearly equal in intensity is the G band at 1081 cm^{-1}. Based on this G band intensity, it is concluded that dodecanethiol forms a more disordered monolayer than butanethiol. This conclusion is consistent with the observation that solid dodecanethiol exhibits greater G intensity than solid butanethiol or octadecanethiol. It should be further noted that the absolute degree of disordering in the surface film may actually be small, because changes in G and T intensities may not be linear with the number of G conformations in the alkane chain.[32] The defects in the dodecanethiol film are thought to be located along the alkane chain in addition to the small number of G conformations near the C–S bond as indicated in the ν(C–S) region. This is supported by the observation that while the surface spectra for all three adsorbed alkanethiols exhibit similar G intensity in the C–S stretching region, only adsorbed dodecanethiol exhibits a large G band in the ν(C–C) region.

Octadecanethiol adsorbed at smooth Ag exhibits three bands in the ν(C–C) region which are all assigned as T vibrations (Figure 7d). The 1101-cm^{-1} band is not assigned to a G conformer, as reported by Sandroff and co-workers for 1-hexadecanethiol at Ag.[15] Such an assignment is inconsistent with the observation of this band in the spectrum of solid octadecanethiol shown in Figure 7a. In total, the surface spectra suggest that the octadecanethiol film in air exists in a nearly perfect all-trans configuration except for the presence of a small number of defects in the vicinity of the C–S bond.

One further experiment was performed to investigate the extent to which disorder could be introduced into the octadecanethiol film. This experiment consisted of acquisition of the Raman spectrum of an octadecanethiol film on a rough Ag surface warmed above room temperature. The temperature of the sample was raised by periodic immersion in ca. 85 °C water for 10 s and spectral acquisition for 20 s. Figure 8a shows the spectrum for octadecanethiol adsorbed to rough Ag before immersion in hot water. Water was chosen as the warming solvent, because it is a weak Raman scatterer in this region. Upon immersion in hot water, the G band at 1082 cm^{-1} becomes evident, shown in Figure 8b, suggesting that the film is disordered by the increased temperature. Nuzzo and co-workers[33] have also presented evidence for increased G conformers in long-chain alkanethiols at Au upon heating to temperatures of 380 K and above using IR spectroscopy. Figure 8c shows the sample after reimmersion of this same film into ca. 20 °C water. The G band at 1082 cm^{-1} has disappeared. Further studies of this type are currently underway in this laboratory and will be reported at a later date.

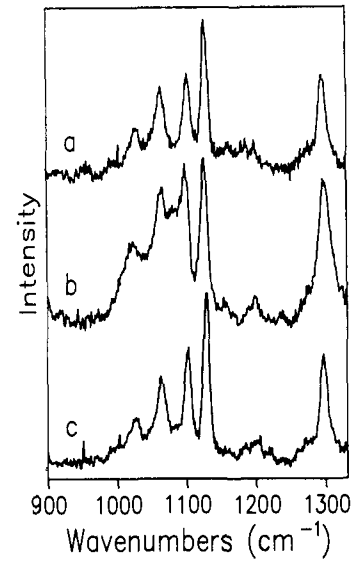

Figure 8. Raman spectra in ν(C–C) region of (a) octadecanethiol adsorbed on rough Ag, (b) octadecanethiol adsorbed at rough Ag immersed in ca. 85 °C water, (c) octadecanethiol adsorbed at rough Ag immersed in ca. 20 °C. Integration times at (a) 1 min, (b) 3 min, (c) 4 min; incident laser power, 150 mW.

