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Optically nonlinear Langmuir–Blodgett films: Influence of the substrate on film structure and linear optical properties

G. H. Cross, N. A. Cade, I. R. Girling, I. R. Peterson, and D. C. Andrews

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Optically nonlinear Langmuir–Blodgett films: Influence of the substrate on film structure and linear optical properties

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Normal incidence transmission measurements and surface plasmon spectroscopy at optical frequencies are used to probe the optical and structural properties of an optically nonlinear dye, deposited onto glass and silver substrates by the Langmuir–Blodgett technique. The particular orientation and proximity to the silver surface afforded by the deposition method reveals strong molecule/metal interactions hitherto unreported for LB film assemblies on silver.

INTRODUCTION

Highly polarizable molecules such as derivatives of mercyanine and hemicyanine possess high optical nonlinearities as demonstrated by strong second harmonic generation when arranged in a suitable morphology.^{1–4} Films of these dyes may be deposited by the Langmuir–Blodgett (LB) method in arrangements which provide the noncentrosymmetry of chromophore dipoles necessary to observe even order nonlinear effects.^{3,4} We have recently shown⁵ that the second harmonic generation (SHG) from an LB monolayer of a hemicyanine dye may be enhanced by utilizing the excitation of a surface plasmon mode at a silver surface to concentrate and align the field of the incident radiation in the dye monolayer. Since this experiment necessarily requires the deposition of the dye onto a silver substrate rather than the glass substrates of previous studies, it is of value to compare the optical and structural properties of the dye films on both substrates. By analogy with this previous study we propose to carry out the initial investigation of the dye/silver system in the same experimental geometry using surface plasmon spectroscopy (SPS).

The value of surface plasmon spectroscopy in probing the optical and structural properties of absorbing LB films has been demonstrated in previous studies.^{6–9} The dispersive properties of the materials are determined by this method and electronic transitions which are subject to little damping are revealed as “back bending”¹¹ in the plasmon dispersion curve. This back bending is a result of molecular exciton–surface plasmon polariton coupling. For dipole aligned dyes, the anisotropy produces a single back bending, however, double back bending may also be possible in films which possess significant optical isotropy.^{10,11}

In addition to this optically mediated interaction, there may be interactions which are Coulombic or chemical in origin, and significant only at distances of less than 1 nm which have not been emphasized in these previous studies. The dye chromophores are usually separated from the silver surface either by their hydrocarbon tails or by a predeposition of inert spacer layers. In this work, the dye is in direct contact with the silver metal surface and in further contrast to the previous studies we propose to study the interaction in which the optical electric field is nearly parallel to the transition moment of the deposited dye.

EXPERIMENTAL

The silver depositions were made by evaporation of silver (99.99%, Goodfellow Metals) from a tungsten basket at a pressure of 5×10^{-5} mbar. The thickness was monitored by following the frequency change of a quartz crystal oscillator during the deposition. Clean glass slides (Chance Prop-er) were used as substrates for the absorption studies, whereas for the attenuated total reflection (ATR) spectroscopy the evaporation was made onto the hypotenuse face of a right angle glass prism (Schott BK7, $n_d = 1.517$). A silver depth of 480 Å was deposited for these studies. The organic overlayers were transferred immediately after removal of the substrate from the evaporator using the Langmuir–Blodgett technique.¹² The deposition conditions for the active dye layers and the inert fatty acid layers are given in Table I.

The dye monolayers were deposited hydrophilically by withdrawing the substrate through a compressed monolayer of dye molecules on the subphase surface. This allows the chromophore head group to be in closest proximity to the silver.

ATR measurements were made in the Kretschmann¹³ configuration and using the equipment shown schematically in Fig. 1. Reflectivities of *p*-polarized incident light in the range 400 to 750 nm were measured and for the thin films considered showed resonant coupling to the single TM surface plasmon mode. The use of glass optics precluded a study of the near ultraviolet region.

The absorption measurements in the range 300–700 nm were made via transmission through the sample and reference substrate at normal incidence using a Cary 2300 double beam spectrophotometer.

