Near-Infrared Surface-Enhanced Raman Scattering Study of Ultrathin Films of Azobenzene-Containing Long-Chain Fatty Acids on a Silver Surface Prepared by Silver Mirror and Nitric Acid Etched Silver Foil Methods

Yuqing Wu,* Bing Zhao, Weiqing Xu, and Bofu Li

Key Laboratory of Supramolecular Structure and Spectroscopy, Jilin University, Changchun, 130023, P. R. China

Young Mee Jung and Yukihiro Ozaki

School of Science, Kwansei-Gakuin University, Uegahara, Nishinomiya 662-8501, Japan

Received December 31, 1998. In Final Form: March 16, 1999

Near-infrared (NIR) Fourier transform (FT) surface-enhanced Raman scattering (SERS) spectra were measured for Langmuir—Blodgett (LB) and dipping films of azobenzene-containing long-chain fatty acids (nAmH, n = 8, 12, m = 3, 5) on silver substrates prepared by silver mirror and nitric acid etched silver foil methods. FT-IR spectra were also obtained for some of the films on silver mirror, silver foil, and CaF2 plate. The dipping films on the silver mirror always show much greater SERS effect than those on the silver foils, revealing that the silver mirror method is more powerful than the silver foil method in preparing the substrates suitable for the SERS measurements. The fatty acids assume the COO− form in the dipping films on the silver mirrors, while they mainly take the COOH form in the LB films on the silver mirror and CaF2 plate. Probably, silver reacts with the COOH groups during the dipping of the silver mirrors into the chloroform solutions of the azobenzene fatty acids. Bands at 1603 and 853 cm−1 due to the phenyl ring modes are enhanced markedly in the NIR-SERS spectra of the dipping films of 8A3H and 12A3H on the silver mirrors. Based upon the SERS “surface selection rule”, it may be concluded that the phenyl rings are nearly perpendicular to the silver mirror surfaces. Such enhancement is much weaker for the dipping film of 8A5H. Therefore, it seems that the length of the spacer (m) of the fatty acid is an important factor for the great SERS enhancement.

1. Introduction

Near-infrared (NIR) Fourier transform (FT) surface-enhanced Raman scattering (SERS) has become an important technique in the structural studies of adsorbed molecules on the roughened metal surface.1–6 The technique has advantages arising from both the NIR excitation and the SERS effect. By use of the NIR excitation, one can avoid both strong fluorescence and unfavorable photo-reaction of chromophoric groups of the adsorbed molecules at the same time. The SERS effect provides high sensitivity and high selectivity.7,8 Even one monolayer film can give a Raman spectrum with a high signal-to-noise ratio with the aid of the SERS effect. NIR-SERS is also very important for exploring the mechanism of SERS because the SERS effect shows a strong dependence upon the excitation wavelength.7,8 In our previous paper we reported NIR-SERS spectra of [4-{4-[(4-(alkyloxy)phenyl)azo]napthyl}oxy]alkyltriphenylammonium (CnAzoNaph(1,4)CnN−Br) in dipping and cast films and of CnAzoNaph(1,4)CnN−sodium dextran sulfate (SDS) in Langmuir—Blodgett (LB) films. In that study, we demonstrated the usefulness of the nitric acid etched silver foil method in yielding a strong SERS effect.4 To make the NIR-SERS method more useful, a more powerful method for preparing the roughened metal surface must be developed. In the present study, we have tried a silver mirror method recently proposed by Xue et al.9 and compared it with nitric acid etched silver foil method10,11 to study the SERS spectra of ultrathin films of azobenzene-containing long-chain fatty acids (nAmH, n = 8, 12, m = 3, 5; Figure 1).

Figure 1. Structure of azobenzene-containing long-chain fatty acids (nAmH, n = 8, 12, m = 3, 5).
LB and dipping films of nAmH and the interaction between the ultrathin films and the silver surface by use of NIR-SERS and FT-IR spectroscopy. IR spectroscopy was also used to provide complementary information about the structure of the films. We measured SERS of the LB and dipping films of nAmH with different alkyl chain lengths \((n = 8, 12; m = 3, 5)\) to investigate the effects of the length of alkyl chains on the SERS spectra and the structure of the LB and dipping films.

The structure and molecular orientation of LB films of azobenzene-containing long-chain fatty acids such as 12A3H and their salts have been studied extensively by ultraviolet and infrared spectroscopy.\(^{12,13}\) For example, Kawai et al.\(^{12}\) investigated the molecular orientation in the LB films of azobenzene-containing long-chain fatty acids and their barium salts by infrared transmission and reflection–absorption spectroscopy. They calculated tilt angles of the chain axis and various transition moments from the surface normal for the LB films of nAmH and their barium salts. Taniike et al.\(^{13}\) carried out spectroscopic studies on the phase transition of a LB film of 12A3H. Thus, comparison of the structure and molecular orientation in LB films of the azobenzene-containing long-chain fatty acids between the present study and previous studies is very interesting.