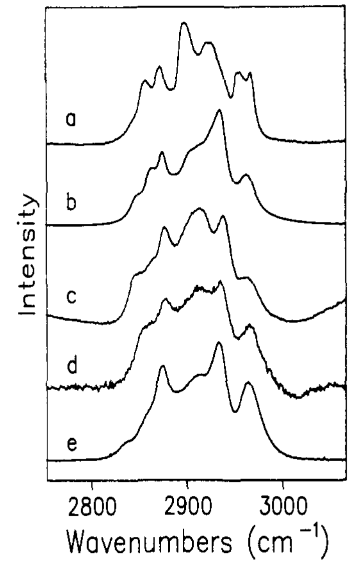

Figure 9. Raman spectra in ν(C–H) region of (a) bulk solid butanethiol, (b) bulk liquid butanethiol, (c) aqueous butanethiolate, (d) butanethiol adsorbed at smooth AG, (e) butanethiol adsorbed at rough Ag.

Little difference between spectra obtained at mirrored and rough Ag is observed for the longer chain alkanethiols, suggesting the generality of the SERS data from ORC-pretreated Ag. No changes in the relative intensities for G and T bands are seen in the ν(C–C) region for dodecanethiol and octadecanethiol at the two surfaces. However, butanethiol shows a change in relative intensity of the 1051-cm^{-1} T and 1069-cm^{-1} G bands between

---

[32] Snyder, R. G.; Cameron, D. G.; Casal, H. L.; Compton, D. A. C.; Mantsch, H. H. *Biochim. Biophys. Acta* **1982**, *684*, 111.

[33] Nuzzo, R. G.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* **1990**, *93*, 767.

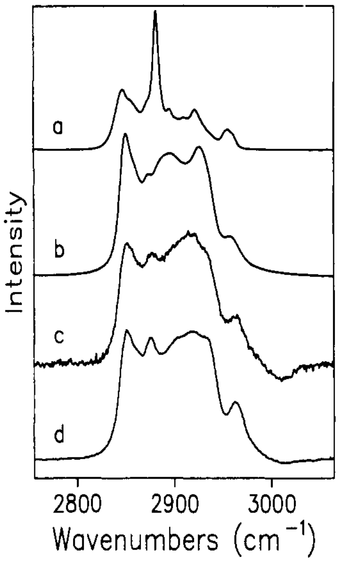

Figure 10. Raman spectra in ν(C-H) region of (a) bulk solid dodecanethiol, (b) bulk liquid dodecanethiol, (c) dodecanethiol adsorbed at smooth Ag, (d) dodecanethiol adsorbed at rough Ag.

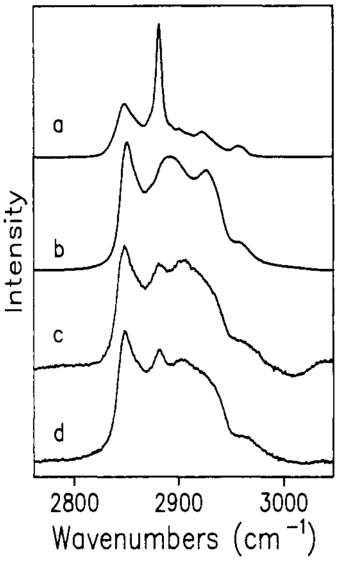

Figure 11. Raman spectra in ν(C-H) region of (a) bulk solid octadecanethiol, (b) bulk liquid octadecanethiol, (c) octadecanethiol adsorbed at smooth Ag, (d) octadecanethiol adsorbed at rough Ag.

smooth and rough surfaces. Therefore, butanethiol monolayer films seem to be slightly more sensitive to surface morphology than the longer chain alkanethiols.

C-H Stretching Region. The ν(C-H) region of these molecules is quite complex and includes symmetric and asymmetric stretches of the methyl and methylene groups and several Fermi resonance bands.[22,25] Figures 9 through 11 show the spectra in this region for butanethiol, dodecanethiol, and octadecanethiol, respectively. Figure 9a shows the spectrum for solid butanethiol. Two $\nu_s(CH_2)$ bands are observed at 2842 and 2857 cm^{-1}. The band at 2857 cm^{-1} is assigned to the $\nu_s(CH_2)$ of the methylene adjacent to the terminal methyl group of the chain.[25] The 2842-cm^{-1} band is for the remaining methylene groups.