RESULTS AND DISCUSSION

The absorption spectrum of a monolayer of hemicyanine hydrophilically deposited on glass is shown in Fig. 2. The wavelength of maximum absorption, λ_{\max} , at 480 nm is very similar to the corresponding value for the absorption of a 10^{-4} M solution of the dye in chloroform ($\lambda_{\max} = 495$ nm). The rise below 350 nm corresponds to higher energy transitions also seen in the spectrum of the dye solution. Unlike the absorption characteristics of squarylium and carbocyanine LB films⁷ there is no evidence here of a dimer

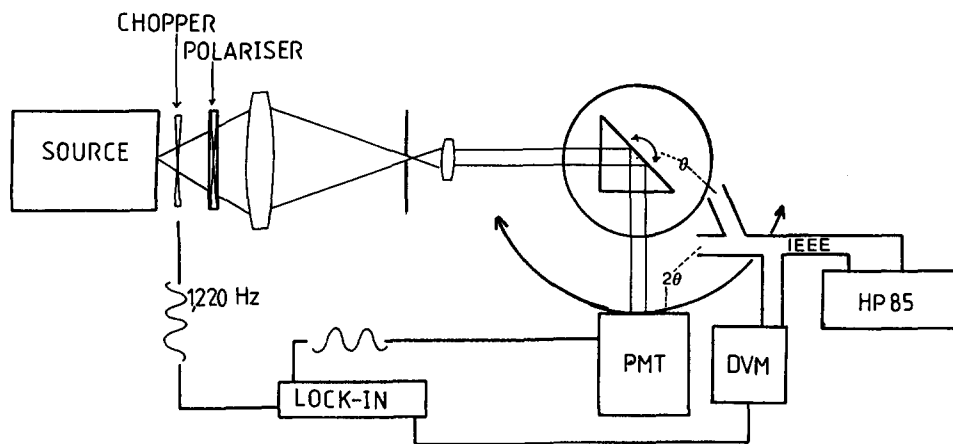


FIG. 1. Experimental configuration for angular scans in ATR studies.

band and we thus assign the absorption peak to a discrete monomer electronic transition. The effective oscillator strength of the transition (as obtained from the absolute area under the peak) was: $f(480) = 0.062$. This is about one order of magnitude lower than the value calculated for the same transition in solution [$f(\text{sol}) = 0.65$]. The solution value represents an isotropic system and corresponds to a maximum possible molecular oscillator strength, $f(m) = 3 \times f(\text{sol})$ for the transition moment aligned along the incident optical field. In the present experiment, the transition moment is coincident with the long axis of the dye chromophore (the LB deposition certainly gives anisotropic optical properties as manifested by the observation of second harmonic generation⁴). The low value of effective oscillator strength obtained is therefore easily reconciled with the much larger solution value if we assume the chromophores are aligned almost normal to the substrate (and also to the optical electric field).

For a polar angle θ , relative to the substrate normal, we have

$$\sin^2 \theta = f(480)/f(m)$$

giving $\theta \approx 10.25^\circ$. It should be emphasized however that the monolayer film is by no means dilute and that the effective oscillator strength obtained will certainly contain a contribution from local field effects. These will act to modify the effective strength of the transition but since their sign and magnitude are not known, these effects are not accounted for in this analysis. Even accepting these considerations it is of interest to compare this result with the value of θ of 20° obtained in Ref. 4 from an analysis of the SHG of a hemicyanine monolayer on glass.

To further probe the optical properties of hemicyanine monolayer films, we have investigated the optical dispersion

TABLE I. Langmuir-Blodgett film preparation conditions.

	Concentration (solvent)	pH	π (mN m ⁻¹)	Subphase
Hemicyanine	10 ⁻³ mol dm ⁻³ (CHCl ₃)	9.5	35	> 20 M Ω cm water
ω -Tricosenoic acid	10 ⁻³ mol dm ⁻³	4.5	30	> 20 M Ω cm water

of the dye by an analysis of the attenuated total reflection (ATR) from dye deposited on a silver substrate. Prism coupling in a Kretschmann¹³ configuration was employed.

The ATR spectra of a bare silver layer and a silver/dye layer system are compared in Fig. 3. The data shown is for 440 nm incident *p*-polarized light. The three empirical parameters of interest and their relationship to the overlay optical properties are:

- (i) The change in coupling angle induced by the dye, $\Delta\theta_c$. This is representative of the change in the real part of the surface plasmon wave vector and qualitatively reflects the real part of the dielectric function of the overlay.
- (ii) The change in width of the surface plasmon resonance, $\Delta\theta^{1/2}$. This mirrors the loss mechanisms (absorption and in-plane scatter) in the overlay and is qualitatively related to the imaginary part of the dielectric function of the overlayer.
- (iii) The change in resonant reflectivity ΔR_{\min} . This is qualitatively similar to $\Delta\theta^{1/2}$.

