



Characteristics of alkanethiol self assembled monolayers prepared on sputtered gold films: a surface enhanced Raman spectroscopic investigation

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Self assembled monolayers (SAMs) of $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ($n=2, 5, 7, 8, 9, 11$ and 17) on polycrystalline gold films have been investigated using FT-Raman spectroscopy. All the thiols chemisorb dissociatively in the thiolate form and the adsorbate-surface interaction is the same in all the cases. Initial chemisorption occurs with fast kinetics and it is complete in the first few hours of exposure of the thiol to the surface. The formation of self assembly occurs rather slowly and the evolution of spectral features continues till 12–15 h of exposure. The change is pronounced particularly on the $(\text{C}-\text{C})_T$ stretching mode. Initial adsorption results in the $(\text{C}-\text{S})_G$ form and equilibration between $(\text{C}-\text{S})_T$ and $(\text{C}-\text{S})_G$ occurs rather quickly. In lower member thiols, equilibration occurs within about 30 min of exposure. Upon heating, the monolayers begin to desorb at about 348 K followed by melting of the close packed assembly. Spectrum upon melting resembles that of the liquid. © 1998 Elsevier Science Ltd. All rights reserved

Introduction

Organised molecular assembly has become one of the most important areas of modern chemical research. Of the variety of approaches used for the formation of organised molecular assemblies, the Langmuir-Blodgett methodology and self assembly are the two foremost important techniques.¹ Self assembled monolayers (SAMs) have been made with thiols,² disulfides,³ siloxanes,⁴ carboxylates⁵ and such other surfactants⁶ on appropriate surfaces. The versatility of SAM methodology to make functional monolayers⁷ has attracted considerable attention in the recent past. Towards this goal, we have been trying to modify the chemical functionality at the air-monolayer interface by low energy ion bombardment.⁸ Our studies have shown that prototypical surface transformations are possible by ion collisions. We have also been extending the ion interfacial chemistry to the solution phase as well.⁹

While investigating this chemistry, it became necessary to characterise monolayers by various techniques. In an earlier investigation¹⁰ of *n*-alkanethiol ($\text{CH}_3(\text{CH}_2)_n\text{SH}$) SAMs on gold by X-ray photoelectron spectroscopy (XPS) we have shown that secondary electron background of the photoelectron spectrum is a good measure of the monolayer thickness. The extent of order in monolayers was found to be maximum when *n* is around 7.

XPS binding energies were used to demonstrate the similarity of the binding environment in these monolayers.¹⁰

Essential tools for the characterisation of monolayers have been methods of electrochemistry¹¹ owing to their enhanced sensitivity. Ellipsometry,¹² wettability,¹³ reflection absorption infrared spectroscopy,¹⁴ sum-frequency spectroscopy,¹⁵ X-ray photoelectron spectroscopy,¹⁶ rare gas atom scattering¹⁷ and ion-surface collisions¹⁸ have been used to characterise SAMs. Although each one of these techniques has focussed on a few of the aspects of self assembly, infrared spectroscopy has shed light on most of the issues concerning their structure. Due to the rather stringent selection rules of surface Raman scattering, the technique can reveal important structural information. However, the poor sensitivity of the technique in its normal mode of operation has substantially hindered its applicability to these systems. Surface enhanced Raman spectroscopy (SERS), although surface sensitive, can be applied only to roughened surfaces.¹⁹ In spite of these limitations, it has been eminently applied to the study of SAMs. Particular relevance to this study are reports from the groups of Pemberton²⁰⁻²¹ and Kim.²²⁻²³

In this report, we present an investigation of *n*-alkanethiol monolayers by SERS. By effectively utilising our methodology to make surface enhanced Raman active gold films for the preparation of monolayers,²⁴ a systematic investigation of their SERS spectra could be undertaken. The study shows that for a given kind of substrate, the Raman intensity is a true measure of the surface concentration of the species of interest. We show that the

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nature of chemical bonding at the surface in a series of monolayers is similar. However, there are changes in orientational symmetry between them. It is shown that upon increasing the chain length, the C—C stretching frequency increases monotonically and the spectral region starts resembling that of the bulk solid, when n approaches 8. In order to investigate the evolution of self assembly, time dependent experiments have been performed. The thermal stability of monolayers is investigated using temperature dependent measurements. It is shown that long chain monolayers melt upon heating to a temperature of 348 K and the spectrum resembles that of the bulk liquid while desorption occurs. It is important to mention that all the thiols upon adsorption lead to the formation of orientationally restricted conformers at the surface, implying a frozen molecular assembly. The present studies are grossly in agreement with those reported in the literature²⁰ and reiterate the fact that the initial adsorption and subsequent assembly are two separate processes with different kinetics.

