# Resonant Interaction of Surface Plasmons with a Dye Monolayer

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Surface plasmons on silver films covered with organic monolayers (dye molecules (S 120) deposited on cadmium arachidate Scheibe or *j* aggregate) are studied in detail. The optical properties of this system derived from reflection measurements can be described by a rather simple one electron oscillator model. The damping of its eigenfrequency is rather small due to the regular arrangement of the dye molecules. ATR measurements showed a strong influence of this narrow resonance on the dispersion relation of surface plasmons. These observations can be well described by the dielectric function derived from the reflection measurements. The dye molecules are deposited on a cadmium arachidate film of 27 Å thickness. In the case of more than one cadmium arachidate space layer between dye and metal the agreement of observed data with those calculated using the oscillator constants gets worse. This is explained by the decreasing order of the dye molecules in the *j*-aggregates with increasing number of space layers.

## I. Introduction

The eigenfrequency of surface plasmons (SP) is strongly dependent on thin coating films which cover the metal (plasma) surface [1]. Such films can have in general a dielectric function nearly independent of the frequency without or with an imaginary part [2]. Special interest have films which have an eigenfrequency with a small damping. E. g. a dye in a j-aggregate has these properties, as Fig. 1 (full line) demonstrates [3]. In t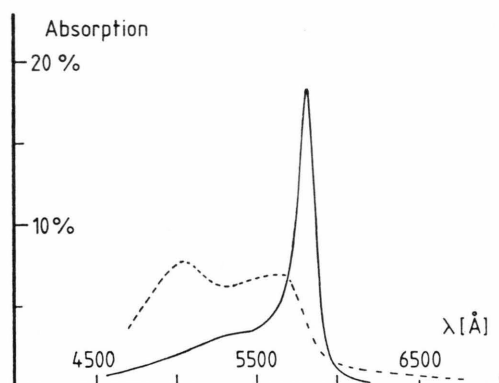he following a more detailed description of experiments with SP on dye covered silver surfaces is given. The first experiments are outlined in [4 – 6].

## II. The Dye Monolayer

The system used in these experiments in drawn in Fig. 2 (system I). In order to excite SP in the boundary metal/dye we have to use a metallic substrate (here silver). The dye (⊔) is deposited (see Appendix A) on the silver surface with a spacer



Fig. 1. Absorption spectra of a well ordered (full line) and of a perturbated dye monolayer (dotted line) on a glass substrate. These measurements were performed with the dye S 120 (see text).
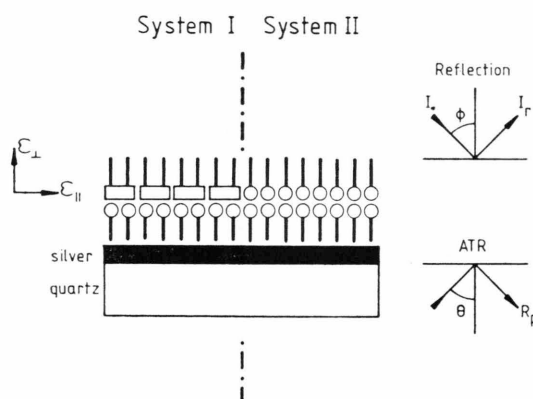


Fig. 2. Sketch of the layer system for reflection (light comes from above) and for ATR experiments (light comes from below). A quartz slide is covered with evaporated silver (black area). This silver film is coated by an organic monolayer of C20 (|: hydrocarbon chain, ○: hydrophillic head of C20; ⊐: chromophore ringsystem of the dye molecule, see text). The dielectric function $\varepsilon_\perp$ is valid in the direction perpendicular and $\varepsilon_{||}$ parallel to the surface of the substrate. The upper Cd arachidate monolayer of system II behaves optically like the hydrocarbon chains of the dye molecule so that system I and II differ optically only by the chromophore ringsystem (⊐) of the dye.