2. Experimental Section

Samples. nAmH (Figure 1) was purchased from Dojin Chemical Co., Ltd., Kumamoto, Japan, and used without further purification. Doubly distilled water was used throughout the experiments.

Etching Silver Foil. Silver foil with a thickness of 0.025 mm was immersed in vigorously agitated 3.5 M HNO\(_3\) solution at ambient temperature for a few minutes until the foil surface became milky.\(^{10,11}\) This procedure generated a sponge-type surface with abundant roughness on a 100 nm scale.\(^{10,11}\) After etching, the foil was thoroughly rinsed with distilled water and dried in the air.

Silver Mirror. A silver mirror was prepared by the Tollén’s test, which is widely used for the identification of aldehyde.\(^{14}\) A CaF\(_2\) or glass plate of 20 mm \(\times\) 10 mm \(\times\) 1 mm was put in a 10 mL beaker. A 5 mL aliquot of 0.02 mol/L silver ammonium solution and 0.05 mL of formaldehyde were mixed in the beaker. About 1 second after the mixing, the solution turned to gray and black. In the meanwhile, the silver ions were reduced and deposited on the CaF\(_2\) or glass plate to form a fine silver film called a silver mirror. After withdrawing, the silver mirror was washed with distilled water. A Shimadzu SPM-9500 atomic force microscope (AFM) and a Hitachi S2500C scanning electron microscope (SEM) were used for the measurements of the silver particle size in the silver mirrors. The results show that the size of the silver particles in the silver mirror is 250–400 nm.

Preparation of Dipping Films.\(^5\) The silver foil roughened with HNO\(_3\) or silver mirror was dipped into a chloroform solution (0.001 M) of nAmH for approximately 30 s in order to yield a reproducible coverage of the monolayer range. After withdrawing, the film was washed with chloroform and then dried in the air.

Preparation of LB Films. A Nima 622 Langmuir–Blodgett trough with a Wilhelmy balance was employed for the fabrication of the LB films. The monolayer was obtained by spreading a chloroform solution of 8A3H (0.001 M) on the subphase. After evaporation of the solvent, the monolayer was compressed at a constant rate of 10 cm\(^2\)/min up to the surface pressure of 20 mN/m. The \(\pi-A\) isotherm showed that the condensed monolayer film was a solid condensed film at this surface pressure. The monolayer films were transferred onto CaF\(_2\) plates and the silver substrates by the vertical dipping method at a dipping and raising speed of 10 mm/min. The above procedures were carried out at 20 ± 0.5 °C.

Spectroscopy. A Bruker IFS 100 FT-Raman spectrometer equipped with a Ge detector was used to obtain the FT-Raman spectra. Continuous-wave (CW) NIR excitation at 1064 nm was provided by a diode laser-pumped Nd:YAG laser (Adlas, DPY 301). The spectra were measured at a 4 cm\(^{-1}\) resolution, and the laser power at the sample point was 100 mW for the films and 15 mW for the solid samples. The FT-Raman spectra reported in this paper are all original and unsmoothed. Infrared measurements were made by a Bruker IFS 66V FT-IR spectrometer equipped with a MCT detector. The reflection attachment used for the IR reflection–absorption (RA) measurement was a homemade set, and the incidence angle was 80°. The spectra of the ultrathin films were taken at a 4 cm\(^{-1}\) resolution and generally several hundred scans were accumulated for an acceptable signal-to-noise ratio.

Results and Discussion

Figure 2 shows a FT-IR transmission spectrum of a one-layer LB film of 8A3H on a CaF\(_2\) plate (a) and reflection–absorption (RA) spectra of its dipping (b) and one-layer LB (c) films on substrates with a silver mirror. Band assignments for the IR spectra of nAmH have been studied in detail.\(^{12,13}\) Although all the spectra in Figure 2 are those of one-layer films, the band intensities in spectra (b) and (c) are much stronger than that in spectrum (a). Bands at 2921 and 2848 cm\(^{-1}\) in spectrum (a), which are assigned to antisymmetric and symmetric CH\(_2\) stretching modes of the alkyl chain, respectively, show a downward shift to 2918 and 2848 cm\(^{-1}\), respectively, in spectra (b) and (c). The frequencies of these two CH\(_2\) stretching bands are sensitive to the conformation of a hydrocarbon chain; low frequencies (~2918 and ~2848 cm\(^{-1}\)) of the bands are characteristic of a highly ordered (trans-zigzag) alkyl tail, while their upward shifts are indicative of the increase in the conformational disorder, i.e., gauche conformers, in the hydrocarbon chain.\(^{15,16}\) Therefore, the observation in Figure 2 suggests that the