Two bands are associated with the $\nu_s(CH_3)$ mode. Snyder and co-workers assign the 2873-cm^{-1} band to $\nu_s(CH_3)$ and the 2937-cm^{-1} to $\nu_s(CH_3,FR)$ which is in Fermi resonance with the overtone of the CH_3 deformation.[22-24] Hill and Levin assign both as $\nu_s(CH_3,FR)$.[25] The notation of Snyder and co-workers will be used here.

The $\nu_a(CH_2)$ appears at 2900 cm^{-1}. There are also two Fermi resonance bands of the symmetric methylene stretch and overtone of the methylene deformation which are observed at 2926 and ca. 2915 cm^{-1}. Two $\nu_a(CH_3)$ bands are seen in the solid butanethiol spectrum. The out-of-plane stretch occurs at 2956 cm^{-1} and the in-plane stretch occurs at 2968 cm^{-1}.[24] These bands overlap in the spectra for the longer chain alkanethiols and the liquid spectra for butanethiol.

The polarization behavior of these bands has been used to confirm symmetric/asymmetric assignments. Polarization studies were performed using excitation with incident radiation polarized perpendicular to the plane determined by the incident beam, sample, and spectrometer entrance slits and collection of scattered radiation parallel and perpendicular to the incident beam. The intensity of the Raman scattering perpendicular ($I_\perp$) divided by the scattering intensity parallel ($I_\parallel$) is defined as the polarization ratio, ρ. Nontotally symmetric (depolarized) vibrations have a depolarization ratio, $\rho = 0.75$, while vibrations containing a symmetrical polarizability component have a ratio $0 \leq \rho < 0.75$.[34] In the polarized spectrum for liquid butanethiol, the strongest bands, which are the nontotally symmetric vibrations, are the $\nu_a(CH_2)$ and $\nu_a(CH_3)$ stretches. The $\nu_s(CH_3)$ stretch decreases to virtually zero in the polarized spectrum.

For butanethiol adsorbed at mirrored Ag (Figure 9d), a large increase in the intensity of the $\nu_s(CH_3)$ and $\nu_a(CH_3)$ vibrations relative to those of the methylene stretches of the liquid is observed. Coinciding with this increase is an increase in intensity of the $\nu_s(CH_3,FR)$ at 2937 cm^{-1}. The increase in intensity of the methyl stretches is also seen by comparing the spectrum for adsorbed butanethiol to that of aqueous butanethiolate (Figure 9c).

Figure 10 shows the ν(C-H) region for dodecanethiol. The intensity of the $\nu_s(CH_3)$ in the solid and liquid spectra, seen as a shoulder at 2873 cm^{-1} in Figure 10, a and b, is small relative to the methylene stretches, because the ratio of methyl to methylene groups has decreased. Likewise, the intensity of the 2938-cm^{-1} $\nu_s(CH_3,FR)$ has become a shoulder on the $\nu_s(CH_2,FR)$ at ca. 2928 cm^{-1}. The $\nu_a(CH_2)$ band at 2882 cm^{-1} dominates the spectrum of the solid (Figure 10a). In both the solid and liquid spectra, the $\nu_s(CH_2)$ band at ca. 2850 cm^{-1} dominates the $\nu_s(CH_2)$ band at 2860 cm^{-1}.

The spectrum of dodecanethiol adsorbed at mirrored Ag (Figure 10c) exhibits an increase in intensity of the $\nu_s(CH_3)$ relative to the spectrum of the liquid (Figure 10c), as was seen for adsorbed butanethiol. The $\nu_s(CH_3,FR)$, which appeared as a weak shoulder in the liquid spectrum, is also more intense. However, the intensity of the $\nu_s(CH_3)$ compared to the $\nu_s(CH_2)$ is less for adsorbed dodecanethiol than for adsorbed butanethiol, reflecting the greater number of methylene groups in dodecanethiol.