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of one monolayer of cadmium arachidate (C20, $\overset{O}{\underset{|}{\phantom{.}}}$ , $n_{C20} = 1.52$, no absorption, 27 Å thick or multiples). This is necessary since the dye does not organize as j-aggregate when in direct contact with the metal film. Usually the dye monolayers are deposited on glass substrates for absorption measurements. If monolayers are transferred from a water surface onto a metallic substrate (see Appendix), they are frequently perturbated as can be seen in the case of dye monolayers from the broad absorption curve Fig. 1 (dashed line).

We used as dye the compound 1-octa-decyl-1-1'methyl-2,2'cyanin perchlorat (S120). As can be seen from the structural formula the dye molecule consists of two parts:
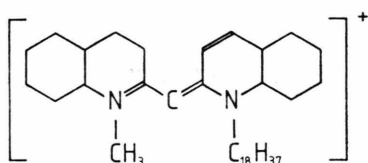
The hydrophyllic chromophore ringsystem ($\square$ in Fig. 2) is 7 Å thick and the hydrophobic hydrocarbon chains (— in Fig. 2) are 15 Å long.

## III. The Determination of the Dielectric Function of the Dye from Reflection Experiments

In order to compare the results of the ATR measurements on dye monolayers described in Sect. IV with calculated values we have to know the dielectric function of the dye monolayer. We describe the optical behaviour of the organic film on the silver substrate by the tensor

$$\begin{pmatrix} \varepsilon_{||} & 0 & 0 \\ 0 & \varepsilon_{||} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix}.$$

Here $\varepsilon_{||}$ means the dielectric function parallel to the surface of the dye monolayer (isotropic in the surface), see Fig. 2, and $\varepsilon_{\perp} = \varepsilon_{\infty}$ the dielectric function of the hydrocarbon chains perpendicular to the surface, which has a value of 2.31 [6]. $\varepsilon_{||}$ is approximated by a one electron oscillator model $\varepsilon_{||} = \varepsilon_{||}' + i \varepsilon_{||}''$ and is written:

$$\varepsilon_{||}' = \varepsilon_{\infty} + C \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2}, \quad (1)$$

$$\varepsilon_{||}'' = C \frac{\Gamma \omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \quad (2)$$

with the eigenfrequency $\omega_0$, the oscillator constant $C = 4 \pi e^2 N/m$ (charge $e$, mass $m$, number of oscillators per unit volume $N$) the damping constant $\Gamma$ and the dielectric function of the dye outside the absorption band: $\varepsilon_{\infty}$. The dielectric function $\varepsilon_{||}$ is determined by measuring the light $I_{r,I}$ reflected at an angle of 45 deg from system I (as is explained in Fig. 2 in the upper right scheme) and $I_{r,II}$ reflected from system II at the same angle. The reflection apparatus at our disposal is constructed to give

$$H = \frac{I_{r,II} - I_{r,I}}{I_{r,II}} \quad (3)$$

for $p$ and $s$ polarized light or the absorption, see below. On the other hand $I_{r,I}/I_0$ and $I_{r,II}/I_0$ ($I_0$: incoming light intensity) can be calculated from the Fresnel coefficients for s and p polarization; thus (3) allows to compute $\varepsilon_{||}'$ and $\varepsilon_{||}''$ or $C$ and $\Gamma$, see (1) and (2), by a fitting procedure. In a first step we have determined $C$ and $\Gamma$ with s polarized light and then with these constants, the dielectric function normal to the substrate $\varepsilon_{\perp}$, so that the p-polarized experimental curve can be calculated. The value of $\varepsilon_{\perp}$ obtained is the same as that given above.

We see that the experimental values in Fig. 3 derived from reflection fit rather well the experimental data. The comparison of observed and calculated values shows less good agreement in the sidewings of the absorption curve which are certainly due to the absorption farer away from $\lambda_0$ having not been taken into account in the model.

In calculating the Fresnel's coefficients containing the dielectric tensor we have profited from the fact that the s polarized Fresnel coefficients can be computed with the dielectric function $\varepsilon_{||}$ as is done in the isotropic case whereas for p polarized light we have to compute with a corrected wavevector $k_x^*$

$$k_x^* = \frac{\varepsilon_{||}}{\varepsilon_{\perp}} k_x ,$$

$k_x$: x-component of the original wavevector $k$ [7, 8].

