

Self-assembled Monolayers of Two Aromatic Disulfides and a Diselenide on Polycrystalline Silver Films: An Investigation by SERS and XPS

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Self-assembled monolayers of diphenyldisulfide (DDS), naphthalenedisulfide (NDS), and diphenyldiselenide (DDSe) on polycrystalline silver films have been investigated by surface enhanced Raman spectroscopy (SERS) and X-ray photoelectron spectroscopy (XPS). DDS adsorbs on Ag through a homolytic cleavage of the S-S bond and resultant thiolate at the surface decomposes upon prolonged exposure to air. The geometry of the molecule is such that the benzene ring is almost horizontal to the surface. The Raman spectrum has been assigned in the light of ab-initio molecular orbital calculations. In DDSe, the Se-Se bond is retained upon adsorption and the molecule sticks up. In contrast, NDS is highly reactive on the microscopically rough surface so that a stable monolayer could not be prepared. A temperature dependent Raman study of the DDS monolayer shows the absence of any reorientation at the surface as one would expect from the adsorption geometry. XPS study complements the SERS data and shows the presence of Ag₂S on an NDS exposed surface. © 1999 Academic Press

Key Words: self-assembled monolayers; surface enhanced Raman spectroscopy; X-ray photoelectron spectroscopy; ab-initio MO calculations.

INTRODUCTION

Self-assembled monolayers (SAMs) have generated considerable excitement among scientists for well over a decade (1). Organic molecular films in general and SAMs in particular can have a wide variety of applications in the fields of chemical sensors (2), nonlinear optical materials, photo patterning methodology (3), etc. Following the early reports of Allara and Nuzzo (4) on the adsorption of organic thiols on gold, various aliphatic thiols were studied (5). Not only thiols but also organic disulfides adsorb on Au (6) and Ag (7) surfaces. The important aspect of self-assembly is to understand the chemical interactions between the underlying surface atoms and head groups of the adsorbent molecules. This necessitates the characterization of SAMs by various surface analytical techniques

such as X-ray photoelectron spectroscopy (XPS) (8), atomic force microscopy (AFM) (9), scanning tunneling microscopy (STM) (10), and surface enhanced Raman spectroscopy (SERS) (11). Other techniques such as ellipsometry (5a) and electrochemical studies (12) are also useful in characterizing the properties of monolayers. In spite of the large number of studies on long chain SAMs, only a few aromatic systems have been studied so far (13, 10c). Very few studies are available on selenium containing systems (14).

We have been investigating the structure and properties of self-assembled monolayers (8c, 15–17) using SERS and XPS. In a recent study (15) we showed that a monolayer undergoes a solid–liquid phase transition beyond 350 K. Monolayers of small aromatic dithiols such as 1,4-benzenedimethane thiol adsorb differently on gold and silver (16). In the case of 2-mercaptobenzothiazole (MBT) monolayers, the difference is not only in the adsorption geometry but also in the chemical state (17). Our earlier studies on the geometrical constraint of small aromatic disulfides by SERS, XPS, and electrochemistry lead to the understanding of SAM formation of diphenyldisulfide (DDS), naphthalenedisulfide (NDS), and diphenyldiselenide (DDSe) on polycrystalline gold films (14b). In this paper, we present comparative studies of SAM structures of DDS, DDSe, and NDS on polycrystalline silver films using SERS and XPS.

EXPERIMENTAL

For SERS measurements, an oxidized aluminum foil of 20- μm thickness prepared by heating it in air at 500°C for 5 h was sputter coated with about 2000 Å silver in an Edwards sputter coater. The silver used for coating was of 99.9% purity. The films prepared this way have been shown to be excellent substrates for SERS work (19). The films show corrugations in the submicrometer scale in scanning electron microscopy. All SERS measurements on these surfaces have given excellent spectra, the intensities of which were reproducible from batch to batch under identical conditions. Raman spectra were recorded with a Bruker IFS 66V FT-IR spectrometer with a FRA