The frequencies of the bands in the spectra of the solid and liquid forms of octadecanethiol (Figure 11, a and b) are similar to those of dodecanethiol. Upon adsorption at mirrored Ag (Figure 11c), the $\nu_s(CH_3)$ of octadecanethiol is only a shoulder on the $\nu_a(CH_2)$ at 2883 cm^{-1}. This reflects the increased ratio of methylene to methyl groups in octadecanethiol compared to dodecanethiol.

Comparing the surface spectra for mirrored Ag (Figures 9d, 10c, 11c) to those for rough Ag (Figures 9e, 10d, 11d) for all three molecules, one notes that in most respects, the spectra are the same. Differences in the relative intensities of the $\nu_s(CH_2)$ bands and the Fermi resonance bands are frequently observed for different samples with adsorbed butanethiol and, to a lesser extent, dodecanethiol.

In general, it is found that surface Raman spectra of long-chain alkanethiols adsorbed at roughened surfaces are similar to spectra obtained from smooth surfaces. Butanethiol appears more sensitive to surface morphology and exhibits more G intensity at roughened surfaces than smooth. These results are consistent with a study published previously.[2] In wetting studies of octadecanethiol at Au films evaporated on smooth and rough Si wafer surfaces, Bain and co-workers reported no significant differences in advancing contact angles between smooth and rough surfaces. They esti-

---

(34) Claassen, H. H.; Selig, H.; Shamir, *J. Appl. Spectrosc.* **1969**, *23*, 8. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 4th ed.; John Wiley: New York, 1986; p 72.

mated their roughness features to be on the order of micrometers. However, they did report an increase in the hysteresis of the measurement at rough samples.

Defects in Films with Change in Chain Length. Previous reports of octadecanethiol adsorbed at Au have hypothesized that the molecules of the film are in the all-trans conformation by analysis of the C–H stretching frequencies obtained with reflection IR spectroscopy.[6,8] Surface Raman spectra for octadecanethiol adsorbed at Ag reported below show conclusively the absence of the G ν(C–C) band, similar to the spectrum for solid octadecanethiol.

In contrast, defects within the alkane chain of adsorbed dodecanethiol are observed. In the ν(C–C) region, a large G intensity is observed. The presence of the G band in the adsorbed spectra correlates to the behavior observed in solid dodecanethiol which also exhibits significant G intensity. The number of defects in the adsorbed film may actually be small, because the intensity of the G band is not linear with G concentration.[32] The behavior of adsorbed butanethiol is similar to that of octadecanethiol. Little G intensity is seen for adsorbed or solid butanethiol.

The disorder implied in the Raman spectra of alkanethiol films of intermediate length is similar to the disorder suggested in the data of Porter and co-workers.[8] They studied a series of films in alkanethiols at Au ranging from butanethiol to octadecanethiol and docosanethiol using reflectance IR spectroscopy. In the plot of absorbance of the $\nu_s(CH_2)$ band versus chain length, experimental values were compared to values interpolated from the absorbance of docosanethiol and the origin. The largest deviation from the interpolated values was the absorbance of dodecanethiol. The other alkanethiols exhibited absorbance values closer to the interpolated plot. While the effect upon the methylene absorbance was not understood, they concluded that molecules shorter than hexadecanethiol form less densely packed films. Whether dodecanethiol represents a unique chain length or whether a minimum in order occurs as chain length increases from butanethiol to octadecanethiol is uncertain at this time. Further work is in progress to determine this aspect of self-assembling monolayer systems.

G conformations are presented in the vicinity of the C–S bond in all of the films studied here as evidenced by the persistent, albeit small, G ν(C–S) intensity. G conformers may be the result of the morphology or grain structure of the polycrystalline Ag surface, because the intensity ratio of the G to T bands is similar for all three alkanethiols adsorbed at Ag. The polycrystalline surface may allow defects to occur in the film, because lateral chain interactions at grain boundaries will be different from those in crystalline domains on the surface.