This evaluation has been made for several samples and the following values of the oscillator constants of the dye S120 have been obtained:

$$C = 2.1 \times 10^{31} \, s^{-2}, \quad \Gamma = 1.1 \times 10^{14} \, s^{-1}$$

and

$$\lambda_0 = 5860 \, \text{Å} .$$

The dielectric function $\varepsilon_{||}$ ((1) and (2)) with these parameters is displayed in Figure 4. These values

can be ascribed to the optical properties of the dye monolayer alone since the experimental results are normalized to the reflection $I_{r,\mathrm{II}}$ of the C20 coated metallic surface.



a)

b)

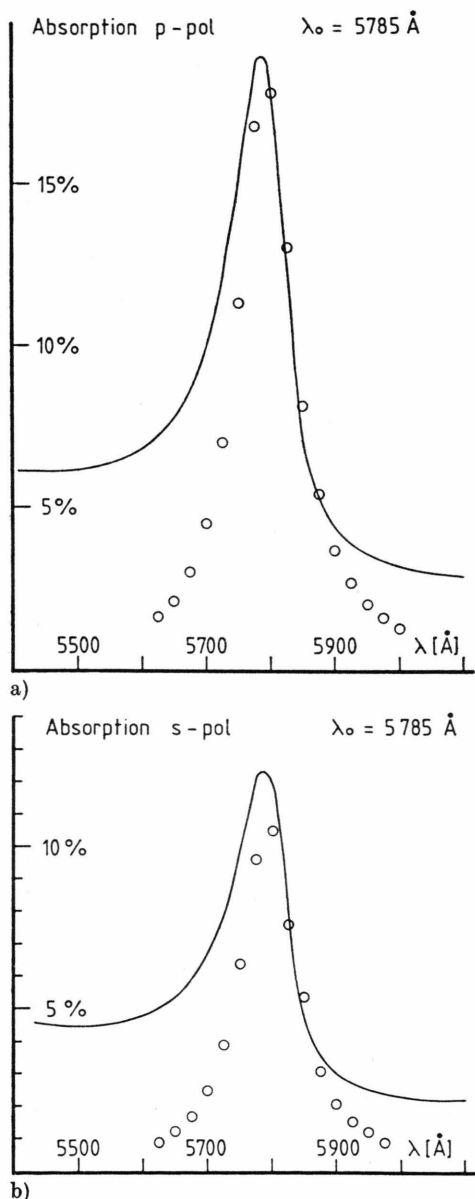Fig. 3. The function $H(\lambda)$, see (3). Figure 3a shows the results for p polarized light at an angle of incidence of 45 degrees and a dye monolayer with one C20 spacer on silver, whereas Fig. 3b displays the same for s polarized light. The full line is measured and the circles are calculated with the oscillator constants $\lambda_0 = 5785$ Å, $\Gamma = 1.1 \times 10^{14}$ s$^{-1}$, $C = 2.1 \times 10^{31}$ s$^{-2}$ and $\varepsilon_\perp = 2.31$. The difference of p and s polarized light comes from the anisotropy of the dielectric function of the dye (and not from the metal).
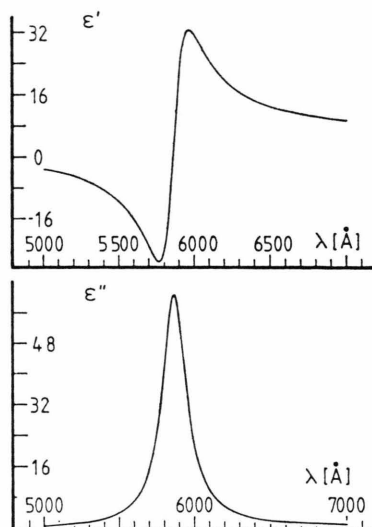


Fig. 4. The dielectric function $\varepsilon_\| = \varepsilon_\|' + i\varepsilon_\|''$ of the dye S120.