As can be seen from the plot of these parameters vs wavelength (Fig. 4) there are no maxima seen in $\Delta\theta^{1/2}$ or ΔR_{\min} in the region of the absorption maximum of the glass deposited dye and the theoretically predicted back bending¹¹ in $\Delta\theta_c(\lambda)$ is not seen.

The monotonic rise of all three functions to short wavelength makes a simple interpretation difficult. Such behavior occurs even for materials without electronic transitions in

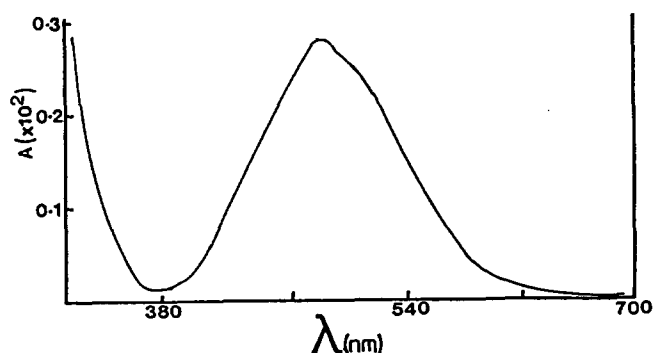


FIG. 2. Normal incidence absorbance of a monolayer of hemicyanine on glass.

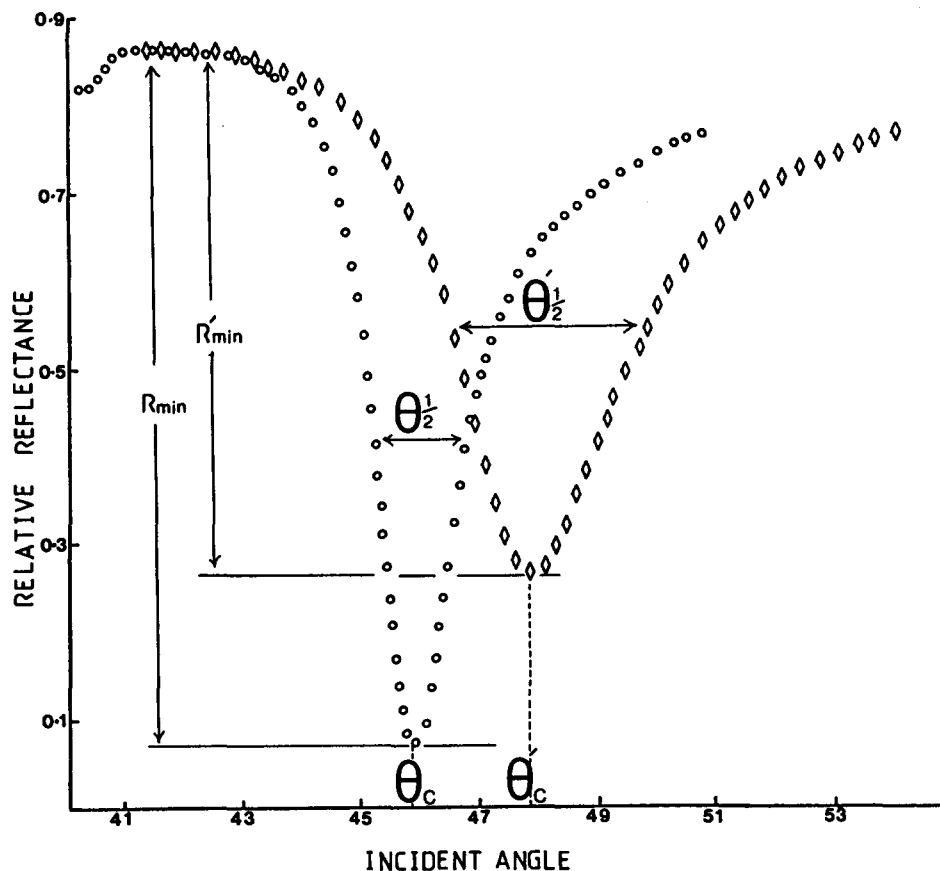


FIG. 3. ATR spectra for silver (circles) and silver + hemicyanine (diamonds) at 440 nm incident light.

this wavelength range.¹⁴ We have thus fit these empirical data to exact Fresnel reflection formulas using a least squares fitting procedure to obtain the real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric function of the dye. The fitting is first made to the reflection data obtained from uncoated silver.

The optical constants and thickness obtained are then held fixed in the least squares fitting of the dye coated silver reflection data. As was found in Ref. 14 we also are unable to improve the confidence in the fit by assuming an anisotropic model for the dye overlayer and have thus assumed instead a simple isotropic scheme.

