Resonant Interaction of Surface Plasmons with a Dye Monolayer

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The interaction of surface plasmons with a dye monolayer having a rather small absorption band is discussed in this paper. Applying the ATR method surface plasmons were excited on a silver surface covered with a monolayer of arachidate (26.8 Å) and a monolayer of the dye.

The position, half-width and the depth of the reflection minimum are strongly dependent on the applied wavelength in the region of the absorption line. The essential features of the measured dependencies can be explained by a simple oscillator model.

It has been shown that monolayers of long chain fatty acids e.g. arachidic acid deposited on thin silver- and gold films can be detected by the ATR-method (excitation of surface plasmons); their optical properties have been derived from such observations [1, 2, 3]. This method has been used now to investigate the influence of a dye monolayer with a strong absorption band in the visible region of the spectrum in an arrangement where the silver film is covered by a monolayer of fatty acid and a dye monolayer (see Figure 1). At the surface of the silver film (500 Å thick) surface plasmons are excited with the aid of a quartz cylinder, see also [4]. For a fixed wavelength the reflected intensity R_p is recorded as a function of the angle of incidence Θ. A minimum of R_p is observed at an angle Θ_0. If the metal film is coated with organic monolayers this minimum displaces. For this purpose we used the dye 1-octa-decyl-1′-methyl-2,2′-cyanine perchlorate (abbrevation S. 120) organized in J-aggregates [5] with a narrow absorption band at about $\lambda_0 = 5750$ Å. Several effects have been observed measuring the reflection curves $R_\mathrm{p}(\Theta)$ with the wavelength of the exciting light as parameter.

1. The depth of the reflection minimum $(1 - R_\mathrm{min})$ passes a minimum at λ_0. Figure 2 shows R_min as a function of the wavelength λ.
2. Parallel to this change the halfwidth of the reflection R_p passes a maximum at λ_0, as shown in Figure 3.
3. The angle Θ_0 depends on λ as shown in Fig. 4, demonstrating an anomalous behaviour around λ_0. This is unusual since the dispersion relation in general has no turning point [4].

These phenomena indicate a strong interaction of the surface plasmons with the excited dye monolayer.

To describe these observations the classical model of an electron oscillator with an eigenfrequency ω_0 can be used as rough approximation, thus we have a dielectric function $\varepsilon = \varepsilon_1 + i\,\varepsilon_2$. To get the numerical data of ε we have performed a transmission experiment to determine the position λ_0 and the halfwidth of the absorption band $\Delta\omega$. The absorption of N oscillators per unit volume (charge e, mass m, frequency λ_0, damping constant Γ, d thickness of the chromophore) in a dielectric medium of refraction index n is given by

$$A = \frac{4\pi}{n\,c}\,\frac{e^2}{m}\,N\,d\,\frac{\omega^2\,\Gamma}{(\omega_0{}^2 - \omega^2)^2 + \omega^2\,\Gamma^2}\,. \qquad \text{(I)}$$

This equation is derived as follows: The absorption A is given by

$$A = 1 - \frac{I}{I_0} = \frac{4\pi\,K\,d}{\lambda} \quad \text{for} \quad K\,d \ll \lambda$$

since

$$\varepsilon_2 = \frac{4\pi\,e^2}{m}\,N\,\frac{\omega\,\Gamma}{(\omega_0{}^2 - \omega^2)^2 + \omega^2\,\Gamma^2}$$

and

$$\varepsilon_2 = 2\,n\,K$$

(K = absorption constant) we obtain the relation (I).

According to this relation the damping constant Γ is related to the halfwidth of the absorption band (if $\Delta\omega/\omega \ll 1$) by

$$\Gamma = \Delta\omega\,. \qquad \text{(II)}$$

In the absorption maximum $\omega = \omega_0$ one has

$$A_\mathrm{max} = \frac{4\pi}{n\,c}\,\frac{e^2}{m}\,N\,d\,\frac{1}{\Delta\omega}\,. \qquad \text{(III)}$$

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If we measure now the absorption maximum in a transmission experiment of light through a dye monolayer on a sheet of glass, we get $A_{\max} = 0.125$ (corrected according to Ref. [6] from the measured value 0.15) and the halfwidth $\Delta\omega = 0.8 \times 10^{14}\ \mathrm{s}^{-1}$, we obtain from Eq. (I) with $\omega = \omega_0$ the value $C = \frac{4\pi e^2}{n c\ m} N d$. These figures are:

$$\lambda_0 = 5750\ \text{Å},$$
$$\Delta\omega = 0.8 \times 10^{14}\ \mathrm{s}^{-1},$$
$$C = 1 \times 10^{13}\ \mathrm{s}^{-1}\ *.$$

With these data we have the dielectric function which we need for calculating the reflection curve $R_p(\lambda, \Theta, \varepsilon(\lambda))$ [7, 8] for the system quartz/silver/Cd-arachidate/air as a function of Θ with λ as parameter. For this computation we assume $d = 7$ Å. This curve yields the position of the reflection minimum Θ_0, its halfwidth $\Delta\Theta$ and the depth of the reflection minimum $(1 - R_{\min})$.