*Remark:*

The above expression $1 - I_{r\mathrm{I}}/I_{r\mathrm{II}}$ (see (3)) can be identified with the absorption $A$ of the dye, if we neglect in the known relation $1 = A + R + T$ the transmission $T$. Calculations of $A$, $R$ and $T$ using (1) and (2) and Fresnel's formula of the systems show that the transmission $T$ amounts to only a few percent and may be indeed neglected. This has allowed to derive in a first good step from the absorption spectrum (Fig. 1)

$$A = C \frac{d}{c \sqrt{\varepsilon_\infty}} \frac{\Gamma \omega^2}{(\omega_0{}^2 - \omega^2)^2 + \Gamma^2 \omega^2} \qquad (4)$$

(which is derived in [4]) the start values $C$, $\Gamma$ and $\omega_0$ for our fitting procedure. The thickness $d$ of the dye (7 Å) has been taken from the model of the dye molecule, see the chemical formula in Section II; the damping constant $\Gamma$ equals in a first approximation the halfwidth $\Delta\omega_0$ of the absorption curve.

## IV. Experimental Results with Surface Plasmons

In the ATR arrangement in Fig. 2 we irradiated the silver film covered with system I from below and measured the minimum of the reflected light intensity as function of angle of incidence $\theta$ at different wavelengths $\lambda$. The thickness $T$ of the silver film has been chosen so that a rather deep minimum in the reflection curve $R(\theta)$ is observed ($T \cong 500$ Å)
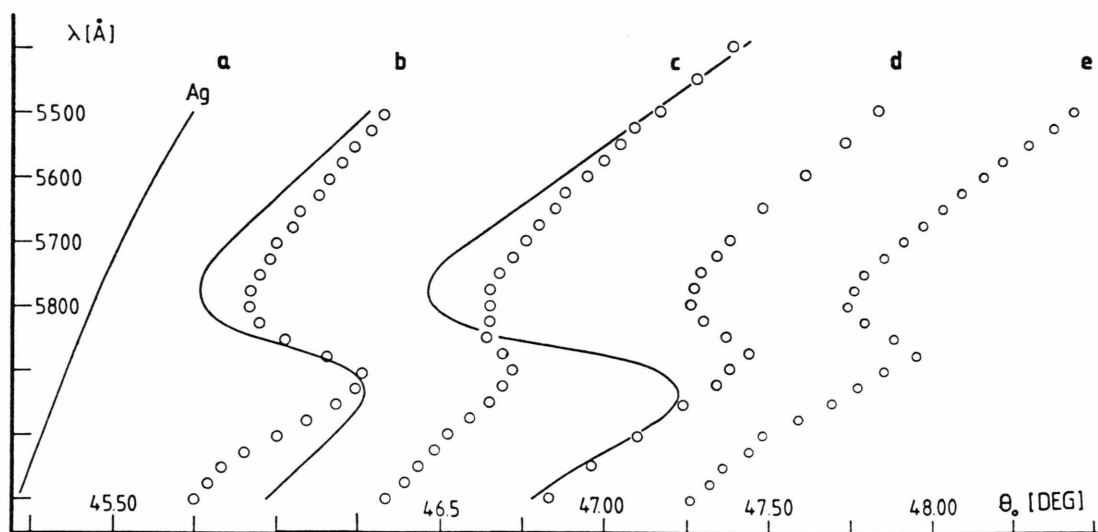
Fig. 5. Dispersion relations of some silver substrates 500 Å thick coated with one dye monolayer in different distances from the metal film. The full lines are calculated with the model parameters given in the text, the circles are measured values. Curve a) dispersion relation of the uncoated silver film; curve b) one C20 spacer between metal film and dye (☐─○─☐); curve c) three C20 monolayers between silver film and dye (☐─○─○─☐); curve d) two C20 monolayers between metal film and dye which is covered with one C20 layer (☐─○─○─☐─○─); curve e) four C20 monlayers between metal film and dye which is covered with one C20 monolayer (☐─○─○─○─○─☐○─). The layer systems d and e are prepared with the touching method. The last C20 monolayer is necessary to protect the dye against oxidation.