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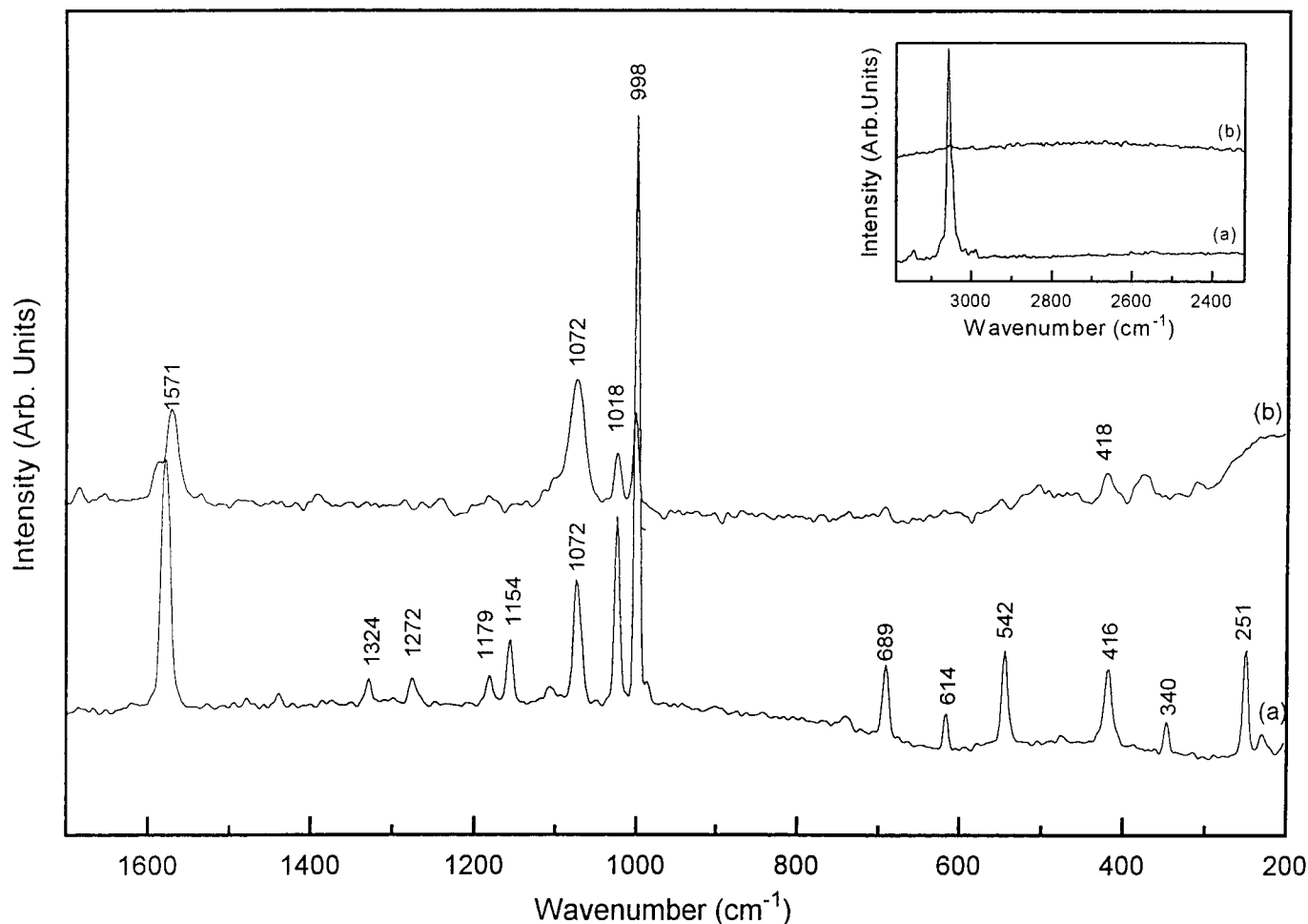


FIG. 1. (a) The normal Raman and (b) the SER spectra of the monolayers on Ag of DDS. Note the feature at 1585 cm^{-1} . The C-H region of the respective systems is shown in the inset.

106 Raman accessory. A Nd-YAG laser of 1064 nm was used as the primary excitation source. A laser power of 70 mW was used. Each spectrum was an average of 500 scans and the spectral acquisition took nearly 30 min. The temperature dependent measurements were done with a home built heater with a programmable temperature controller.

XPS measurements were performed on the SAMs using a VG ESCA LAB Mk II spectrometer operating at a pressure better than 10^{-9} torr. The time interval between preparation of the SAM and its mounting in the XPS chamber was kept to a minimum (ca. 30 min) in order to reduce contamination. The $\text{MgK}\alpha$ -induced core level spectra in the C 1s, Ag 3d, O 1s, and S 2p (or Se 3p) regions were recorded at an overall instrumental resolution of 1 eV. All the binding energies (BE) were referenced to the Ag $3d_{5/2}$ peak at 368.2 eV . The X-ray flux was kept low to reduce beam-induced damage (electron power, 70 W).

Ab-initio MO calculations were performed with the Gaussian 94 system of programs (20) in the HF/3-21G* level on

DDS. Calculations were performed on two geometries, a C_{2v} conformer in which two phenyl rings face each other and a C_{2h} conformer in which the two phenyl rings lie on paper in a transconfiguration. Both these geometries gave similar vibrational frequencies and therefore, only the C_{2h} values are presented.

