



Enhanced infrared spectra of azobenzene carboxylic acid LB monolayer on discontinuous silver film

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Abstract

Enhanced infrared spectra of a Langmuir–Blodgett (LB) monolayer of C_8AzoC_3COOH on silver-coated CaF_2 substrates are reported, in which much larger enhancement for the $COOH$ groups residing in the gap between silver islands than the COO^- groups on silver islands are observed. The enhancement factor for the $\nu(C=O)$ mode of $COOH$ was estimated to be a value much larger than 150. The data clearly show the collective electron resonance mechanism of the surface enhanced infrared spectroscopy (SEIRS). © 1997 Elsevier Science B.V.

Surface enhanced infrared spectroscopy (SEIRS) on rough metal surfaces has been attracting considerable research interests since its discovery [1–5], not only because of its prospective applications [11–17], but also because it can help us understand surface enhanced spectroscopy fundamentally. Efforts have been made to elucidate the mechanism of this kind of surface enhanced phenomenon [1–8]. Similar to the surface enhanced Raman spectroscopy (SERS), this kind of enhancement effect may have two main contributions: an *electromagnetic mechanism (EM)* involving the excitation of a localized surface electromagnetic wave, or in other words, the local surface plasmon [1–5], and a *chemical mechanism* of charge transfer from the probe molecules to SEIRS active substrate [7,9,10]. Regarding the electromag-

netic mechanism, many studies suggest that the collective electron resonance is responsible for SEIRS [2–5]. The mutual coupling of the local surface plasmon on different metal islands (or particles) of the rough surface plays the most important role. As studied by measuring the optical absorption of the substrates, when the metal particles (e.g., Ag particles) are aggregated, the absorption peak of the surface plasma resonance of the metal film is red-shifted into the IR region and enhanced infrared absorption is observed [3]. It is also suggested that the enhancement effect is predominant in the region between the silver islands comparing to that on the silver islands, which was proved indirectly either by the polarization property of the enhanced spectra [2] or by theoretical calculation [4]. In this Letter, we report the surface enhanced infrared spectra of the Langmuir–Blodgett (LB) monolayer of the $CH_3-(CH_2)_7-Azo-O-(CH_2)_3-COOH$ molecule (referred as C_8AzoC_3COOH) on a discontinuous silver film.

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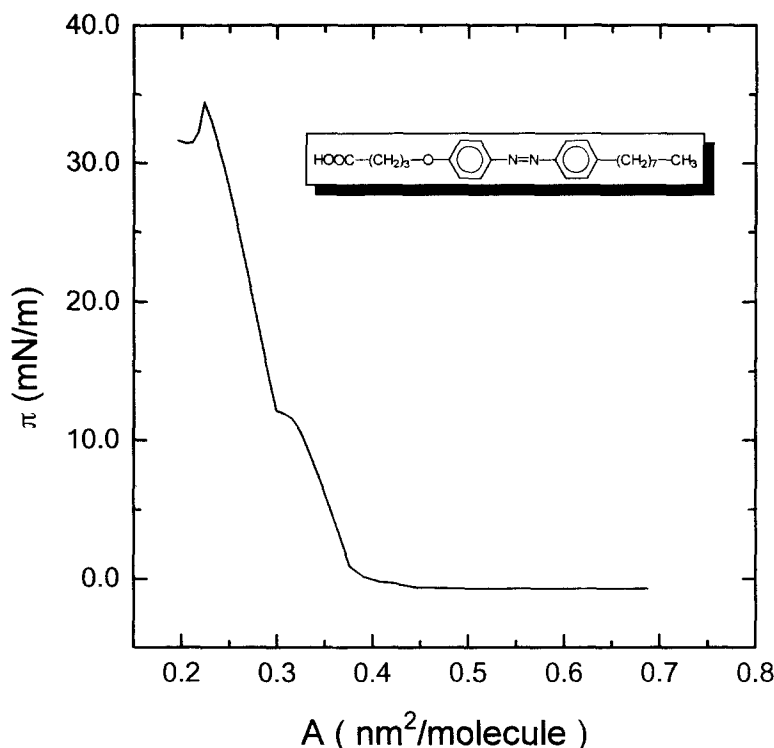


Fig. 1. π - A isotherm of the monolayer of C_8AzoC_3COOH molecule on air/water interface. Inset: the molecular formula of C_8AzoC_3COOH

The different IR absorption behavior of the carboxyl group (COOH) between the silver islands and the carboxylate group (COO⁻) on the silver islands allows us to distinguish and to make a direct comparison of the enhancement effect in the region between the silver islands and on the silver islands.

