Resonance Raman Spectra
of Thin Langmuir-Blodgett Films
# of Cetyl Orange*

Junzo UMEMURA, Hitoshi MATSUDA,** Takeshi KAWAI,*** and Tohru TAKENAKA

Langmuir-Blodgett (LB) films of cetyl orange were prepared from spread monolayers on water at pH 8.7 and 1.5. Uv-visible absorption spectra of these LB films gave K and Q bands ascribed to the π-π^* transition of the azo and hydrazone forms, respectively, of the azobenzene chromophore. We could observe resonance Raman spectra of these LB films as thin as monolayer. Excitation profiles of the observed bands were also examined.

KEY WORDS: Resonance Raman spectra/ Cetyl orange LB films/ Langmuir-Blodgett films/ Excitation profiles/ Azo hydrazone tautomers/

INTRODUCTION

The Langmuir-Blodgett (LB) technique[1] is a powerful means to fabricate novel thin organic films of well-organized and functionalized molecular assemblies which can be utilized as microelectronic or microoptical devices. To investigate the structure of these films with thickness at the monolayer level by spectroscopy, an extremely high sensitivity is required. Use of resonance Raman scattering (RRS) is one of the useful techniques for this purpose and has been widely applied to biological systems with chromophores.[2] However, applications of this technique to LB films are quite limited.[3-6] In a previous paper,[7] we reported surface enhanced resonance Raman spectra (SERRS) of 1- and 2-monolayer LB films of cetyl orange (sodium p-dicetylaminoazobenzenesulfonate), since the RRS sensitivity was still insufficient for obtaining high-quality spectra of 1-monolayer LB films.

In the present work, we measured RRS of 1-, 4-, and 10-monlayer LB films of cetyl orange deposited from spread monolayers on basic and acidic aqueous solutions using an intensified photodiode array detector which has higher sensitivity than the previous one.[7] The excitation profiles of RRS of the two kinds of LB films (azo and hydrazone forms illustrated in Fig. 1) were examined in the wavelength range of 406 to 647 nm.

梅村 純三, 松田 仁史, 河合 武史, 竹中 亨: Laboratory of Surface Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611
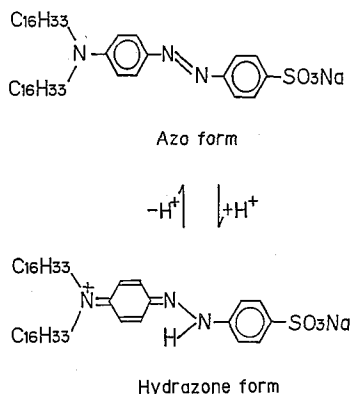
Azo form

$-H^+$ $+H^+$

Hydrazone form

Fig. 1. Tautomeric equilibrium in cetyl orange.

EXPERIMENTAL

Cetyl orange was kindly synthesized by Wako Pure Chemical Industries, Ltd., Osaka using the method described previously.[8] A Kyowa Kaimen Kagaku Model HBM-AP Langmuir trough with a Wilhelmy balance was used for LB film fabrications. Water used as a subphase was purified by a modified Mitamura Riken automatic lab still consisting of a reverse osmosis module, and ion exchange column, and a double distiller. It was adjusted to pH 8.7 by adding 1.3×10^{-3}M $NaHCO_3$ and 2.3×10^{-4}M Na_2CO_3, or to pH 1.5 by aqueous H_2SO_4 solutions. Cetyl orange monolayers spread on water surfaces from a 1.0×10^{-3}M chloroform solution were compressed at 10°C to the surface pressure of 40 mN/m (at pH 8.7) or 32 mN/m (at pH 1.5) where the monolayers are in the solid-condensed phases (see the surface pressur-area isotherms in Fig. 2), and then transferred onto quartz plates. The 1-monolayer LB film was deposited by the
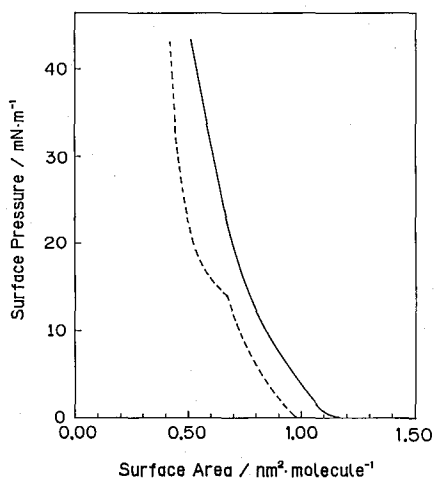
Fig. 2. Surface pressure-area isotherms of spread monolayers of cetyl orange on water at 10°C at pH 8.7 (dotted line) and 1.5 (solid line).
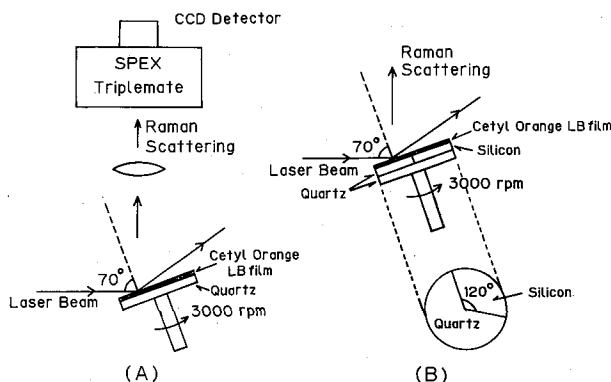
Fig. 3. Experimental set up for obtaining (A) resonance Raman spectra and (B) excitation profile for cetyl orange LB films.