RESULTS AND DISCUSSION

SERS Studies

Figure 1 shows the ordinary Raman (OR) and SER spectra of DDS on Ag. The peak at 542 cm^{-1} corresponding to the S-S stretching (21) in the OR spectrum is completely absent in the SER spectrum. This indicates the breaking of the S-S bond upon adsorption on Ag, which presumably involves homolytic cleavage of S-S bonds (7). Support for the silver-sulfur interaction on the surface is obtained from the weak broadband in the low frequency region (22) of the SER spectrum. Evidence for the breaking of S-S bonds on adsorption also came from the

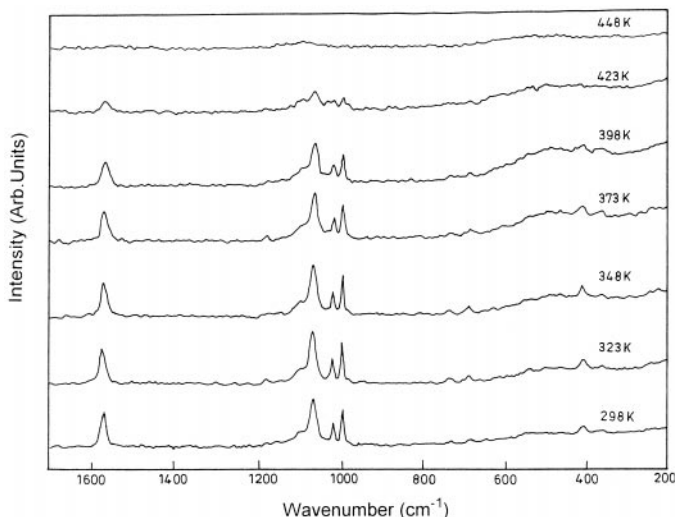


FIG. 2. The temperature dependent SER spectra of DDS on Ag. Note that the spectra were measured immediately after the preparation of the monolayer.

absence of the C_6H_5-S-S bending mode, which is appearing at 340 cm^{-1} in the OR spectrum. The peaks at 998 , 1018 , and 1072 cm^{-1} are characteristic of the benzene thio group (7). Relative intensities of the peaks at 1571 and 998 cm^{-1} are decreased with respect to the peak at 1072 cm^{-1} upon adsorption. The ring mode appearing at 1571 cm^{-1} shifts substantially to a lower frequency on adsorption, indicating that there is significant π interaction with the surface (23). Along with this, the C-H stretching appearing at 3047 cm^{-1} in the OR spectrum is completely absent (see the inset of Fig. 1).

A reaction between organic disulfides and silver could occur as per the scheme, $RSSR' + 2Ag \rightarrow RSR' + Ag_2S$, where R and R' are organic groups. The reaction would be exothermic for diphenyl disulfide, considering the thermochemical values. Catalytic decomposition of dibenzyl disulfide (DBDS) on iron powder yields dibenzyl sulfide (7), which is in accordance with the above reaction scheme. In the case of DDS, the adsorbed species on the surface is C_6H_5-S , which is clear from the data presented. Therefore, it has been suggested (7) that the monosulfide (RSR') route is followed in the adsorption of DDS. This conclusion is supported by the weak peak around 1600 cm^{-1} in the spectrum (7), which is observed in DDS and DBDS adsorption but not in phenyl mercaptan adsorption. This is attributed to an organic by-product, which occurs during the adsorption. Therefore, the suggested scheme of adsorption pathway is



R' gets adsorbed on the surface contributing to the peak around 1600 cm^{-1} .

However, our studies suggest that such a scheme does not occur. As shown in Fig. 2, when the spectrum of a freshly prepared DDS is measured immediately, the 1585 cm^{-1} peak is not observed. This peak occurs in samples which have been exposed to air for a day or more. Therefore, it appears that initial adsorption occurs via a homolytic cleavage of the disulfide. However, the adsorbed thiolate species is susceptible for decomposition. It is important to note that thermal activation does not induce the formation of such a species. Therefore, it is likely that the decomposition of mercaptide species occurs by itself. Direct silver sulfide formation is also not suggested by XPS investigation (see below).

Schoenfish and Pemberton have recently examined the air stability of alkanethiol monolayers (11h). They concluded that exposure to laboratory air leads to oxidation of the thiolate group to sulphonate, sulfate, and other moieties and the major

TABLE 1
Optimized Structural Parameters Obtained from
ab-initio MO Calculations

Parameters	Values ^a
$R_{1,2}$	2.085
$R_{1,3}$	1.781
$R_{3,9}$	1.384
$R_{9,11}$	1.387
$R_{11,13}$	1.380
$R_{13,7}$	1.386
$R_{7,5}$	1.379
$R_{5,15}$	1.076
$R_{7,17}$	1.072
$R_{13,23}$	1.071
$R_{11,21}$	1.072
$R_{9,19}$	1.069
$R_{5,3}$	1.392
$\angle_{2,1,3}$	101.9
$\angle_{1,3,9}$	125.6
$\angle_{3,9,11}$	119.9
$\angle_{9,11,13}$	120.7
$\angle_{1,3,5}$	115.0
$\angle_{3,5,7}$	120.3
$\angle_{5,7,13}$	120.3
$\angle_{7,13,11}$	119.4
$\angle_{3,5,15}$	120.3

Note. The C_{2h} point group is assumed. The schematic structure illustrating the atomic labels is also given.

