Incident-Angle Dependence of the Sensitivity of Second-Harmonic Generation of an Oxacyanine Dye in an LB Film

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The second-harmonic generation of a cyanine dye in an LB film was investigated by varying the incident angle of the excitation laser. There was a clear dependence on the incident angle, which was simulated by a simple model. Thus, a highly sensitive determination should be carried out at such an angle where the efficiency of the second-harmonic generation shows its maximum.

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Second-harmonic generation (SHG) is a surface-sensitive technique and has been applied to orientational analyses of molecules on a surface.¹⁻⁴ Structural analysis in LB films⁵⁻⁷ and on water surfaces^{3,8-12} has been one of major research targets. This method has also been used for highly sensitive determinations in LB films.^{13,14} However, the incident angle of the excitation laser is usually set at 45°, and the incident-angle dependence of the SHG efficiency has scarcely been measured.

In the present study, we constructed a new instrument to investigate the incident-angle dependence of SHG signals, and applied it for determining a cyanine dye (DOOC) in LB films. We found that the signal was dependent on the incident angle and that the detection limit could be improved by using the most efficient incident angle.

Experimental

The experimental apparatus is schematically shown in Fig. 1. Its optical units are essentially identical to that described previously,^{8,13} except for a goniometer, which was installed in order to change the incident angle continuously. An Ar-ion laser (Coherent, Innova 310) exited Ti:Al₂O₃ laser (Coherent, MIRA900D; pulse width, 200 fs; average power, 1 W; pulse repetition rate, 76 MHz) was used as the excitation source. The laser beam was focused onto a sample on a glass plate set on a goniometer (Shimadzu, VG207RA), which was operated by a computer (NEC PC9801RX2). Its polarization was set at either s-polarized (polarized along the surface) or p-polarized (polarized perpendicular to s) by using a half-wave plate. The reflected beam was passed through a filter to remove the fundamental laser light and through a Glan-Taylor prism to select its polarization. The second-harmonic (SH) light was

measured using a monochromator (JASCO, CT10), a photomultiplier (Hamamatsu R212UH or R5600P-03) and a photon counter (NF PC545A). The wavelength of the monochromator was set at the half wavelength of the incident laser. The signal was accumulated for 5 s on a spot of the sample, and several signals were averaged to obtain the observed data using the same computer.

The LB film was prepared in a Teflon LB trough (Kyowa Kaimen Kagaku). A cyanine dye, 3,3'-dioctadecyl-2,2'-oxacyanine perchlorate (DOOC; shown in Fig. 1), was obtained from Nippon Kankou Shikiso Kenkyusyo and used as received. The dye was mixed with a certain amount of arachidic acid in benzene and spread on the water surface. Deposition was carried out on a quartz plate (non-fluorescent grade) at a surface pressure of 25 mN/m; three layers of arachidic acid were deposited on the quartz plate in advance. The concentration of

Fig. 1 Experimental apparatus and molecular structure of DOOC.

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Fig. 2 Absorption spectrum of DOOC in an LB film; the ratio of DOOC to arachidic acid was 1:5. (a) One layer of DOOC-arachidic acid on three layers of arachidic acid. (b) Three y-type layers of DOOC-arachidic acid on three layers of arachidic acid.

Fig. 3 Incident angle dependence of the SHG signal for an LB film of one layer of DOOC-arachidic acid (1:5) on three layers of arachidic acid. ●, *Ippp*; ○, *Isss*; □, *Issp*; △, *Ipps* (these data were taken to measure the angle dependence as accurately as possible; thus, the relative intensity among 4 polarization combinations is not very accurate).

DOOC was varied by changing the ratio of DOOC to arachidic acid.

Results and Discussion

DOOC molecules in an LB film showed an absorption band of the monomer at 390 nm, a band of the dimer at 365 nm and a band of J-aggregates at 405 nm.⁸ The band of J-aggregates was negligibly weak, as shown in Fig. 2, when the ratio of DOOC to arachidic acid was 1:5, which was the typical experimental condition in the present study. The laser wavelength was set at 780 nm so that the SH light was resonant to the monomer absorption. The SH light appeared sharply at 390 nm, and its intensity was quadratically proportional to the pulse energy of the incident laser.