vertical dipping method with a withdrawing speed of 5 mm/min (transfer ratio = 1.0 ± 0.1). The 4- and 10-monolayer LB film was deposited by the horizontal lifting method (transfer ratio = 2.0 ± 0.2) onto the quartz plate precoated with a 3-monolayer LB film of cadmium stearate.

The experimental setup used for RRS measurements of cetyl orange LB films is shown in Fig. 3. Generally, we used a circular quartz plate (diameter = 22.5 mm, thickness = 0.65 mm) as a solid substrate of the LB film, and rotated it at 3000 rpm to avoid photodegradation (Fig. 3A). For measurements of excitation profiles, we cut off a sector with an interior angle of 120° from the above quartz plate, and replaced it by a bare silicon wafer of the same shape. This configuration makes it possible to use the 520-cm^{-1} Raman peak due to the Si lattice vibration as an external intensity standard, after correction for the wavelength dependent sensitivity of our Raman measurement system. The p-polarized excitation beam with the output power of 5 mW from a Spectra Physics Model 164-03 Ar$^+$ laser or a Coherent Inova-90 Kr$^+$ laser was incident on the film surface with an angle of incidence of 70° after passing through appropriate interference filters (Fig. 3). Raman scattering was observed in the direction perpendicular to the excitation beam and detected by a Tracor Northern Model TN-6134 intensified photodiode array detector cooled down to −20°C through a Spex Triplemate 1877 monochromator. Data processing was performed by a Seki MDS program on a NEC PC-9801VX personal computer connected through a Seki MDS interface to the detector. The observation time was 10-60 min and the spectral resolution was 4-5 cm^{-1}. Uv-visible absorption spectra were recorded on a Hitach Model U3400 spectrophotometer.

RESULTS AND DISCUSSION

Figure 4 shows absorption spectra of the 10-monolayer LB films of cetyl orange prepared at pH 8.7 and 1.5. For the LB film prepared at pH 8.7, a peak appears at 415 nm which is called 'K band' and is ascribed to the π-π* transition of the azo form of the trans azobenzene moiety (Fig. 1).[7-10] For the LB film prepared at pH 1.5, on the other hand, a peak is observed at 515 nm which is designated as 'Q band' and is
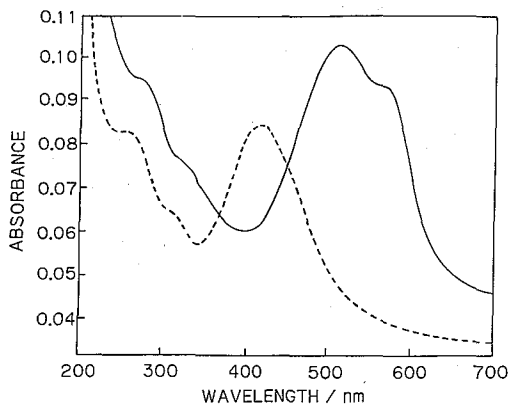
Fig. 4. Uv-visible absorption spectra of 10-monolayer LB films of cetyl orange prepared at 10°C at pH 8.7 (dotted line) and at 1.5 (solid line).
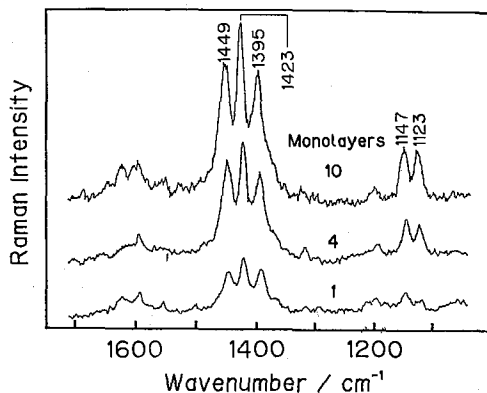