Experimental

Methodology to make surface enhanced Raman active gold films has been discussed in detail elsewhere.²⁴ Briefly, the method involves sputter coating gold up to a thickness of 2000 Å on oxidised aluminium foil in an Edward sputter coater. Aluminium foils of 20 μm thickness, were oxidised by heating in air for 5 h at 773 K. The foils were introduced into the sputter coater, immediately after heating and sputtering was done for 40 min in an argon plasma (discharge conditions: 1.3 kV, 5 mA). The evaporated gold films were characterised by scanning electron microscopy (SEM) which showed the presence of roughness in sub-micron dimensions.

Alkanethiol monolayers were prepared by following literature procedures.¹ One millimolar solutions of thiols in absolute ethanol were prepared and the freshly evaporated gold films were immersed in the solutions overnight. The films upon removal from the solution were washed repeatedly in absolute ethanol and air dried before the Raman measurement. The thiols were purchased from Aldrich and were used as received.

SER spectra were taken using a Bruker IFS 66v FT-IR spectrometer with a FT Raman attachment. Nd-YAG laser at 1064 nm was used for the excitation. All the spectra were collected with 500 scans. For the time dependent measurements, gold foils were exposed to the solutions for the appropriate period of time and the Raman spectra were measured immediately after taking them out of the solution. Temperature dependent measurements were performed using a home built heater with a programmable temperature controller. All the spectra are presented as raw data without smoothening or spectral manipulations.

Results and Discussion

Figures 1 and 2 present the SER spectra of $\text{CH}_3(\text{CH}_2)_n\text{S-Au}$ ($n = 2, 8, 11$ and 17) monolayers in the high and low frequency regions, respectively. Although we have studied the monolayers of various thicknesses for $n = 2$ to 18 , only representative spectra are shown. The frequencies observed and the assignments for representative monolayers are given in Table 1. Since the spectra of alkanethiols and thiolates have been discussed in detail in the literature²⁰ in the following we shall discuss only certain important regions pertaining to self assembly.

The C—H stretching region ($2800\text{--}3000\text{ cm}^{-1}$) shows five prominent peaks assigned to the characteristic aliphatic C—H

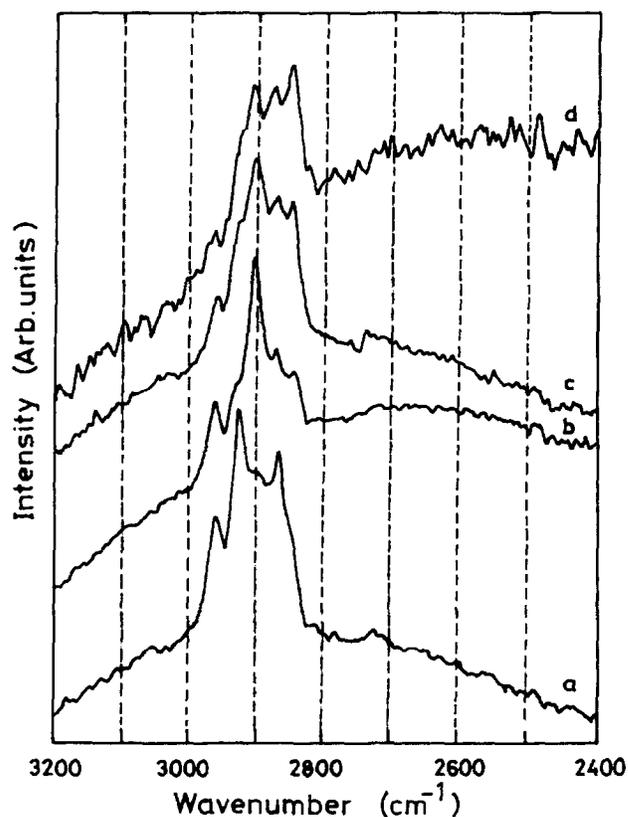


Figure 1. SER spectra in the C—H region of $\text{CH}_3(\text{CH}_2)_n\text{S-Au}$ monolayers. a, b, c and d represent $n = 2, 8, 11$ and 17 respectively. Spectra of only selected chain lengths are shown for the sake of clarity.