^a Distances (R) are in Å and angles (\angle) are in degrees. CCH angles were also optimized but were close to 120.3° and therefore, only one value is given.

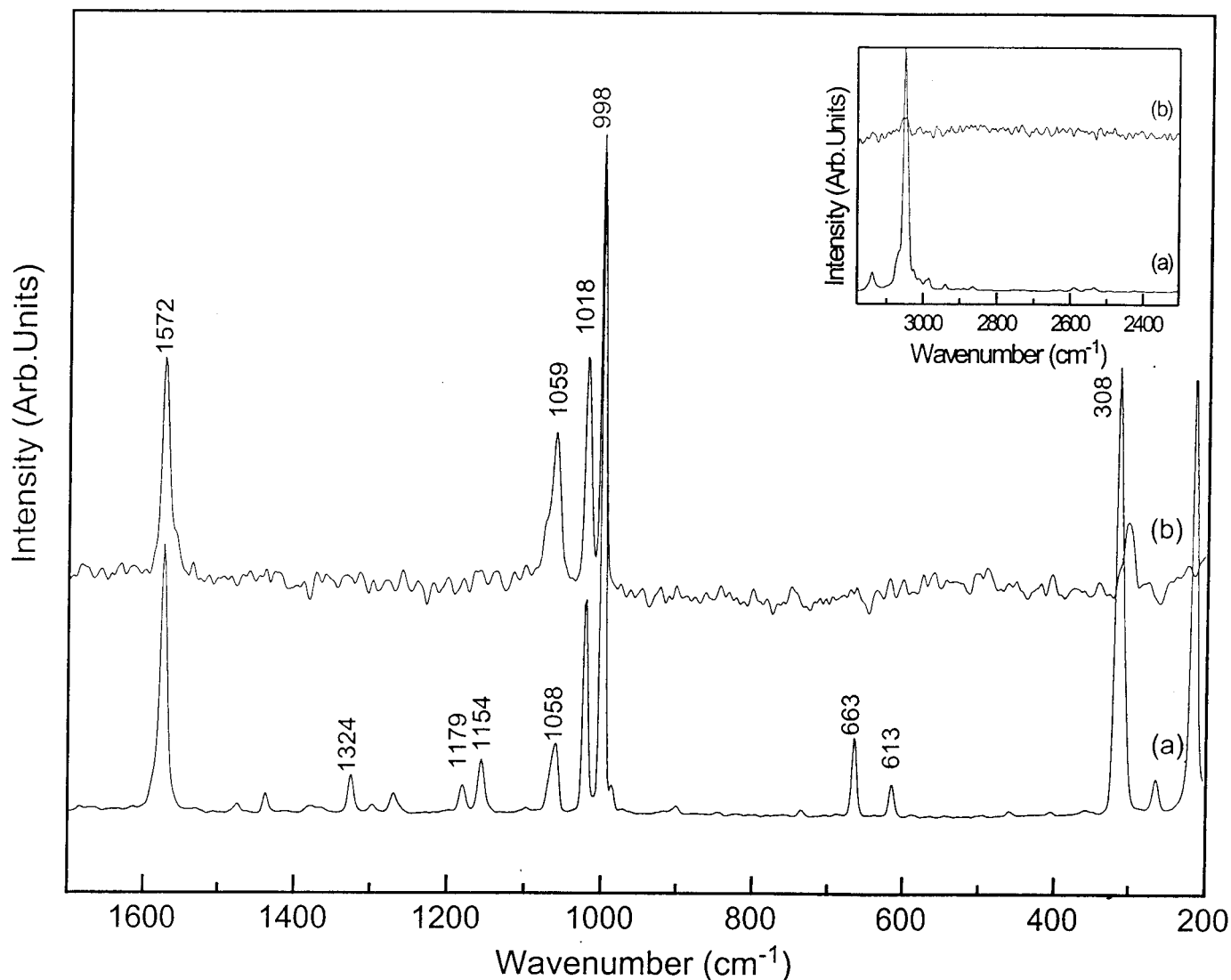


FIG. 3. (a) The normal Raman and (b) the SERS spectra of the monolayers on Ag of DDS. The C-H regions of the respective systems are shown in the inset.

culprit in the observed chemistry is ozone. Aromatic thiolate monolayers were believed to be more stable toward oxidation, but they also react with ozone. Oxidation occurs either directly or through a surface oxide. In the spectra presented in Figs. 1 and 2, no signatures of sulfate or sulfonate (or other oxidized sulfur) species are observed. However, the broad feature around 250 cm^{-1} is indicative of the Ag-S bond at the surface (22). This region is quite different for the fresh monolayer (Fig. 2) suggesting that the band may have a contribution from surface sulfide as well.