Fig. 5. Resonance Raman spectra (457.9 nm excitation, 60 min exposure) of 1-, 4-, and 10-monolayer LB films of cetyl orange prepared at 10°C at pH 8.7.

ascribed to the same electronic transition of the protonated hydrazone form (or the quinoid form if the dicetyl aminobenzene ring, i.e. N'-ring, is referred).[8-11] On the higher wavelength sides of the K and Q bands in Fig. 4, there are shoulders at ca. 470 nm (less pronounced) and 561 nm (more pronounced), respectively. As described later, these shoulders can be ascribed to the vibronic 0-0 components, while the main peaks are ascribed to the other (0-2 or 0-1) vibronic components.

Figure 5 shows RR spectra of the 1-, 4-, and 10-monolayer LB films of cetyl orange prepared at pH 8.7 and excited by the 457.9 nm line of the Ar^+ laser. The spectral features of these LB films are similar to those of the azo-form of p-dialkylaminoazobenzenesulfonates.[7,12-15] The doublet at 1423 and 1395 cm^{-1} is assigned to the coupling mode between the N=N stretching vibration and the 19b vibration (after Wilson's numbering[16,17]) of the sulfonated benzene ring (S-ring).[14] The peak at 1449 cm^{-1} is assigned to the 19b mode of the N'-ring.[14] Further, the 1147- and 1123-cm^{-1} peaks are attributed to the ϕ-N and SO_3^- stretching vibrations, respectively.[12-15]

In Fig. 6, the excitation profiles for the 1423 and 1147-cm^{-1} peaks are given. The excitation profiles for the two peaks are clearly different from each other. Although
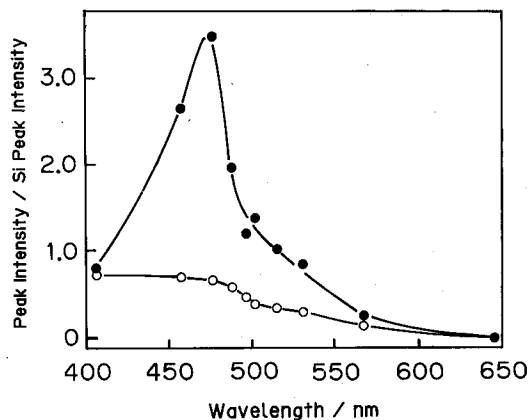
Fig. 6. The excitation profiles of the 1423- (●) and 1147-cm$^{-1)}$ (○) Raman peraks of the 10-monolayer LB films of cetyl orange prepared at 10°C and pH 8.7.

the profile for the 1147-cm^{-1} peak roughly follows the absorption curve of the azo form with the peak maximum at 415 nm (K-band, 24096 cm^{-1}) in Fig. 4, the profiles for the 1423-cm^{-1} peak (as well as those for the 1449- and 1395-cm^{-1} peaks, not shown) is maximized at ca. 470 nm (21277 cm^{-1}) which is the position of the shoulder ascribable to the vibronic 0-0 component. The maximum intensity enhancement often occurs by excitation under the 0-0 transition, because the vibrational overlap integrals (also known as Frank-Condon factors) are maximized at this transition.[2] The separation between the 415-nm peak and 470-nm shoulder in Fig. 4 amounts to 2819 cm^{-1}, which is almost the double of the frequencies of the three bands around 1400 cm^{-1} in Fig. 5. Therefore it is reasonable to consider that the main peak at 415 nm in Fig. 4 is due to the vibronic 0-2 component of the electronic π-π^* transition. More accurately, the 0-2 component is generally the envelope of all the active vibronic transitions in which the vibrational quantum numbers increase from 0 to 2.[2] The stronger intensity of the 0-2 component than that of the 0-0 component indicates that the overlapping of the wavefunctions between the electronic ground and excited states is maximized at the former transition.[18] The similar phenomenon has been observed in the absorption spectrum of astaxanthin.[2]
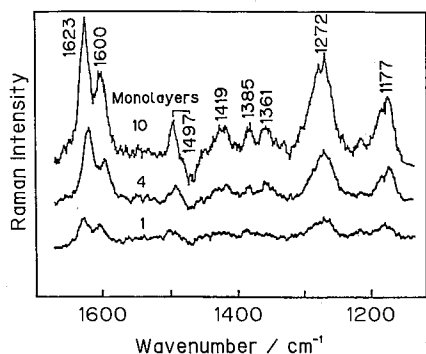