Underpotential deposition (UPD) of Pb was used to determine whether gross defects in the monolayer films at polycrystalline Ag surfaces were present. At bare Ag electrodes, a separate deposition wave corresponding to the formation of a Pb monolayer on Ag is observed at potentials positive of the bulk deposition potential of Pb. The surface area of bare Ag can be quantitated by measuring the amount of charge contained under the UPD stripping wave.[35] Figure 12 shows the cyclic voltammograms of Pb UPD at bare Ag and Ag modified with a monolayer of dodecanethiol. At bare Ag, the Pb UPD stripping wave peak is observed at −0.32 V, and the bulk Pb stripping wave is observed at ca. −0.44 V. For dodecanethiol-covered Ag, a bulk Pb stripping wave is observed at −0.43 V, but no Pb UPD stripping wave is observed. It is concluded that less than 0.5% of a monolayer of bare Ag is exposed in the dodecanethiol monolayer. Therefore, the polycrystalline Ag substrate does not produce gross defects in these alkanethiol films.

Orientation of Alkanethiols at Ag. A simple model for the orientation of alkanethiols adsorbed at Ag can be deduced using surface selection rules for Raman scattering. These rules are often called "propensity rules",[36] because the magnitude of the dielectric constants in the visible wavelength region result in less rigorous rules than those applicable in the infrared. These rules have been described elegantly by Moskovits[37] and Creighton[38] for rough surfaces.

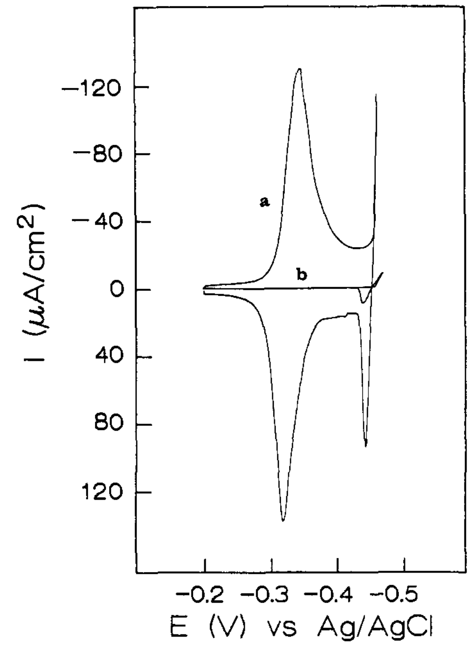

Figure 12. Cyclic voltammetry of Pb UPD from 0.1 M KCl/1 × 10^{-3} M Pb^{2+} with scan rate of 15 mV/s at (a) bare smooth Ag, (b) smooth Ag with adsorbed dodecanethiol.

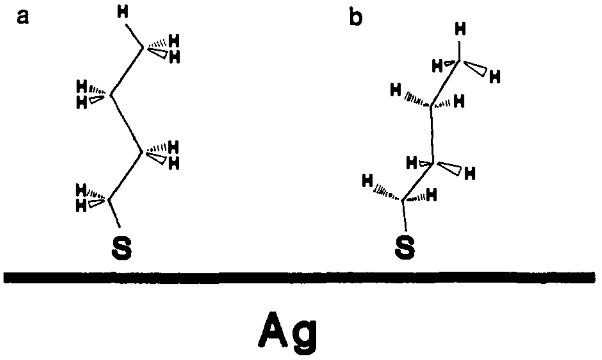

Figure 13. Models of orientation of 1-alkanethiols at Ag: (a) directly perpendicular, (b) tilt of 15° in the plane of the carbon backbone and rotation of 45° about chain axis.

Consider a molecule with its x, y, and z axes oriented such that the z axis is perpendicular to the surface. At SERS-active Ag surfaces with excitation red of the surface plasmon wavelength, vibrations of the molecules with a component along the z axis will be enhanced more than vibrations without a z tensor component. Vibrations with zz tensor components will be enhanced to a larger extent than vibrations with xz or yz components. Vibrations of the molecule having large components along the x or y will be only very weakly enhanced, and thus will result in low-intensity bands in the SERS spectrum.