stretching features. An important aspect of the spectra is the gradual evolution of the CH_2 symmetric stretching mode at about 2850 cm^{-1} which gains in intensity upon increasing the chain length. Along with this, the asymmetric and symmetric CH_3 modes decrease in intensity. The peaks upshift upon increasing the chainlength as reported before.²⁰ The evolution in the band profile is comparable to that reported in the literature. Since the spectral region is complicated with the presence of $\delta(\text{C—H})$ overtones, we have reported only the prominent features in Table 1. In nonanethiol (see Fig. 1), $\nu_a\text{CH}_2$ band is anomalously intense for which we do not have an explanation. It appears that this is correlated with the intensity of the $(\text{C—S})_T$ conformer (see below).

Direct evidence of the cleavage of the S—H bond is provided in Fig. 1, where no S—H stretching mode is visible. The band is expected around 2570 cm^{-1} . Complete absence of this band and the downshift of the C—S frequencies from the free thiol values suggest that thiols dissociate at the surface and adsorb as the thiolate form. A discussion of the chemisorption event may be found in Refs 20–23. It is also important to note that in the time dependent measurements (see below) at no instant we observed S—H stretching.

Figure 3 shows the C—S stretching region ($600\text{--}750\text{ cm}^{-1}$) of the monolayers. The C—S region is characterised by two distinct peaks around 709 cm^{-1} and 635 cm^{-1} due to the C—S trans and gauche conformers, respectively. Adsorption results in the downshift of these bands by about 20 cm^{-1} consistent with the thiolate geometry. Except in the case of nonanethiol, which shows

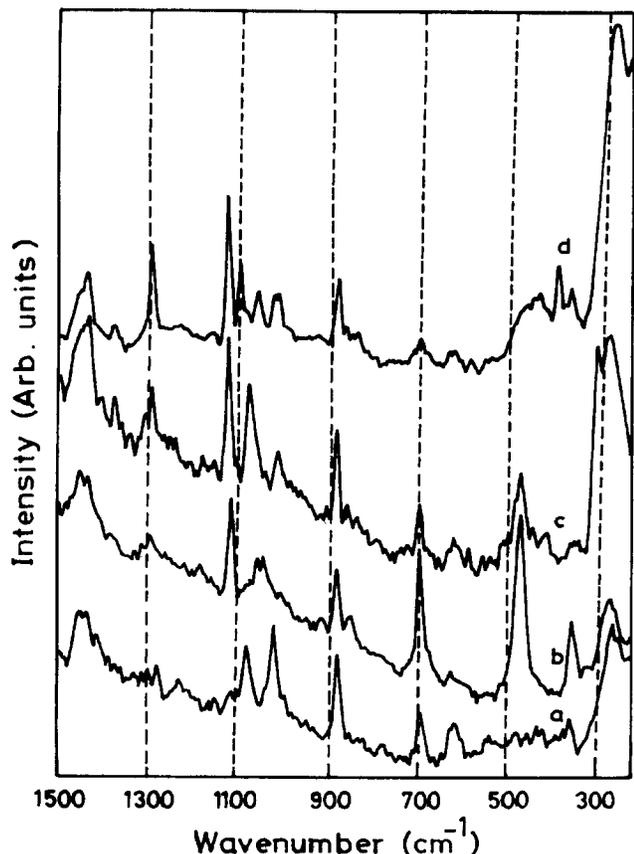


Figure 2. SER spectra in the low frequency region of $\text{CH}_3(\text{CH}_2)_n\text{S-Au}$. a, b, c and d represent $n = 2, 8, 11$ and 17 respectively.