[9]. The characteristic data of the minima of the ATR reflection curves, i. e. the position $\theta_0$ of the maximum excitation of surface plasmons, the halfwidth $\theta_{1/2}$ and the reflected intensity in the minimum $R_{\mathrm{pmin}}(\theta_0)$, are then plotted vs. the wavelength. The experimental values are displayed by the open circles in the Figures 5 to 7.
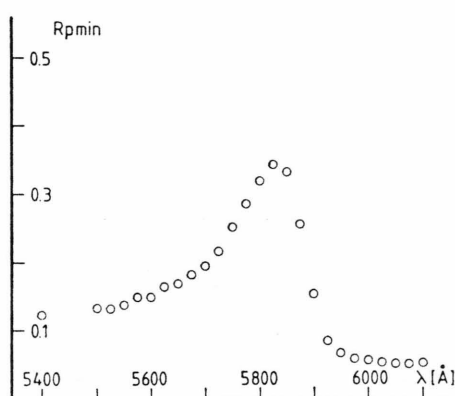


Fig. 6. The measured minima $R_{\mathrm{pmin}}(\lambda)$ of the ATR reflection curves as function of wavelength $\lambda$. The dye S120 is deposited onto the silver substrate with the touching method. The spacer is four C20 monolayers thick and the dye is coated with one C20 monolayer. (case e of Figure 5).



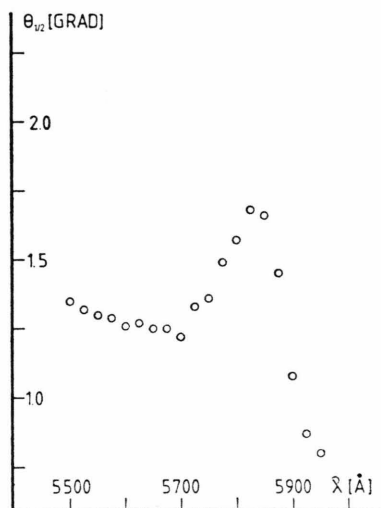Fig. 7. The halfwidths $\theta_{1/2}(\lambda)$ of the ATR reflection curves (minima) displayed in Figure 6.

The general result can be resumed as follows:

1) The position of the reflection minimum $\theta_0$ shifts with decreasing wavelength to higher angles of incidence, turns back and increases again, after passing the eigenfrequency $\omega_0$ or the correlated wavelength $\lambda_0$ (Fig. 5),

2) the intensity in the reflection minimum $R_{pmin}$, Fig. 6, and

3) the halfwidth $\theta_{1/2}$ go through a maximum (Figure 7).

Some of these results for one C20 layer have been briefly published in [10, 4].

Similar experiments have been performed with other dyes, e. g. 3,3'di-octa-decyl-2,2'thiacyanin perchlorat (S11) and 1,1'di-octa-decyl-3,3'diethyl-5,5',6,6'tetrachloro-2,2'imidazolocarbocyanin p-toluol-sulfonat (OB6). These dyes show in principle the same optical behaviour as the dye S120 (one C20 monolayer as spacer between dye and metal film).

Table 1 shows the characteristic data of the absorption and ATR experiments of the two dyes:

Table 1.

| dye | $\lambda_0$ [Å] | $H(\lambda_0)$ [%] | $R_{pmin}$ [%] | $\lambda_0$ [Å] | $\theta_{1/2}$ [deg] |
|-----|-----|-----|-----|-----|-----|
| S11 | 4555 | 12 | 27 | 4555 | 2.8 |
| OB6 | 5870 | 7.5 | 33 | 5925 | 1.1 |

Outside the absorption band ($H(\lambda_0) = 12\%$) of the dye S11 there exist sidewings (5%); thus the maxima of $R_{pmin}(\lambda_0)$ and $\theta_{1/2}(\lambda_0)$ are not strongly pronounced. The dye OB6 behaves optically like the dye S11; besides this the transfer of the OB6 monolayer from the water surface onto the metallic substrate is difficult due to its stiffness.