1-Alkanethiol molecules have very low symmetry and belong, at best, in the C_s point group. Therefore, all vibrations of the adsorbed molecule have a component perpendicular to the surface in all orientations. Stretching vibrations, however, are assumed to have a larger contribution from the tensor component along the axis of the vibration. The stretching vibrations can therefore be used for interpretation of orientation in these systems. Stretches that are orthogonal will be enhanced by different amounts when comparing the Raman surface spectra to those of the bulk molecules.

A simple model of an adsorbed alkanethiol with the S atom attached to the Ag substrate and the alkane chain perpendicular

---

(35) Guy, A. L.; Bergami, B.; Pemberton, J. E. *Surf. Sci.* **1985**, *150*, 226.
(36) Otto, A. *Colloids Surf.* **1989**, *38*, 27.
(37) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.
(38) Creighton, J. A. In *Spectroscopy of Surfaces*; Clark, R. J. H., Hester, R. E., Eds.; John Wiley: Chichester, 1988; p 37.

Table IV. Peak Area Ratios for ν(C–S), ν(C–C), and ν(C–H) Regions in Bulk and Adsorbed Alkanethiols

	$I[\nu(\text{C–S})]/I[\nu(\text{C–H})]$	$I[\nu(\text{C–C})]/I[\nu(\text{C–H})]$
butanethiol		
liquid	0.13	0.10
adsorbed smooth Ag	0.64	0.44
dodecanethiol		
liquid	0.11	0.11
adsorbed smooth Ag	0.84	0.26
octadecanethiol		
liquid	0.084	0.080
adsorbed smooth Ag	0.52	0.24

to the Ag surface is shown in Figure 13a. The methylene ν(C–H) vibrations are orthogonal to the ν(C–C) vibrations. The intensities of the ν(C–S), ν(C–C), and ν(C–H) bands in the liquid and surface spectra were determined from the results discussed above for all three molecules. The ratios of the intensity of the ν(C–S) to ν(C–H) bands and the ν(C–C) to ν(C–H) bands were then calculated and are given in Table IV. The ν(C–S)/ν(C–H) ratio for butanethiol adsorbed at Ag increases by a factor of 5 relative to that of the bulk. The ratio for dodecanethiol adsorbed at Ag increases by a factor of 7.5 relative to that of the bulk, while the ratio for octadecanethiol adsorbed at Ag increases by a factor of 6. The significant increase in the intensity ratio for the surface spectra relative to the liquid spectra suggests that the C–S bond has a significant component perpendicular to the surface.

The ν(C–C)/ν(C–H) ratio for these molecules also increases in going from the liquid state to the adsorbed state. The increases are a factor of 4 for the butanethiol, 2.5 for dodecanethiol, and 3 for octadecanethiol. The carbon backbone must therefore also have a large component perpendicular to the surface.

Figure 9 shows the ν(C–H) region for solid and liquid butanethiol, aqueous butanethiolate, and butanethiol adsorbed at mirrored and rough Ag. Comparing the surface spectra to the thiolate spectrum, it is clear that the methyl stretches at ca. 2870, 2935, and 2960 cm^{-1} for adsorbed butanethiol are greater in intensity than the methylene bands. Furthermore, the $\nu_a(\text{CH}_3)$ band at 2967 cm^{-1} is enhanced more than the $\nu_s(\text{CH}_3)$ at 2878 cm^{-1}. Similar behavior can be seen for dodecanethiol in Figure 10. For octadecanethiol in Figure 11, the $\nu_s(\text{CH}_3)$ at 2876 cm^{-1} can be seen as a small shoulder in the surface spectra, but it is buried in the liquid spectrum. From these data, it is concluded that the plane of the methylene groups is mostly parallel to the surface and the C–S bond and the C–C bonds are mostly perpendicular to the surface.