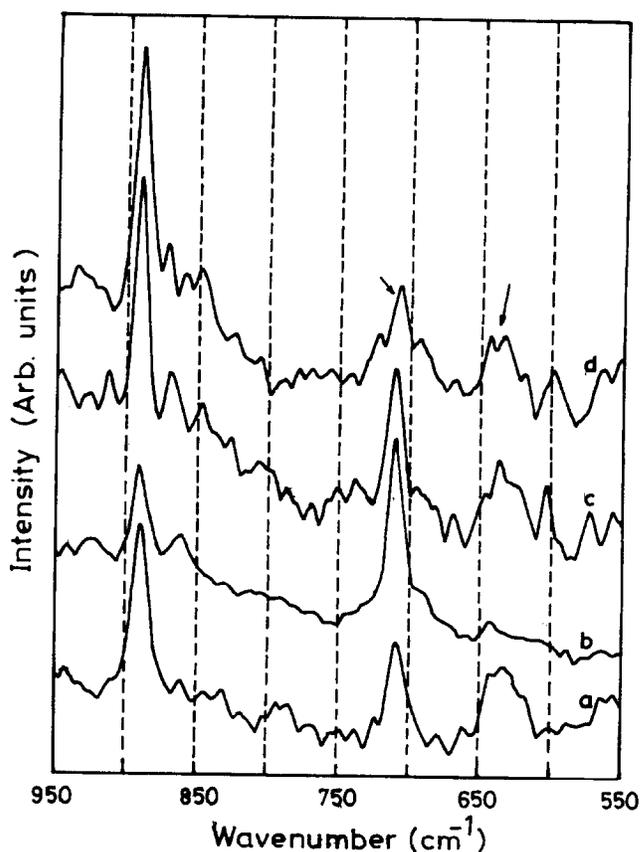


Figure 3. SER spectra in $\nu(\text{C-S})$ region for the monolayers. Note the changes in the $(\text{C-S})_T$ and $(\text{C-S})_G$ peaks (marked). a, b, c and d represent $n = 2, 8, 11$ and 17 respectively.

Table 1. The observed SERS frequencies (in cm^{-1}) of $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ($n = 2, 5, 7, 8, 9, 11$ and 17) monolayers and their assignments

Assignment	$n = 2$	$n = 5$	$n = 7$	$n = 8$	$n = 8^a$	$n = 9$	$n = 11$	$n = 11^b$	$n = 17$	$n = 17^c$
CCSdef(G)	289	292	294	294	—	286	294	—	283	—
CCCdef(G)	379	397	384	377	—	365	372	—	376	—
CCCdef(T)	—	—	—	—	—	—	—	—	408	—
CCCdef(T)	453	452	447	—	—	432	431	—	453	—
CCCdef(G)	—	488	487	490	—	461	489	—	489	—
$\nu(\text{C-S})_G^d$	634	637	—	—	641	634	634	641	638	642
$\nu(\text{C-S})_T^d$	707	710	707	709	706	704	709	709	709	713
$\text{CH}_2(\text{rock})_G$	—	848	834	863	—	862	867	—	862	—
$\text{CH}_3(\text{rock})_T$	889	891	890	891	—	891	892	—	891	—
$\nu(\text{C-C})_G$	—	—	1005	—	—	—	—	—	—	—
$\nu(\text{C-C})_T$	1026	1014	1032	—	—	1029	1020	—	1022	—
$\nu_s(\text{C-C})_T$	—	1070	1062	1062	1064	1062	—	1064	1064	1065
	1087	1109	—	—	—	—	—	1080	1101	1103
$\nu_s(\text{C-C})_T$	—	—	1119	1122	1120	1123	1127	1125	1130	1129
CH_2 wag	1284	1301	1303	1297	—	1301	1297	—	1297	—
CH_3 sy.def	—	1383	1376	1380	—	1380	1378	—	1377	—
CH_3 sy.def	1439	1439	1436	1437	—	1439	1437	—	1439	—
CH_3 as.def	1457	1453	1454	1456	—	1453	1458	—	1458	—
$\nu_s \text{CH}_2$	2854	2855	2851	2849	2854	2852	2850	2853	2850	2851
$\nu_s \text{CH}_3$	2870	2874	2874	—	—	—	—	—	—	—
$\nu_a \text{CH}_2$	—	—	—	2875	2880	2873	2873	2879	2879	2883
$\nu_a \text{CH}_2$	2900	2907	2905	2907	2907	2908	2905	2904	2908	2903
$\nu_s \text{CH}_3, \text{FR}$	2929	2933	2932	2934	2936	2932	2930	2932	2926	2932
$\nu_a \text{CH}_3$	2962	2962	2963	2965	2967	2962	2963	2963	2965	2965