Fig. 7. Resonance Raman spectra (514.5 nm excitation, 60 min exposure) of 1-, 4-, and 10-monolayer LB films of cetyl orange prepared at 10°C and pH 1.5.
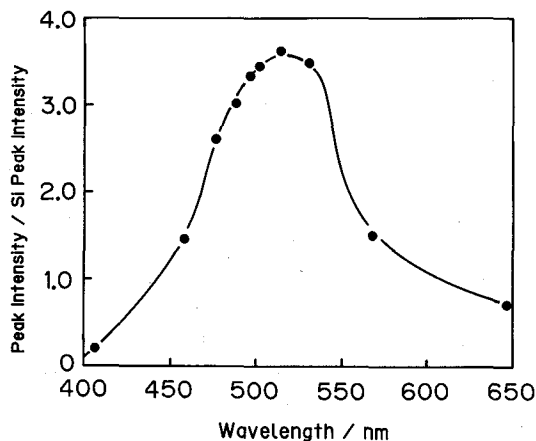
Fig. 8. The excitation profile of the 1272 cm^{-1}
Raman peak of the 10-monolayer LB film of
cetyl orange prepared at 10°C and pH 1.5.

Figure 7 shows RR spectra of 1-, 4-, and 10-monolayer LB films of cetyl orange prepared at pH 1.5 and excited by the 514.5-nm line of the Ar$^+$ laser. In this case, the spectral features are very similar to that of the protonated, hydrazone form reported for methyl orange in acidic media.[13,14] The 1623-cm^{-1} peak is assigned to the C=C stretching mode of the N'-ring, the 1600-cm^{-1} peak to the 8a mode of the S-ring, the 1272-cm^{-1} peak to the C-N stretching mode, and the 1177-cm^{-1} peak to the 9a mode of the S-ring which has some contribution from the N-N stretching mode.[14] Reflecting the position of the C=C bonds in the chromophore, the C=C stretching band of the quinoid ring (N'-ring) becomes the strongest instead of the N=N stretching band of the azo form in Fig. 5. As described before, the Q band at 515 nm (19417 cm^{-1}) has a shoulder at ca. 562 nm (17794 cm^{-1}) as shown in Fig. 4. The frequency difference between them amounts to 1623 cm^{-1}, which coincides with the vibrational frequency of the C=C stretching mode of the quinoid ring. Therefore, it is reasonable to assign the shoulder and main bands to the vibronic 0-0 and 0-1 components, respectively, of the electronic π-π^* transition.

The excitation profiles of the 1272-cm^{-1} Raman peak is shown in Fig. 8. In this case, the profile roughly follows the absorption curve of the hydrazone form represented in Fig. 4. If we compare them carefully, however, there is a small discrepancy between them. In Fig. 8, Raman intensity ratio at the 568.2-nm excitation line is 0.42 of that at the 514.5-nm line, while in the absorption curve of Fig. 4, the corresponding absorbance ratio is about 0.86. This fact indicates that the 0-0 component at the 562-nm shoulder has a smaller enhancement factor than the 0-1 component at 515 nm. In other words, the Frank-Condon factor is smaller in the resonance process at the former transition.[2] The excitation profiles of other RR peaks were also similar to that in Fig. 8.

In the acidic media, the hydrazone form is generally in equilibrium with other type of the azo form protonated at the N'-atom position which is responsible for the weak 320-nm shoulder band in Fig. 4.[14,15,19] In fact, we observed a different Raman spectrum

at the 350.7-nm (Kr⁺ laser) excitation of the LB film prepared at pH 1.5 (not shown). However, since the absorbance at 320 nm is fairly small, the amount of the protonated azo form may be very small.

We have also investigated the equilibrium shift on compression of spread monolayers of cetyl orange on the water surface and on transfer of the monolayers to solid substrates. These results have been reported separately.[20,21]

ACKNOWLEDGMENT

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