For the reasons mentioned above we have preferred the dye S120 and have performed a smaller number of experiments with the dyes S11 and OB6.

The experiments with S120 at different distances between dye and silver film were evaluated and compared with calculated data:

Using the Fresnel relations which contain the distance $d$ between dye and silver film one can calculate the influence of $d$ on the ATR minima just described. The following results are obtained:

1) The position of the minima shifts monotonically to larger angles $\theta_0$ with increasing thickness $d$.
   The amplitude of the swing of the dispersion relation increases with increasing distance $d$. The full lines of Fig. 5 curve (b) and (c), show this effect; they are calculated with the same oscillator constants.

2) The reflection $R_{pmin}(\lambda_0)$ increases with increasing distance (d) between dye and metal film from 55% at one C20 spacer to roughly 70% at more than 12 C20 monolayers. This dependence passes a flat maximum at 14 C20 monolayers.

3) The halfwidth $\theta_{1/2}(\lambda_0)$ increases monotonically from about 2 degrees to 20 degrees for 16 C20 monolayers spacer. For a thicker spacer the halfwidth remains nearly constant.

These calculations have to be compared with the experimental results. The main features of these results are displayed in Table 2, which gives a survey over the experiments with the dye S120. Two results are evident: contrary to the calculation, the halfwidth $\theta_{1/2}(\lambda_0)$ remains nearly constant (1.8 degrees) and the reflection $R_{pmin}(\lambda_0)$ as well as the absorption $H(\lambda_0)$ decreases with increasing spacer between dye and metal film. The curves (b) and (c) represent 1 and 3 spacelayers of C20. The layers are described in Figure 5. The experimental curve (b) is in more or less good agreement with calculated values. With the constants derived from curve (b)

Table 2. Experimental results from the dye S120. $m$: Number of the C20 monolayers between dye and silver film in the case of the LB Method, with the Touching Method this quantity is $m - 1$. LB: Langmuir Blodgett Method; T: Touching Method.

| Curve (Fig. 5) | $m$ | | Reflection Measurement | | | | | | | ATR-Measurement | | | Calculated ATR results: * | | |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | | | | p-pol. | | | s-pol. | | | | | | | | |
| | | | $\lambda_0$ [Å] | $H(\lambda_0)$ [%] | $\Delta\omega_0$ [$10^{12}$ s$^{-1}$] | $\lambda_0$ [Å] | $H(\lambda_0)$ [%] | $\Delta\omega_0$ [$10^{12}$ s$^{-1}$] | $\lambda_0$ [Å] | $R_{pmin}$ [%] | $\theta_{1/2}$ [deg] | $\lambda_0$ [Å] | $R_{pmin}$ [%] | $\theta_{1/2}$ [deg] |
| b | 1 | LB | 5785 | 19 | 85 | 5785 | 12 | 85 | 5860 | 60 | 1.9 | 5860 | 55 | 2.1 |
| c | 3 | LB | 5890 | 10 | 91 | 5890 | 7 | 83 | 5875 | 45 | 1.8 | 5890 | 78 | 3.4 |
| d | 3 | T | 5845 | 11 | 83 | 5850 | 10 | 83 | 5825 | 43 | 1.8 | 5825 | 75 | 2.2 |
| e | 5 | T | 5830 | 7.7 | | 5825 | 6.4 | | 5825 | 31 | 1.6 | 5825 | 78 | 3.2 |

* with the mean value parameters.

the curve (c) is calculated. The amplitude of the swing of the experimental curve (c) is smaller than is calculated; it does not increase with $d$. The same difference is noticed in $R_{\mathrm{pmin}}(\lambda_0)$ which decreases and in $\theta_{1/2}(\lambda_0)$ which does not increase but remains nearly constant in contrast to the calculated results. Table 2 shows further the results for the resonance wavelength $\lambda_0$ (left column).