^{a,b,c} from Ref. 20, ^d for propane thiol, the $(\text{C-S})_T$ and $(\text{C-S})_G$ peaks have been reported to occur at 635 and 705 cm^{-1} (Ref. 22).

only (C—S)_T form, all others show these two forms in varying intensity. The lack of (C—S)_G intensity in nonanethiol is surprising and may be correlated with the changes in the C—H region. Bryant and Pemberton²⁰ reported that upon increasing the roughness of the gold surface the (C—S)_G peak gains in intensity. Our surfaces are the same for all the monolayers and the absence of (C—S)_G cannot be attributed to a decrease in roughness. It tends to suggest that there is a range of chainlength in which (C—S)_G is preferred. It could also be correlated to the enhanced intensity observed for C 1s and S 2p in XPS around this chainlength.¹⁰ It is important to note that in lower member thiols, the intensity of the gauche form is substantially higher. However, the ratio of intensities do vary depending upon the film characteristics. It may be mentioned that the presence of (C—S)_G does not result in overall disorder in the system²⁰ as will be discussed later.

In Fig. 4 we present the C—C stretching region (1000–1200 cm⁻¹) of the monolayers. The evolution of the band shape is very similar as discussed by Bryant and Pemberton²⁰. In the lower member thiols the (C—C)_T gradually upshifts, on increasing the chain length and reaches a rather constant value of 1130 cm⁻¹ in octadecanethiol. Beyond octanethiol, the region resembles the spectrum of bulk solid, although the enhanced (C—C)_T intensity even in lower thiols is apparent. This suggests enhanced ordering resulting from frozen conformers even in short chain thiols. In the higher member thiols such as octadecanethiol monolayers, four peaks are seen in the spectrum whereas in lower member thiols less number of peaks are seen. In propanethiol SAM for

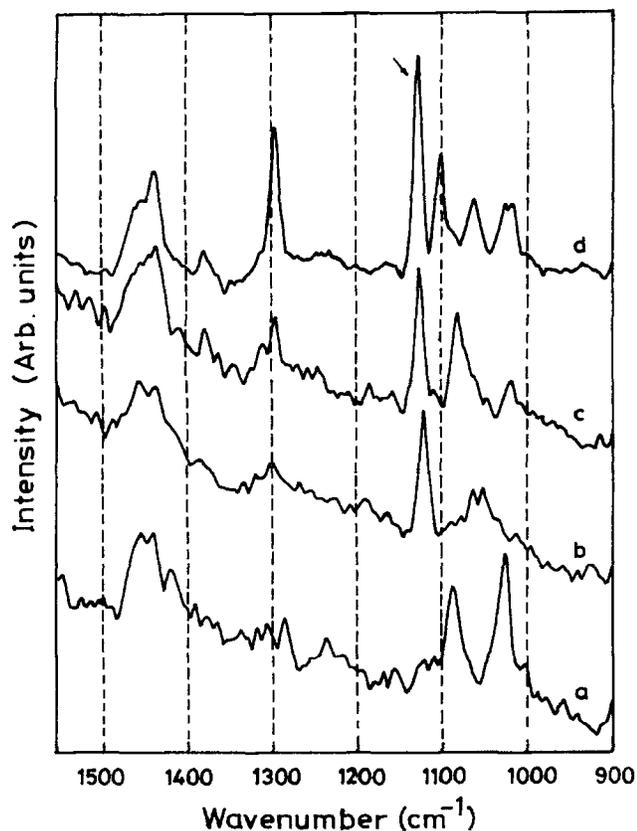


Figure 4. SER spectra of $\nu(\text{C—C})$ region of the monolayers. a, b, c and d represent $n = 2, 8, 11$ and 17 respectively. Note the upshift of the (C—C)_T peak (marked).

example, only two peaks are seen, this behaviour is similar to the corresponding liquids.

An important aspect to be noted in the spectrum of nonanethiol is that although the C—H and C—S regions show distinct differences from the rest of the thiols, there is no marked difference seen in the C—C region. In particular, although no (C—S)_G form is seen in nonanethiol, the C—C region does not show distinct differences from the other thiols. It can therefore be argued that the presence of (C—S)_G does not affect the arrangement of the alkyl chain above it. It may be stated that the formation of self assembly is complete irrespective of the substrate morphology.