The incident-angle dependence was measured using the goniometer, with which the incident angle could be changed equally and simultaneously with the observation angle. A typical result on an LB film, which had one layer of DOOC with arachidic acid at 1:5, is shown in Fig. 3. The intensity of

Fig. 4 Comparison of the angle dependence of the observed SHG signals to that of the calculated one. ●, the observed signals; —, the calculated angle dependence. (a) *Ippp*, (b) *Issp*, (c) *Isss*, (d) *Ipps*.

Ippp was the strongest, but those of *Isss*, *Issp* and *Ipps* were observable, where *Issp* (*Isss*, *Ippp*, *Ipps*) represents the intensity of the SH light in which two photons of the s-polarized (s-, p-, p-, respectively) incident beam create one photon of the p-polarized (s-, p-, s-, respectively) output beam. The intensity peaked at about 37° for *Ippp*, but at about 70° for *Isss*, *Issp* and *Ipps*. Because both *Isss* and *Ipps* had a considerable intensity, the DOOC molecules should be distributed non-isotropically around the vertical axis of the surface.

The SH intensity can be calculated based on its theory.¹⁻³ In order to simplify the calculations, we assumed that only β_{yyz} was large and that other components of β were negligibly small, where β is the molecular non-linear polarizability tensor element. This assumption would be acceptable because the SH light was resonant to the monomer absorption. The calculation was also based on a previous finding, that the molecular surface of the DOOC molecules lay approximately parallel with the vertical axis of the surface.⁸ The observed results of the incident-angle dependence are compared with the calculated values in Fig. 4. They agree approximately, but not exactly. This finding indicates that the assumption that β was small, except for β_{yyz} , would be approximately correct, but not very accurate. A calculation without this assumption requires further information on the molecular orientation, which was not available in the present investigation.

Fig. 5 Concentration dependence of the SH intensity of DOOC in LB films. The ratio of DOOC to arachidic acid was varied. The incident angle was 70° (the noise levels for the three polarization combinations were approximately identical). $\diamond$, I_{ssp} ; $\times$, I_{pps} ; $\blacksquare$, I_{ssp} .

The observed finding, however, clearly indicates that the intensity of the SH light depended on the incident angle of the laser. Thus, the analytical merits should also depend on the incident angle.

The intensity of the SH light was quadratically proportional to the surface concentrations, as shown in Fig. 5, as expected according to the theory^{1,2} of SHG. The detection limits were obtained as the concentration where the signal-noise ratio was 3, which is shown as the broken line in Fig. 5.

Because the SHG intensity depended on the incident angle, the detection limit should have a similar dependence. The detection limits obtained at 45° , 60° and 70° are compared in Fig. 6. The detection limits for I_{ssp} , I_{ssp} and I_{pps} were lowest at 70° , as expected from the angle dependence of their intensity. However, the detection limit for I_{ppp} was better at 45° than at 70° , probably due to a small intensity change of I_{ppp} between 45° – 70° . Although the SHG signals of I_{ppp} were much larger than those of other three polarization combinations (Fig. 3), the detection limit for I_{ppp} was larger than expected from its SHG intensity, mainly because I_{ppp} had the largest background noise, probably due to the high reflectivity of this polarization component. The lowest detection limit, which was defined as the intersection between the analytical curve and the $S/N = 3$ line, was 34 pmol/cm^2 , which was obtained at 70° incident angle for I_{ssp} . This value corresponded to approximately 0.1 of the monolayer coverage.

The first observation on the incident-angle dependence of the detection efficiency clarifies the importance of the angle

Fig. 6 Incident-angle dependence of detection limits for four polarization combinations of the SH light. $\circ$, I_{ppp} ; $\square$, I_{ssp} ; $\triangle$, I_{pps} ; $\diamond$, I_{ssp} .

dependence.

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