In another series of experiments, see curves (d) and (e), the dye was arranged as indicated in Figure 5.
The experimental curves show the same tendency.

The differences of observed and calculated data are very probably due to the fact that well ordered dye monolayers on thicker films of C20 are difficult to deposit on silver substrates. The j-aggregates exist apparently as islands between non organised molecules.

A similar conclusion can be drawn from the difference ob $H(\lambda_0)$ at s and p polarisation which decreases with $d$, see Table 2. This can be interpreted as: the less the difference of the absorption of s and p polarized light becomes, the more non-organized molecules exist in the layer.

As we see, the optical properties of a dye layer covering one C20 layer can well be described with the one electron oscillator model. However the effects calculated for several C20 layers could not be observed due to difficulties in preparing well ordered j-aggregates.

## Appendix

### Preparation of the Monolayers

In order to deposit a dye monolayer onto a metallic surface on which we excite surface plasmons, first a Cadmium-Arachidate (C20) monolayer is transferred onto the metal film. These can be deposited onto the substrate by using the following methods:

### Langmuir Blodgett Method [11, 12]

First a fatty acid (C20) is spread on water containing $30 \times 10^{-4}$ mol $CdCl_2$ at pH 6.4. In order to get densely packed monolayers, a surface pressure of 30 dyn cm$^{-1}$ is applied after evaporation of the solvent. This monolayer can be transferred onto a metallic substrate by dipping it through the monolayer into the water. In this way the hydrophobic

hydrocarbon chain of C20 is attached to the metallic substrate, see Fig. 2 in [6]. The dye monolayer is transferred onto the metal film in the same way. The dye molecule consists of a hydrophillic chromophore ringsystem with hydrophobic hydrocarbon chains. First one (or three or five) C20 monolayers are transferred, then the substrate being in water, the water surface is cleaned and the dye monolayer is produced. After stabilization of the dye monolayer it is deposited onto the substrate by drawing the substrate slowly out of the water.

### Touching Method

The monolayers are produced on water in the same way as in the Langmuir-Blodgett case, but the dye monolayer is transferred onto the metallic substrate in another way. First two (or four) C20 monolayers are deposited onto the silver film by the Langmuir-Blodgett method, then this substrate is dipped through the dye monolayer into the water, see Figure 8 a. But different from the Langmuir-Blodgett method the normal of the substrate slide is parallel to the normal of the water surface.
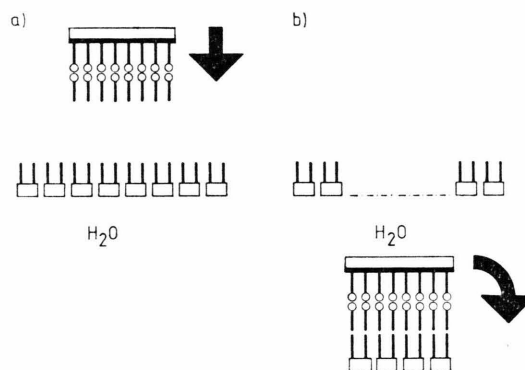


Fig. 8. Touching Method:
⊥⊥: dye molecule; the box represents the hydrophillic chromophore ringsystem, the bars the hydrocarbon chains of the dye molecule. The metallic substrate covered with two monolayers of C20 ($2 \times 27$ Å) just before being dipped through the dye monolayer into the water (a).

In (b) the substrate has been dipped. The water surface is the cleaned from the dye layer and replaced by a C20 monolayer. Now the substrate is turned by $90°$ inside the water and drawn out of the water as in the Langmuir-Blodgett case, see Fig. 2 in [6]. It is now covered with a C20 monolayer

which protects the dye from oxydation. Its hydrophobic side forms the exterior side.

To control the stability of the film the value of $H(\lambda)$ (see (3)) has been measured 2 and 24 hours after preparation. The samples were stored under reduced pressure and different protective gases. The

variation of the curves $H(\lambda)$ was less than that of different samples.

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