Ulman and co-workers have calculated possible orientations of long-chain 1-alkanethiols at Au by computer modeling.[18] These researchers used the calculated minimum in energy of van der Waals interactions to predict the tilt and rotation of alkanethiols adsorbed at single-crystal Au. Two possible degrees of tilting, 0° and 30°, result in minimization of the free energy of the film. The free energy is lower for the 30° case. The degree of rotation about the chain axis that results in the minimum in free energy is ca. 55°.

Harris and co-workers have reported that methyl thiolate adsorbs to Ag(111) with the C–S bond perpendicular to the surface based on sum-frequency-generation spectroscopy.[39] Nuzzo and co-workers have determined that long-chain alkanethiol molecules at Au have a tilt of the alkane chain of ca. 40° with respect to the surface normal and a rotation about the chain axis of 50° from IR spectroscopy.[6] Porter and co-workers estimate the chain tilt to be 20° to 30° using IR spectroscopy and ellipsometry.[8] Strong and Whitesides estimate the tilt angle to be 25° to 35° using electron diffraction.[9] Ulman has reported that the tilt angle of octadecanethiol at Ag is less than 25° using IR spectroscopy.[12]

The results reported for Ag are generally consistent with the orientations proposed previously in the literature. However, a different value of the rotation about the chain axis is suggested by these data in order for the C–S bond to be mostly perpendicular to the surface. This is shown in Figure 13b. The plane of the carbon-backbone in the molecule in Figure 13a has first been tilted ca. 15° such that the C–S bond becomes largely perpendicular to the surface. Then the molecule is rotated about the chain axis ca. 45°. This proposed orientation in Figure 13b allows the C–S bond and C–C backbone to be largely perpendicular to the surface. The methylene groups are mostly parallel to the surface in this orientation. In addition, rotation of ca. 45° about the chain axis would position the methyl group somewhat parallel to the surface. The larger enhancement of the $\nu_a(\text{CH}_3)$ band compared to the $\nu_s(\text{CH}_3)$ band at 2876 cm^{-1} corresponds to the methyl group positioned more parallel to the surface. This picture of adsorbed alkanethiols at Ag is consistent with previous models. More detailed orientation information of alkanethiols adsorbed at Ag and Au substrates will be presented in a later publication.

Conclusions

Surface Raman scattering has been used to characterize self-assembled monolayers at smooth, polished Ag and electrochemically roughened Ag electrodes. Raman scattering is a very useful technique for investigating self-assembling alkanethiol monolayers, because vibrational information can be obtained from all locations within the molecule. For example, ordering and defect structure of the alkane chains can be directly investigated by observing G conformations of the carbon backbone. The alkane chain of adsorbed butanethiol is mostly in the all-T conformation. The alkane chain of adsorbed octadecanethiol appears totally free of G conformers. In contrast, adsorbed dodecanethiol shows a large number of G defects in the alkane chain. This behavior is consistent with that observed in the solid alkanethiols. The conformation of the C–C bond adjacent to the C–S bond is mostly T for all three alkanethiols.

These alkanethiols are proposed to be oriented with their alkane chain largely perpendicular to the Ag surface with the S head group bonded to the Ag surface. A chain tilt of ca. 15° with a rotation of ca. 45° about the chain axis is consistent with the surface Raman spectral intensities.

The Raman scattering results obtained from mirrored surfaces were found to be similar to those from electrochemically roughened surfaces. While it has been shown that surface Raman spectra can be obtained from smooth surfaces, it also has been shown that SERS results from surfaces with extensive roughening can be generalized to those from mirrored surfaces.

Acknowledgment. We are grateful for support of this work by the National Science Foundation (CHE-8614955). Helpful discussions with Dr. Marc D. Porter are also gratefully acknowledged.

Registry No. Ag, 7440-22-4; 1-butanethiol, 109-79-5; 1-dodecanethiol, 112-55-0; 1-octadecanethiol, 2885-00-9.

---

(39) Harris, A. L.; Rothberg, L.; Dubois, L. H.; Levinos, N. J.; Dhar, L. *Phys. Rev. Lett.* **1990**, *64*, 2086.