The calculated ϵ_r and ϵ_i are shown plotted vs wavelength inset in Fig. 4. It is worth noting here that the absolute values for these functions obtained by this method are sensitive to the calculated silver parameters which are held fixed in the analysis. The LB film protects the silver surface from the tarnishing which is known to occur^{14,15} and which can significantly modify the reflectivity properties. An XPS study of a 500 Å silver film prepared in this laboratory and exposed to the atmosphere for 24 h, shows a thin (< 5 Å) layer of chemisorbed oxygen and physisorbed hydrocarbons. The effects of this surface layer are left uncorrected for in the analysis.

If we assume a single pole model for the optical properties of the dye the experimental dispersion might be described by

$$\epsilon(\omega) = \epsilon_\infty + \frac{A}{(\omega - E) + i\eta},$$

where ϵ_∞ is the static dielectric function with E and η repre-

senting the frequency and width, respectively, of the transition. Separating the real and imaginary parts of the above expression gives

$$\epsilon_r = \epsilon_\infty + \frac{A(\omega - E)}{(\epsilon - E)^2 + \eta^2} \quad \text{and} \quad \epsilon_i = \frac{-\eta A}{(\omega - E)^2 + \eta^2}.$$

Thus ϵ_r should pass through a minimum at a slightly higher energy than the maximum in ϵ_i (i.e., where $\omega = E$) which coincides with the transition frequency of the dye. These ATR measurements (Fig. 4) clearly indicate that the transition frequency of the silver/dye system lies at wavelengths below 400 nm.

Normal incidence transmission measurements have been performed on monolayer samples of hemicyanine deposited hydrophilically on 350 Å of evaporated silver, the absorption spectrum is shown in Fig. 5(a). The major differences between this result and that obtained for glass deposited hemicyanine are (i) the apparent large (> 100 nm) hypsochromic shift (consistent with the SPS spectrum) of the transition frequency, with the appearance of a shoulder at longer wavelengths and (ii) an apparent enhancement, by at least one order of magnitude, in the strength of the absorption.

The enhancement of the Raman scattered signal of molecules adsorbed on metal surfaces has been extensively studied both experimentally¹⁵⁻¹⁸ and theoretically¹⁹⁻²⁴ and enhancements of between four and six orders of magnitude have been observed. The enhancement may be optically mediated as in the surface plasmon enhancement or mediated through static (Coulombic/chemical) interactions. The en-