---


troscopy,17 so that the COO transition moments in the direction of the bisector of its stretching mode has its transition moments perpendicular to the surface are enhanced in a RA spectrum. Therefore, the fact that the relative intensities of the two CH2 stretching bands are medium in the RA spectra in Figure 2 indicates that the hydrocarbon chain is tilted on the average with respect to the substrate (a). In the films deposited on the silver substrates and less ordered in that on the CaF2 plate. Accordingly, we may be able to draw a schematic view as shown in Figure 3 for the molecular orientation and structure of 8A3H in the LB and dipping films on the substrates. The alkyl chain of 8A3H is nearly perpendicular to the surface of the silver particles. Of particular note in Figure 2 is that the LB films on the CaF2 plate and silver foil show a band at 1703 cm⁻¹ due to a C=O stretching mode of the COOH group, while the dipping film on the silver mirror gives strong bands at 1580 and 1395 cm⁻¹, which are assigned to the antisymmetric and symmetric stretching modes of the COOH group, respectively.20 These two bands are also observed in Figure 2c, even though they are very weak. Therefore, there are clear differences in the structure of 8A3H between the dipping and LB films on the silver mirrors. It seems very likely that during the spontaneous absorption of the dipping films, the chemical reaction between the COOH groups and the silver particles proceed more effectively compared to the LB films.

Another important point in Figure 2b is that the symmetric COO⁻ stretching band is stronger than its antisymmetric counterpart. In general, the antisymmetric stretching band of COO⁻ is much stronger than its symmetric stretching band. It is very unusual that the reversal of the intensity between the antisymmetric and symmetric bands occurs. Thus, the observation must be explained by the surface selection rules of the RA spectroscopy. The symmetric COO⁻ stretching mode has its transition moments in the direction of the bisector of OCO angle, so that the COO⁻ groups seem to assume the molecular orientation shown in Figure 3. Judging from the frequency of the C=O stretching band of the COOH group, it may be concluded that the COOH groups are involved in hydrogen bonds in a lateral fashion in the LB films.13,21,22

Table 1. Frequencies (cm⁻¹) and Assignments for Raman Bands of 8A3H in Various States

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>solid state</th>
<th>dipping film</th>
<th>LB film</th>
<th>assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1599</td>
<td></td>
<td>1603</td>
<td>1603</td>
<td>v(Ph–C–C–Ph) + v(Ph19a/b)</td>
</tr>
<tr>
<td>1450</td>
<td>1454</td>
<td>1445</td>
<td>1457</td>
<td>v(–N–N–) + v(–N–Ph)</td>
</tr>
<tr>
<td>1409</td>
<td>1409</td>
<td>1402</td>
<td>1402</td>
<td>v(–N–N–)</td>
</tr>
<tr>
<td>1312</td>
<td>1195</td>
<td>1195</td>
<td>1188</td>
<td>v(Ph–C–C–Ph)</td>
</tr>
<tr>
<td>1190</td>
<td>1190</td>
<td>1188</td>
<td>1188</td>
<td>v(–N–N–)</td>
</tr>
<tr>
<td>1138</td>
<td>1140</td>
<td>1141</td>
<td>853</td>
<td>ring breathing mode</td>
</tr>
</tbody>
</table>

Figure 4 shows FT-Raman spectra of dipping films of 8A3H both on silver foil (a) and silver mirror (b) substrates and that of a one-layer LB film of 8A3H on a silver mirror substrate (b). A FT-Raman spectrum of 8A3H in a solid state is depicted in Figure 4d for comparison. We also measured a FT-Raman spectrum of a 20-layer LB film of 8A3H on a CaF2 plate, but the observed bands were very weak. Band assignments for the Raman spectra of 8A3H in various states are summarized in Table 1. These assignments were made by referring to Raman spectra of various azobenzene derivatives for which vibrational assignments have been well established.23–27 A band near 1410 cm⁻¹ in the spectra of Figure 4 is due to the −N=N− stretching mode, while an intense feature near 1456 cm⁻¹ is assigned to the −N=N− stretching mode with a contribution from the phenyl ring mode (v19). The frequency of the −N=N− stretching band of azobenzene derivatives is very sensitive to the conformation around the −N=N− group; a trans conformer gives the −N=N−...
stretching band near 1430 cm\(^{-1}\), while a cis conformer provides it near 1510 cm\(^{-1}\). Therefore, the observation in Figure 4 indicates that 8A3H assumes a trans conformer in the LB and dipping films.