Figure 2 shows the temperature dependent SERS spectra of DDS on silver. Like in the case of BDMT on Ag (16), no dynamics involving the monolayer is observed with an increase in temperature. The monolayer desorbs around 175°C . This implies that the monolayers are stable and the molecule is adsorbed strongly on the surface, which does not permit the

phenyl ring to move freely to show any dynamics. Except for the split of 1018 cm^{-1} peak at 150°C , no apparent changes are seen in the variable temperature spectra of DDS on Ag. The splitting may be due to small conformational changes happening in the molecule but we are unable to suggest the exact nature of changes due to a lack of adequate intensity of these features.

In order to assign the SERS spectrum of the DDS monolayer, ab-initio MO calculations were performed. The optimized structural parameters are predicted in Table 1. The predicted frequencies presented in Table 2 match well with experimental values. This particularly lends support to the assignment of the S-S stretching mode, which is not observed upon monolayer formation. The calculations also suggest that the 3-21G* basis set is reasonably adequate to describe the molecular properties accurately.

TABLE 2
Comparison of the Normal Raman Frequencies of DDSe and DDS and the SERS Frequencies of the DDSe and DDS Monolayers on Ag with the Theoretical Raman Frequencies of DDS from HF/3-21G* Calculation

DDSe ^a		DDS ^a		Scaled (0.9) Raman frequencies from HF/3-21G* calculation on DDS	Assignments ^b
Solid	SERS	Solid	SERS		
				239	
256		262		261	
308	301	340			ν Se-Se δ C ₆ H ₅ -S-S
351			367		
		416	418	413	δ (o) C-H
				447	δ C-S
493	485		504	490	δ C-H
		542		541	ν S-S
613		614			
663		689		701	δ (i) ring
729	734				
897					
997	998	997	998	990	Phenyl ring vibrations
1019	1018	1019	1018	1028	
1058	1059	1072	1072	1072	
		1099		1083	
1154		1154			
1178		1179	1184(w)		C-C-H deformation
1268		1272			
1293					
1324		1324		1366	C-H deformation
1362					
1474		1474(vw)			
1572	1572	1572	1571	1572	ν C=C (symmetric)
2944(w)					
				3017	ν C-H
3054(s)	3047	3051	3047	3048	ν C-H
				3064	

Note. The molecular point group is assumed to be C_{2h}.

^a S, W, and VW refer to strong, weak, and very weak bands, respectively.

^b ν , δ , o, and i refer to stretching, bending, out-of-plane, and in-plane vibrations, respectively.

Figure 3 shows the ordinary Raman spectrum of DDSe and the SER spectrum of the DDSe monolayer on Ag. The characteristic bands of the phenyl group appear at 998, 1018, and 1058 cm⁻¹ as in the case of DDS. The intensity of 998, 1018, 1058, and 1571 cm⁻¹ bands is similar to that of the solid. Unlike the case of DDS on Ag, it is apparent from the preservation of the Se-Se stretching vibration (24) at 308 cm⁻¹ that the Se-Se bond is not broken on the surface. Preservation of the dichalcogenide (S-S or Se-Se) bond upon adsorption on Ag is reported for the first time. The Se-Se stretching vibration undergoes a red shift of 7 cm⁻¹ upon adsorption suggesting a weak chemisorption. The ring mode appearing at 1571 cm⁻¹ shows negligible shift suggesting that the phenyl rings are not lying parallel to the surface. The presence of a C-H vibration at 3047 cm⁻¹ (shown in the inset of Fig. 3) also supports the

above geometry. A list of Raman frequencies and assignments are given in Table 2.

For NDS, although a monolayer could be formed on polished surfaces, on roughened surfaces such as in the case of a SERS active substrate, high reactivity is observed. Upon exposure to such a surface, the compound appears to decompose and a blackened surface results, presumably due to Ag₂S. SERS measurements gave a featureless spectrum. However, on polished surfaces, good quality monolayers compatible for XPS measurements were obtained, which of course did not show SERS activity.

SERS selection rules (25) imply a large enhancement of modes whose transition dipole moments are perpendicular to the surface and a relatively poor enhancement of modes parallel to the surface (26). This general principle has been used to