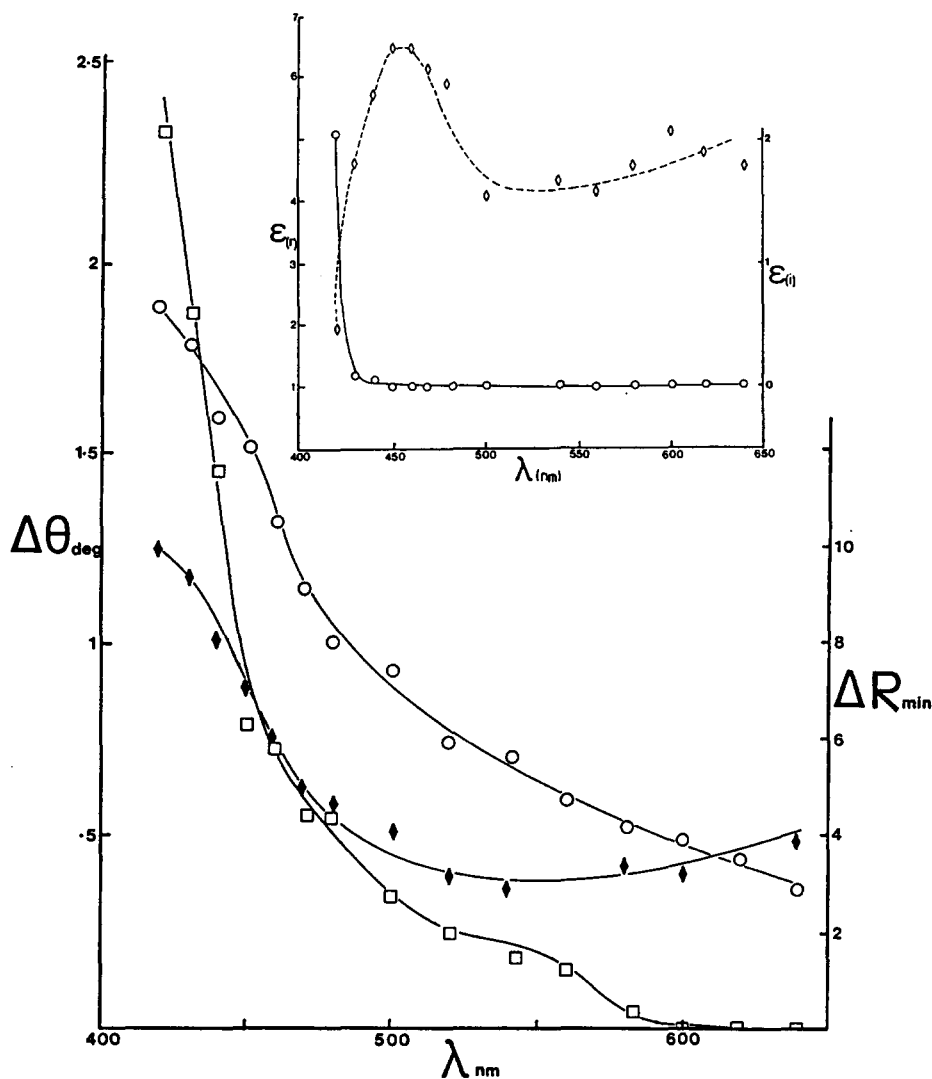


FIG. 4. Qualitative parameters determined from ATR measurements; $\Delta\theta^{1/2}$ (squares), $\Delta\theta_i$ (circles), ΔR_{\min} (diamonds). Inset; dispersive properties of the hemicyanine on silver calculated from Fresnel reflection formulas.

enhancement in the absorption seen in the present study could be explained by any of these mechanisms of field enhancement, particularly since the deposition method arranges the chromophore in close proximity to the metal.

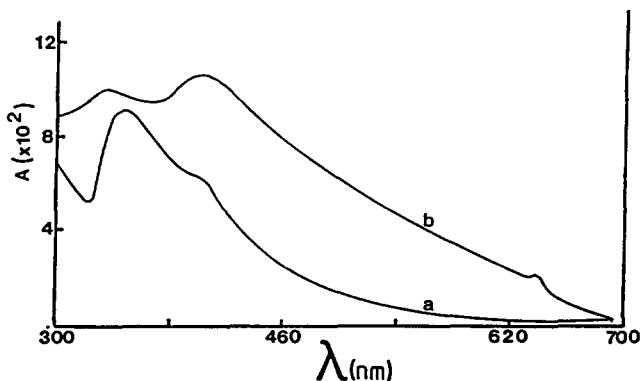


FIG. 5. (a) Normal incidence absorbance of a monolayer of hemicyanine on 350 Å of silver. (b) As for (a) but including a monolayer of ω -tricosenoic acid as a spacer between dye and silver.

Equally, the apparent enhancement in the absorption could be due to a more favorable alignment of the dye to the incident optical field, that is with the chromophores aligned with an average polar angle greater than that for the dye on glass. A point in favor of this suggestion, is that Earls *et al.*²⁵ have found a quasicrystalline form of hemicyanine deposited on silicon with an average polar angle of 40°.

The apparent shift in the transition frequency to higher energy may be explained by postulating the formation of a dye/silver charge transfer complex in which the dye is partially oxidized and transfers charge to the continuum states of the metal. [A hypsochromic shift of similar magnitude is known to occur upon protonation (in acidic solution) of the nominally neutral and structurally analogous stilbazolium betaine.²⁶] Such a mechanism can only be significant when the donor is within a few angstroms of the metal and should be suppressed with the inclusion of an inert spacer layer. Correspondingly we have prepared a system in which the dye is separated from the metal surface by the predeposition of a monolayer of ω -tricosenoic acid. The optical absorption of this system is shown in Fig. 5(b).

The sharp feature at 360 nm seen in trace (a) is now seen as only a shoulder on a broad absorption whose maximum lies in the region of 400 nm. The broadness is indicative of increased disorder in the hemicyanine layer. It is however clear that a separation of the dye from the silver of 30 Å is sufficient to give a substantial shift of the spectrum towards partially restoring the qualitative features of the spectrum of the dye deposited on glass.

Moreover, the resulting shift and shape of the spectrum is qualitatively similar to that observed on partial reduction of the merocyanine dye of Ref. 26.

SUMMARY

We have shown that the electronic characteristics of the highly polarizable hemicyanine dye are radically altered when brought into proximity with a silver metal surface. In particular we have observed a short range interaction which we tentatively ascribe to charge transfer between the discrete levels of the adsorbate and the continuum states of the metal.

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