Silver films on CaF₂ substrate were prepared by thermal evaporation of silver in a vacuum chamber (pressure $\sim 4.0 \times 10^{-4}$ Pa). The film thickness was monitored and controlled by a quartz thickness monitor and the evaporation rate was kept as 0.1 nm/s. To obtain the morphological information of the silver film, a Nanoscope III atomic force microscope (AFM) (Digital Instruments) was adopted.

The molecule adopted for LB monolayer fabrication was 4-octyl-4'-(3-carboxytrimethylenoxy) azobenzene (Dojindo, Japan) (see the inset in Fig. 1). The LB monolayer was vertically deposited onto solid substrates using a commercial Langmuir-Blodgett trough (FACE Co. Ltd., Japan). Milli-Q water with a resistance of $> 17 M\Omega$ cm was used as the subphase. The azobenzene compound, dissolved in chloroform with a concentration of 1.0×10^{-3} M,

was spread onto the air/water interface with a micro-syringe. The π - A isotherm of the monolayer on water is presented in Fig. 1. All of the LB films were prepared at a constant surface pressure of 20 mN/m and the subphase temperature was kept at 20°C. The transferring ratios for both coated and uncoated substrates were identical and were nearly unity.

After the LB monolayers were prepared, transmission infrared spectra were measured. The measurement was done with a Perkin-Elmer System 2000 FTIR spectrometer, equipped with a liquid-nitrogen-cooled narrow-band MCT detector. The resolution of the system was set to be 4 cm^{-1} .

Fig. 2a and b shows the AFM images of ~ 10 nm, and ~ 25 nm thick silver film coated CaF₂ substrate¹. It is seen that in the ~ 10 nm thick silver

¹ Although relatively larger errors occurred in measuring the film thickness because of the instability of the quartz thickness monitor, the film thickness could also be estimated by AFM results.