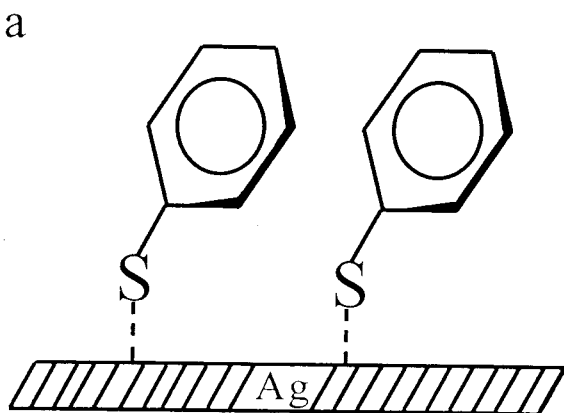
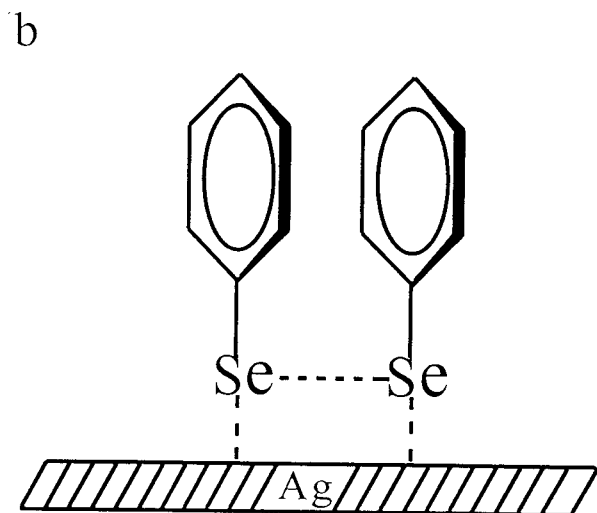


FIG. 4. Schematic representations of (a) DDS and (b) DDSe monolayers on the Ag surface.

infer the adsorption geometry of a large number of systems (27). Looking at Figs. 1 and 3 it is clear that the ring mode at 998 cm^{-1} is more enhanced relative to the ν_s mode in DDSe than in DDS. It is also clear that more or less the intensity pattern of the solid is retained in the DDSe monolayer, whereas in DDS a rather different intensity pattern is observed. This, along with the retention of the Se-Se bond in DDSe, implies that its molecular geometry is less affected upon adsorption. In DDS, the distortion is more. It is also seen that the bands are much broader in DDS than in DDSe upon adsorption. All these indicate a stronger electronic interaction in DDS than in DDSe. An increase in the width of certain bands indicates a more efficient way of relaxation of the vibrational quantum, which could arise due to the coupling of the modes with the surface. It is important to note that this coupling is more intense on bands which are essentially along the plane of the phenyl ring. This indicates that the ring lies flat on the surface. The absence

of aromatic C-H stretching modes also supports the same argument.

The "lying flat" geometry of the molecule also makes it possible for the facile cleavage of the C-S bond making the formation of silver sulfide. The cleavage can also produce aryl groups. Note that a new frequency appears at 1585 cm^{-1} in surfaces exposed to the laboratory air for some time. This frequency is higher than that of the free molecule. This suggests that the new species responsible for this mode cannot be benzenethio group. Therefore, we attribute it to the adsorbed phenyl group or benzene, although the origin of hydrogen is unclear. Thus, initial adsorption occurs via the homolytic cleavage of the disulfide bond and in a subsequent reaction, presumably, $\text{RS-Ag} + \text{Ag} \rightarrow \text{R} + \text{Ag}_2\text{S}$, the adsorbed benzenethio moiety decomposes. This reaction appears to involve a constituent of air, which requires further study. The phenyl group generated could be adsorbed to the surface.