The Raman spectrum of the LB film (Figure 4b) is very similar to that of the solid sample (Figure 4d) in terms of both the frequencies and relative intensities. However, significant changes are observed between the spectrum of the dipping film on the silver mirror and that of the solid state. Of particular note is a change in the relative intensity of a band near 1603 cm\(^{-1}\) and the appearance of a new band at 853 cm\(^{-1}\). These two bands are assigned to the phenyl ring stretching mode \((v_\theta)\) and the skeleton vibration, “ring breathing” of the phenyl ring, respectively.\(^{23}\) The frequency of the latter band is characteristic of a 1,4-disubstituted phenyl ring.\(^{23}\) The marked enhancement of the bands at 1603 and 853 cm\(^{-1}\) may be explained by the SERS “surface selection rule”.\(^{7,28,29}\) According to this rule, if a phenyl ring is “standing up” on the surface, bands due to CH stretching, \(v_\theta\), and breathing modes of the phenyl ring show great SERS effect.

Therefore, the observation in Figure 4c suggests that the phenyl ring is nearly perpendicular to the silver mirror surface.

Kawai et al.\(^{12}\) calculated the tilt angles of the chain axis and various transition moments from the surface normal for NaNmH and their barium salts in the LB films. It was concluded that the barium salts are more highly orientated as compared with the corresponding acids. The present result is in good agreement with their conclusion.

Comparison of the Raman spectrum of the dipping film on the silver foil (Figure 4a) with that of the film on the silver mirror (Figure 4c) shows that the bands in the latter are much stronger than those in the former. It is noted that the bands at 1603 and 853 cm\(^{-1}\) are enhanced markedly in the spectrum of the film on the silver mirror (Figure 4c); the band at 853 cm\(^{-1}\) is not observed in the spectrum of the film on the silver foil (Figure 4a). These observations suggest that the molecular orientation and the structure are different significantly between the two kinds of substrates. Because the size of silver particle is much larger in the silver mirror than in the silver foil. As we described in the Experimental Section, we measured the size of the silver particles in silver mirrors by the AFM and SEM measurements. The results show that the silver particles size in silver mirrors is between 250 and 100 nm.\(^{6,10,11}\) Comparison between the two spectra in Figure 4a,c demonstrates that the size of the silver mirror is more active than that of the silver foil.

Parts a and b of Figure 5 depict NIR-SERS spectra of dipping films of 8A5H on silver foil (a) and silver mirror (b), and Figure 5c shows a FT-Raman spectrum of 8A5H in a solid state (c).

Figures 5 and 6 depict NIR-SERS spectra of dipping films of 8A3H and 12A3H on silver foil (a) and silver mirror (b), and FT-Raman spectra of 8A3H and 12A3H in a solid state (c).

More careful inspection of the spectra of the silver mirror films of 8A3H and 12A3H reveals that the enhancement of the bands at 1603 and 853 cm\(^{-1}\) is more significant for 8A3H. In this respect, the length of the tail also controls the molecular orientation of the phenyl ring to some extent.

Conclusions

The present study has provided new insight into NIR-SERS of the organic thin films on a silver surface. On the basis of the above discussion, the following conclusions can be reached: (i) The silver mirror method is more powerful than the HNO\(_3\) etching silver foil method to

---

obtain great SERS effect. The former method is very promising for various SERS studies. (ii) The marked enhancement of bands at 1603 and 853 cm\(^{-1}\) due to the phenyl ring modes in the SERS spectra of the dipping films of 8A3H and 12A3H on the silver mirrors indicates that the phenyl rings are nearly perpendicular to the surface of the silver mirrors. (iii) The dipping film of 8A3H on the silver mirror has exclusively COO\(^-\) groups while the LB films of 8A3H on the CaF\(_2\) plate and silver mirror have mainly COOH groups. It seems likely that during the spontaneous adsorption for the dipping film, the chemical reaction between the COOH group and the silver particles proceeds effectively compared with the LB films. (iv) Comparison of the NIR-SERS spectra of the dipping films of 8A3H, 8A5H, and 12A3H on the silver mirrors suggests that the length of spacer is important to yield marked SERS effect.

**Acknowledgment.** The authors are grateful to Professor G. Xue (Department of Polymer Chemistry and Physics, Nanjing University, P. R. China) and Dr. J. Dong (Department of Biochemistry, Case Western Reserve University, Cleveland, OH) for valuable discussion and also to Mr. S. Morita (School of Science, Kwansei-Gakuin University, Japan) and Dr. D. W. Park (Kyungpook National University, Korea) for the help in the AFM and SEM measurements. The authors of Jilin University thank the financial support from Project 29633010 of NSFC.