In order to investigate the evolution of self assembly, time dependent measurements were performed on propanethiol, octanethiol and octadecanethiol SAMs. In these measurements, we exposed several films to the same solution for different intervals of time and the spectrum at each exposure time was measured keeping the experimental conditions the same. Evolution of the C—C region in octanethiol with time is shown in Fig. 5. At short exposure times, the spectra show the presence of all possible conformers and gradually the solid like spectrum evolves. The gradual emergence of $\nu(\text{C—C})_{\text{T}}$ is particularly noteworthy. The spectral change after 5 h of exposure is only marginal. The spectrum after 2.5 h of exposure resembles that of the solid with four prominent features which are assigned in Table 1. In addition to the changes in the C—C region, the spectrum also manifests the

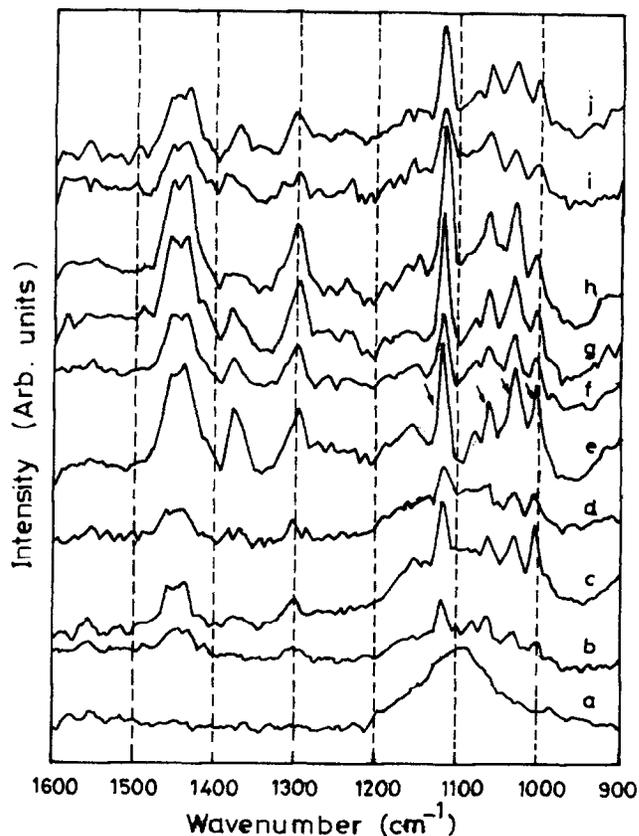


Figure 5. SER spectra of $\nu(\text{C—C})$ region of the octanethiol as a function of exposure time. The exposure times are, $t = 5$ min, 30 min, 1.5 h, 2 h, 2.5 h, 5 h, 10 h, 15 h, 20 h and 26 h for a, b, c, d, e, f, g, h, i and j, respectively. Note the evolution of the (C—C)_T bands.

evolution of band profiles of the CH₃ rocking and CH₂ wagging modes which also support the conclusions above.

The C—S region (Fig. 6), however, shows a marked change with time. Initially all the intensity is observed for (C—S)_G and gradually the (C—S)_T intensity picks up. It can be seen from these two Figures (5 and 6) that although the C—C region continues to evolve even after 5 h of exposure, the C—S region is more or less remaining the same. This may be used to argue that initial adsorption geometry is defined rather earlier and organisation of the alkyl chain continues to evolve even after this. Another important observation is that at no point any S—H stretching is observed. This excludes the possibility of initial thiol adsorption and its subsequent dissociation to the thiolate form.

In order to investigate the time dependence of adsorption geometry, we performed a study of time evolution of propanethiol monolayer (Fig. 7). Evolution of the two C—S forms is rather more clear here, where the two forms have almost the same intensity after long exposure. As in octanethiol, the initial exposure leads to the preferential formation of the gauche form and trans begins to gain intensity quickly. It may be recalled from the earlier spectra that the trans form begins to manifest only after 2.5 h of exposure in octanethiol. In propanethiol the (C—S)_T frequency is visible even after 30 min exposure suggesting