The schematic structures of DDS and DDSe monolayers on

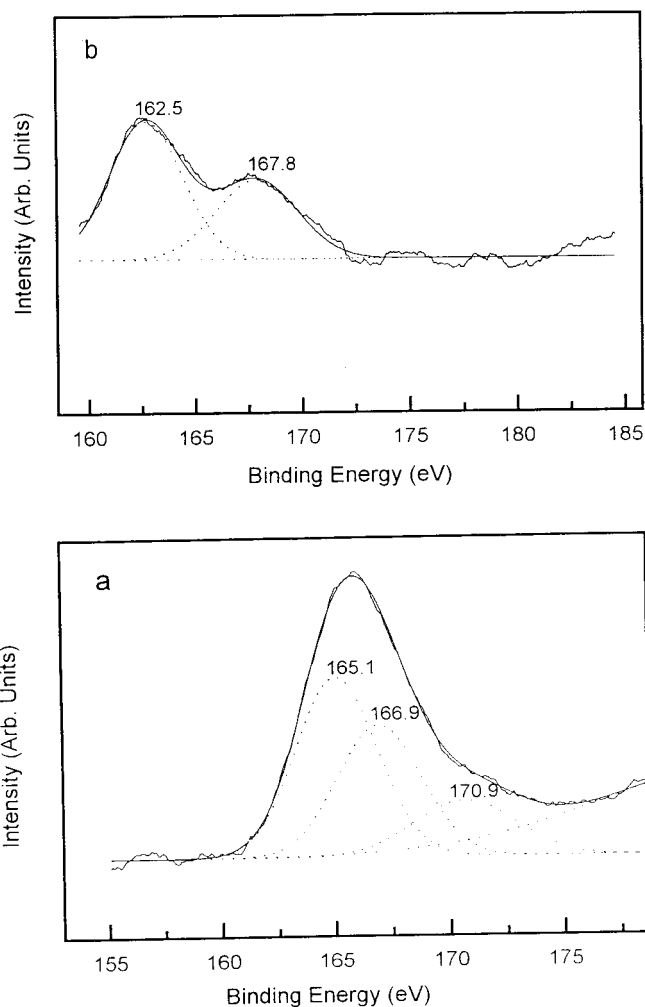


FIG. 5. $\text{MgK}\alpha$ -induced XP spectra of the monolayers. (a) $\text{S}2p$ of DDS and (b) $\text{Se}3p$ of DDSe. The spectra have been fitted with gaussians after background subtraction. The original data, component peaks, and the fit are shown.

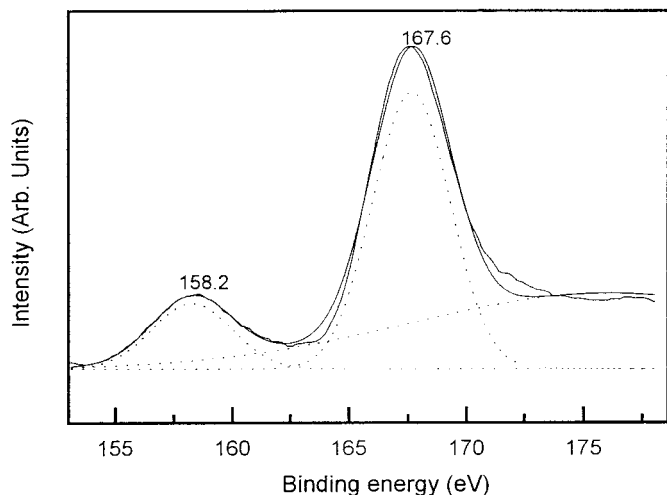


FIG. 6. $MgK\alpha$ -induced XP spectrum of the NDS monolayer in the S2p region. The spectra have been fitted with gaussians after background subtraction. The original data, component peaks, and the fit are shown.

Ag are shown in Fig. 4. Adsorption of alkanethiolates (1a) on Ag(111) results in a $(\sqrt{7} \times \sqrt{7}) R10.9^\circ$ overlayer with a S...S distance of 4.41 Å, which is smaller than the interchain distance of crystalline paraffins. Thiophenolate monolayers are also suggested to have similar adsorbate structure (1a, 10c). In this structure, both the on-top and the hollow sites are occupied by the thiolate groups. Although this structure is possible for DDS, it is not likely for DDSe, because of the preservation of the Se-Se bond. The Se-Se bond length (2.29 Å) (28) is considerably smaller than the lattice constant of Ag (2.89 Å) and therefore, if one Se occupies a threefold or on-top site, the other can only bind to a bridge site. This kind of adsorption, to the best of our knowledge, is reported for the first time.

XPS Studies

XPS measurements provide valuable information on the structure and the extent of beam induced damage on the above three monolayers. Fig. 5 shows the S2p region of DDS and NDS monolayers and the Se3p region for the DDSe monolayer. For DDS on Ag, the S2p appears as a broad structure peaking at 165 eV shifted substantially from thiolate structure which is observed at 162 eV for alkane thiol on Au and Ag (5a, 16). A gaussian fitting of the peak shape resulted in three structures (after appropriate background subtraction). The widths of the first two deconvoluted peaks are comparable for those seen for S2p (see below). The higher BE structure, having a higher width, may be a composite peak. All of these structures correspond to X-ray beam induced products of the thiolate. Various species such as sulfate, sulfite, and sulphonate have been reported in the literature (18). The main line, at 165.1 eV, has been assigned to the nearly integral monolayer.

The $Se3p_{3/2}$ and $3p_{1/2}$ structures are observed at 162.5 and 167.8 eV BE, respectively. These values are close to the values

at 162.2 and 167.8 eV obtained for tetramethyltetraselenofulvalenes (TMTSF) (29). The retention of the Se-Se bond at the surface implies that there can be two kinds of seleniums at the surface. It may be noted that if selenium atoms occupy the three-fold hollow sites (the normal binding site) separated at a distance of 2.89 Å, both selenium atoms cannot occupy the preferred sites retaining the Se-Se bond. If both have to be bound to the surface, either the on-top or the bridge sites have to be involved. In either case, the two kinds of seleniums will have similar charges and the binding energies of these species