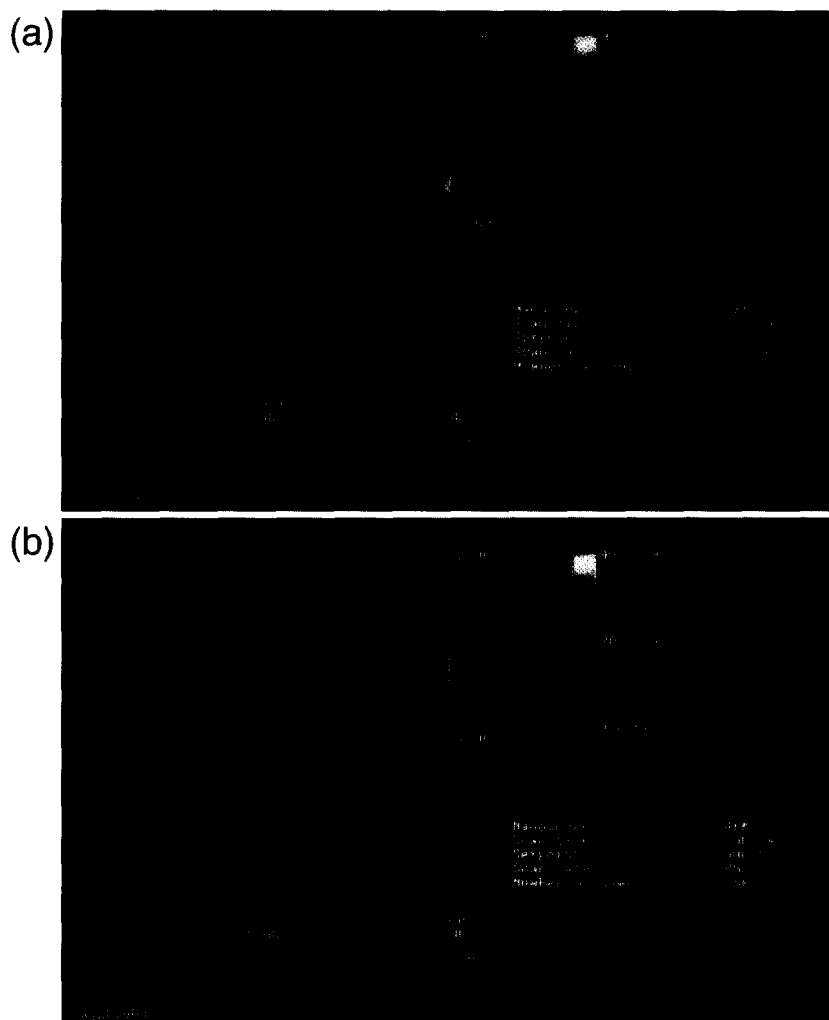


Fig. 2. AFM images of the surface of CaF_2 substrates coated with (a) ~ 10 nm and (b) ~ 25 nm silver film.

film, most of the area is covered by silver and there are small areas uncovered (i.e., tiny holes). The dimension of these uncovered areas is on the scale of several tens of nanometers. The largest hole in the area is about $80 \text{ nm} \times 120 \text{ nm}$. In contrast, as shown in Fig. 2b, the ~ 25 nm silver film is continuous: all of the area is covered with silver particles and no holes are observed. Therefore, two different substrates are prepared, i.e. the discontinuous ~ 10 nm thick silver film and the continuous ~ 25 nm thick silver film, coated CaF_2 substrates.

The transmission infrared spectra of the one-layer LB film deposited on uncovered CaF_2 substrate and

the ~ 10 and ~ 25 nm thick silver coated CaF_2 substrates were measured, which are shown by spectra a, b and c in Fig. 3, respectively. It is seen that the IR spectra of the LB monolayers are greatly enhanced on the silver coated substrates, especially on ~ 25 nm thick silver film. Attention is paid to the absorption of the vibration mode of the carboxyl group (COOH). When the COOH group is in contact with silver, reactive adsorption occurs, and the COOH group is converted to COO^- , as evidenced by a strong absorption band of $\nu_s(\text{COO}^-)$ appearing at 1391 cm^{-1} and the disappearance of the stretching vibration mode of the carbonyl group, $\nu(\text{C}=\text{O})$, in

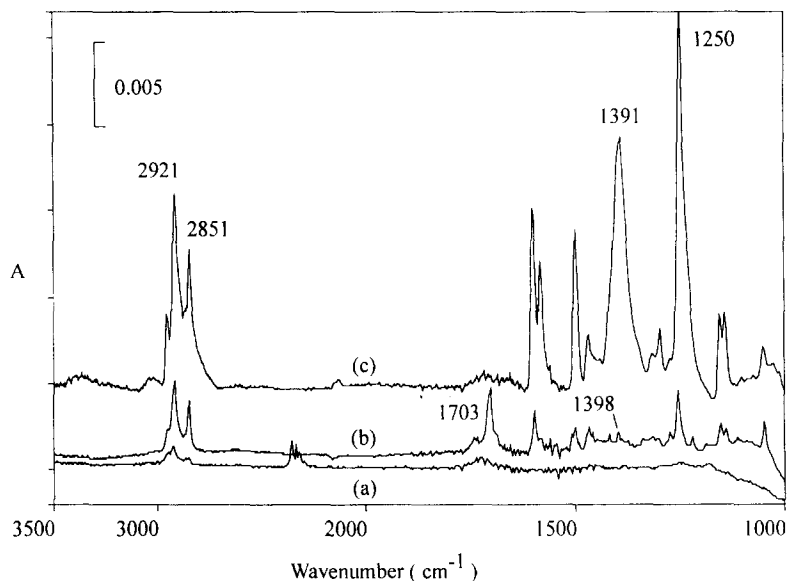


Fig. 3. Transmission infrared spectra of LB monolayer of C_8AzoC_3COOH on (a) bare, (b) ~ 10 nm silver film coated, and (c) ~ 25 nm silver film coated CaF_2 substrates.