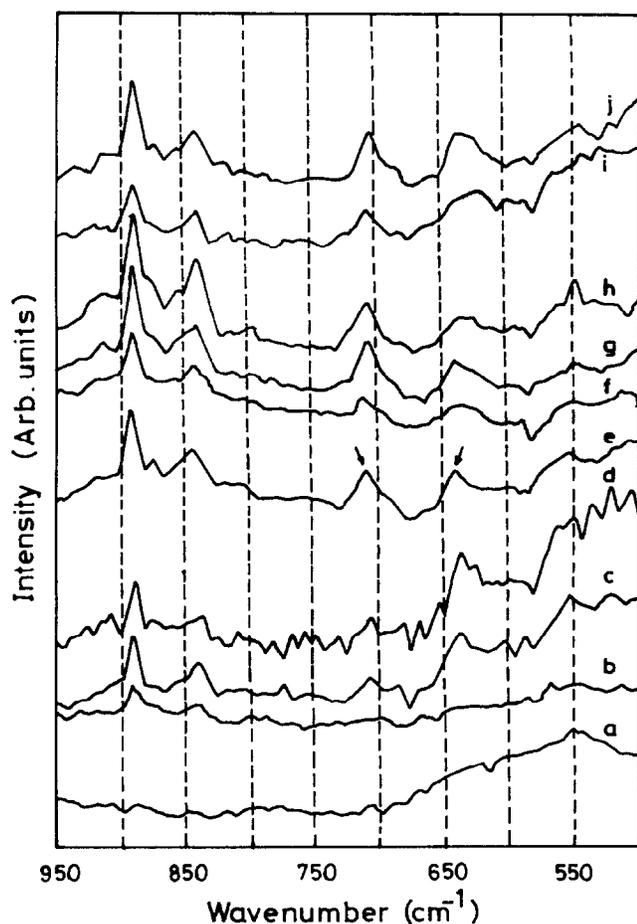


Figure 6. The SER spectra of $\nu(\text{C—S})$ region of octanethiol at various exposure times. The exposure times are, $t = 5$ min, 30 min, 1.5 h, 2 h, 2.5 h, 5 h, 10 h, 15 h, 20 h and 26 h for a, b, c, d, e, f, g, h, i and j, respectively. The (C—S)_T and (C—S)_G peaks are marked.

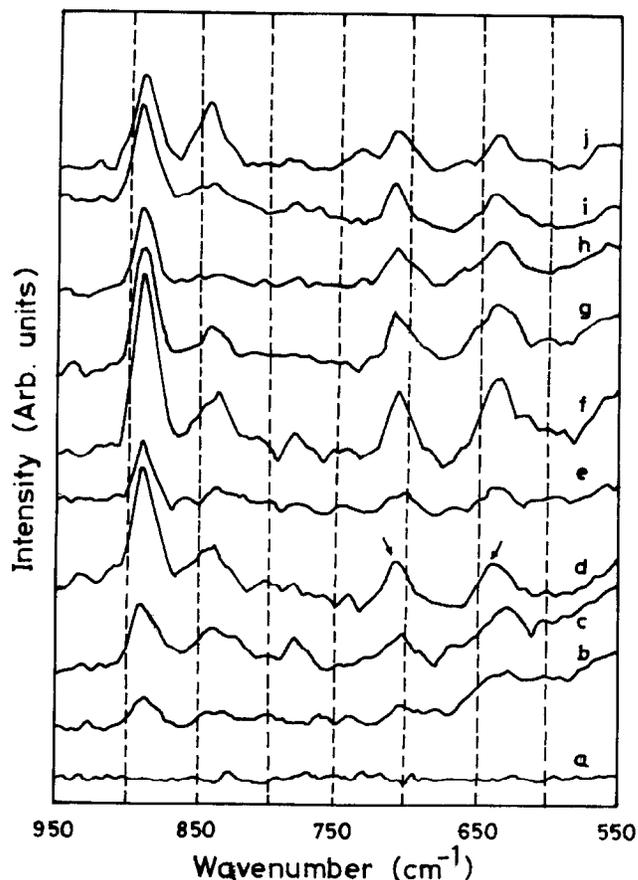


Figure 7. $\nu(\text{C—S})$ region of propanethiol monolayers at various exposure times. The exposure times are, $t = 5$ min, 10 min, 20 min, 30 min, 2.5 h, 3.5 h, 6 h, 8 h, 12 h and 15 h for a, b, c, d, e, f, g, h, i and j, respectively. The (C—S)_T and (C—S)_G peaks are marked. Compare the time evolution of these features with Fig. 6.

an early equilibration between the two forms in lower member thiols.