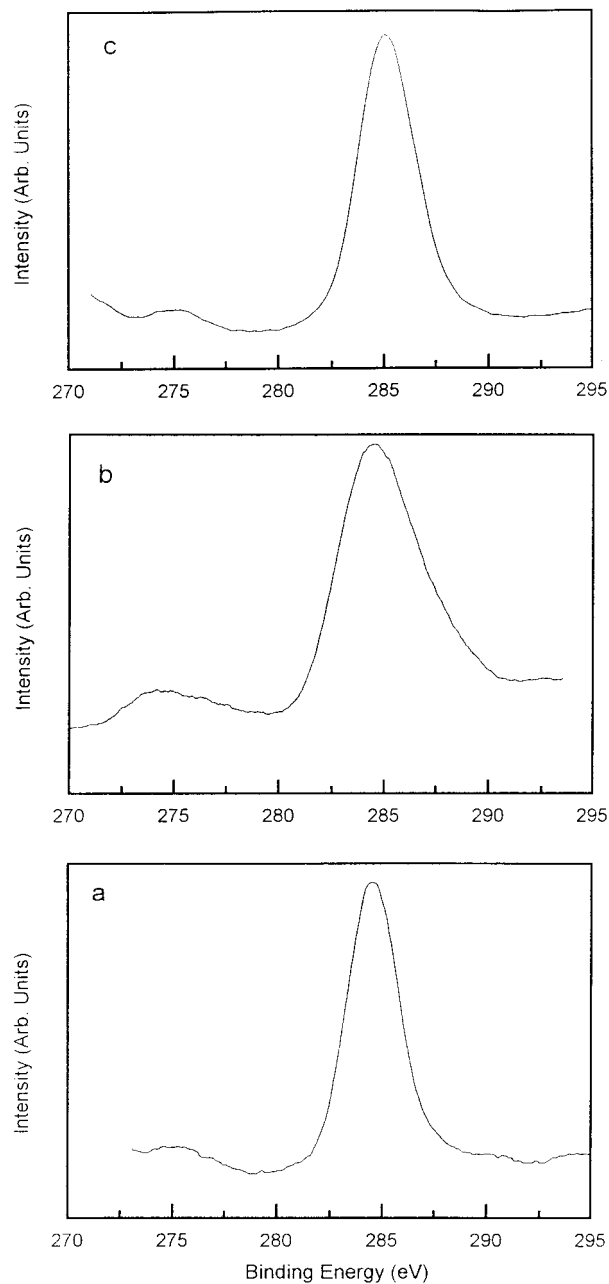


FIG. 7. $MgK\alpha$ -induced XP spectra of (a) DDS, (b) DDSe, and (c) NDS monolayers in the Cls region.

will be within 1 eV, which will not be resolvable in the present measurements. It is seen that seleniums do not show oxidation at the surface; a similar situation is observed for DDS on Au as well (14b).

In NDS on Ag (smooth film), there are two sulfur peaks, one appearing around 158.2 eV and the other around 167.6 eV (Fig. 6). The former peak occurs at a much lower value than the thiolate (RS^-) species which shows a BE of 162 eV. The low BE peak is attributed to Ag_2S at the surface. The observation of this peak supports the blackening of the SERS active rough surfaces upon exposure to NDS solutions. The latter peak appearing at 167.5 eV is attributed to the beam induced damage product, sulfate, or sulphonate (18). It may be pointed out that the beam-induced damage is more severe on more disordered monolayers (30). The higher intensity of this structure indicates that the surface is more disordered than that of DDS.

At this point, it may be mentioned that a similar effect is seen in our studies on the corresponding monolayers on Au (14b). Temperature dependent SERS studies of the Au monolayers show that the NDS monolayer is the least stable one thermally (14b). This monolayer shows a more severe X-ray induced damage. The DDS monolayer, although susceptible for damage, shows also the thiolate-like structure at 165.1 eV.

Figure 7 shows the C1s region of the XPS spectrum for DDS, DDS_e, and NDS monolayers on Ag. In all three cases, the carbon peaks occur at 285 eV. In the case of DDS_e, the peak shape is asymmetric in the higher binding energy region. This may be due to a difference in the binding sites for the two selenium atoms and consequent changes in the electron densities of the two phenyl rings.

CONCLUSION

The above results clearly indicate that DDS forms an organized and stable monolayer on Ag compared to DDS_e and NDS on Ag. SERS study shows that the monolayer formation involves the breaking of the S-S bond on the Ag surface in the case of DDS and the preservation of Se-Se bonds in DDS_e. The initial chemisorption of DDS involves the homolytic cleavage of the S-S bond but the thiolate at the surface is susceptible to decomposition. The temperature dependent SERS study of the DDS monolayer shows that it is stable and no dynamics is observed upon an increase in temperature. SERS provides clear evidence for the flat geometry of the phenyl rings in the case of DDS. This geometry appears to enhance the cleavage of the S-R bond leading to the formation of Ag_2S . There is damage of the monolayer upon X-ray exposure. The damage is severe in NDS compared to DDS and DDS_e on Ag. This increased damage may be due to the unavailability of proper adsorption sites on the Ag surface for both the sulfurs causing weaker binding for one sulfur atom.

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