spectrum c [2,4]². However, in spectrum b, the intensity of the $\nu_s(COO^-)$ (at 1398 cm^{-1}) is very weak and a relatively intense band of $\nu(C=O)$ is observed at 1703 cm^{-1} , indicating the co-existence of carboxyl group (COOH) and carboxylate group (COO^-) on the ~ 10 nm thick silver film. As mentioned above, the 10 nm thick silver film consists of large areas covered with silver and tiny holes with no silver. When the Langmuir monolayer of C_8AzoC_3COOH was transferred onto such a substrate, the COOH group reacts with silver and is converted to COO^- in the regions covered by silver, while the COOH group remains unchanged within the regions uncovered by silver, i.e., in the holes. From the AFM image of the 10 nm silver film, the area of the regions uncovered by silver is much smaller than those covered by silver³. The uncov-

ered areas are measured to be $\sim 2\%$ of the whole area. Therefore, the number of the COOH groups on the 10 nm thick silver film is estimated to be only 2% of that on bare CaF_2 substrate. The much larger intensity of $\nu(C=O)$ in spectrum b than in spectrum a, shows the great enhancement experienced by the carboxyl groups in the gaps between the silver islands on the 10 nm thick silver film. We can estimate the enhancement factor for $\nu(C=O)$ by comparing the integrated absorbance of $\nu(C=O)$ in spectra a and b, which gives a value of 150, supposing that the orientation of carboxyl group is identical in the holes and on the bare CaF_2 surface. Actually, the EM enhanced IR absorption is a short-range effect, whose working distance is within 5 nm [3,5], much less than the dimension of the holes. Therefore, the number of COOH groups which experience enhancement should be much less than the estimated ratio of 2% and therefore, the practical enhancement factor should be higher than 150.

When the thickness of silver film is increased to 25 nm, the substrate surface is completely covered by silver particles and no hole can be observed (Fig. 2b). The spectra of the LB monolayer on such a substrate show a dominant feature of COO^- , and the absorption band of $\nu(C=O)$ disappears.

It is important to have a comparison of the enhancement in the holes and on the top of the silver

² The absence of $\nu_{as}(COO^-)$ is attributed to the selection rule of SEIRS, i.e., only those vibrational modes whose transition dipole moments are perpendicular to the metal surface will give rise to absorption [4].

³ It is possible that some changes happen to the silver substrate during the LB monolayer fabrication, for example, some of the silver particles may fall off the substrate when it is dipped in the water subphase. However, this influence is relatively small because the discontinuous and continuous nature of the silver films are still reflected in the spectra of the LB monolayers.

islands. In spectrum b of Fig. 3, the absorbance of $\nu_s(\text{COO}^-)$ at 1398 cm^{-1} is about 1/25 of that of $\nu(\text{C}=\text{O})$ at 1703 cm^{-1} , a much lower level considering their relative amount. This indicates that the COO^- groups on silver experience much less enhancement than COOH groups in the hole area. In spectrum c, all of the vibration modes are much more greatly enhanced, including $\nu_s(\text{COO}^-)$. This is because of the larger amount of silver islands on the substrate, as evidenced by the AFM images (shown in Fig. 2b) and therefore, more voids between the silver islands are created, which are believed to be the most effective places for enhancement [2–5].

Previous studies on SEIRS have given deep insights into its mechanism [1–5]. Both theoretical and experimental results strongly suggest that it is collective electron resonance, or, in other words, multiple excitation of surface plasma that is responsible for surface enhanced infrared spectroscopy [2,4]. When silver particles become aggregated, the excited local surface plasmon of each isolated particle interacts with those on the adjacent particles. This coupling has strong influence on the optical property of the particle assembly, red-shifting its electron resonance absorption from the visible into the near-infrared region. In the spectral measurement, when IR radiation is incident, multiple surface plasma are generated, resulting in the much more intense electromagnetic field in the area between the silver particles than on the particles. This is the reason why the COOH groups in the holes experience much stronger enhancement than the COO^- groups on the silver islands, which could also be direct evidence of the collective electron resonance mechanism of surface enhanced infrared spectroscopy (SEIRS).

Acknowledgements

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