In the bulk liquid, the (C—S)_G form exists predominantly.²⁰ The presence of the (C—S)_G in the short time exposed samples is in accordance with direct adsorption from the liquid state, but from the thiolate form. The gradual conversion of the (C—S)_G to (C—S)_T suggest rapid equilibration of the gauche form to trans dictated by the energetics of adsorption. The fact that this equilibration is rapid in lower member thiols points to the lower energy barrier for the transformation between them.

In order to investigate the temperature stability of the monolayers, a temperature dependent study was undertaken. In Fig. 8 we show the temperature dependence of the C—C region of octanethiol. The monolayer begins to desorb at around 348 K as reported before.² Important aspect to be noticed is the remarkable reduction of $\nu(\text{C—C})_{\text{T}}$ intensity around that temperature. The spectrum at this temperature can be compared well with that of the liquid suggesting melting of the monolayer. Intensities of all the peaks decrease within a narrow temperature window of 348–373 K. Upon cooling the surface back to room temperature no features reappear suggesting the absence of any adventitious species at the surface. Substantial changes upon heating is seen in C—S region also (not shown). The (C—S)_T intensity decreases with temperature beginning at 348 K, a corresponding gain in the (C—S)_G feature is also observable. Beyond

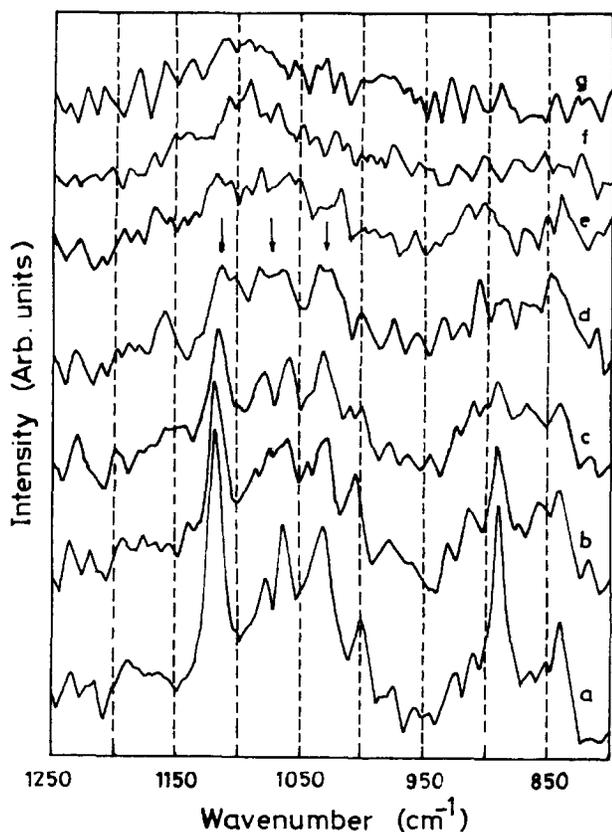


Figure 8. SER spectra of $\nu(\text{C—C})$ region of the octanethiol monolayer as a function of temperature. a. 301 K, b. 323 K, c. 348 K, d. 373 K, e. 398 K, f. 423 K and g. 448 K. Important features are marked.

373 K no C—S intensity is seen. The results suggest that the monolayer desorbs as an integral unit, a conclusion supported by earlier studies of thermal stability of monolayers.^{2,25} XPS measurements of alkyldisulfide monolayers also support the same conclusion, although the desorption occurs at higher temperatures.³

Conclusions

SERS study of a series of alkanethiols on gold has reaffirmed the earlier conclusions and has given some additional information on the formation and stability of self assembly. The thiols dissociatively chemisorb at these surfaces losing the S—H protons. The chemical state of the adsorbed species is same for all the thiols. Monolayer structure begins to resemble that of the solid around $n = 8$. The results suggest that the kinetics of adsorption and that of self organisation are distinctly different, this is par-

ticularly manifested in the time evolution of bands in the C—S and C—C regions. Adsorbate-surface equilibration occurs rather quickly in short chain thiols. The monolayer desorb around 373 K after melting to form a liquid like structure.

Acknowledgments

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