For the calculation we took average optical properties of silver and Cd-arachidate [3]. The dielectric constant of the Cd-arachidate was assumed to be independent of the wavelength λ in the experimental range. The silver film was 500 Å and the Cd-arachidate monolayer 27 Å thick.

The calculated function R_p did not agree satisfactorily with the measured values, therefore we tried to fit the experimental results by using different values of C, Γ and λ_0. A rather good

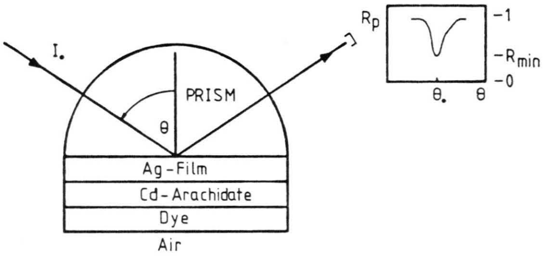

Fig. 1. Experimental arrangement. P-polarized light of intensity I_0 (wavelength λ) is totally reflected at the boundary quartzprism-silver and is detected with a photomultiplier. Surface plasmons are excited at the boundary silver-Cd-arachdate, if the dispersion relation is fulfilled. This excitation is detected as a minimum in the reflected light.

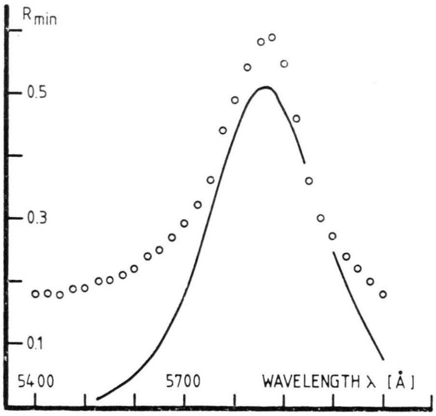

Fig. 2. The minima ($R_{\min}$) of the reflection curves R_p obtained with the ATR-method as a function of wavelength λ on the system Ag/Cd-arachidate/dye (the circles are experimental points, the full line is calculated).

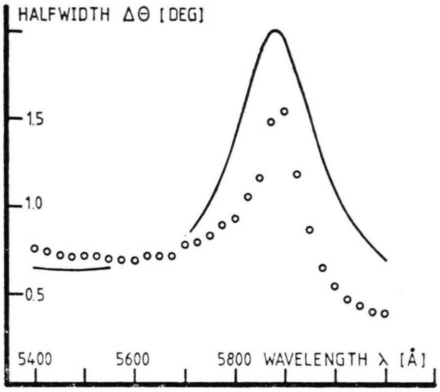

Fig. 3. The halfwidth's of the reflection curves R_p as a function of wavelength λ (the circles are experimental points, the full line is calculated).

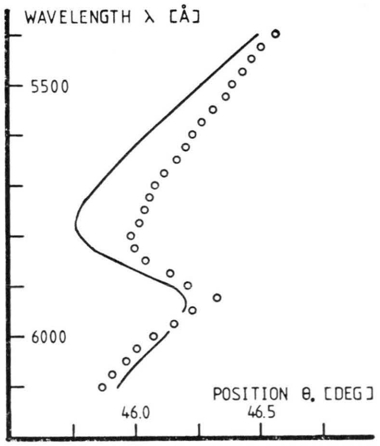

Fig. 4. Dispersion relation. The position Θ_0 of the reflection minima ($R_{\min}$) as a function of the wavelength λ are plotted in Figure 4 (the circles are experimental points, the full line is calculated).

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* Note: It shall be mentioned that assuming one electron oscillator per dye molecule the value of $N \cdot d = 15.6 \times 10^{-3}$ Å^{-2} is obtained from measuring the monolayer isotherm [6]. From the absorption measurement we get in good agreement $N \cdot d = 14.2 \times 10^{-3}$ Å^{-2}.

agreement was obtained with the values

$$\lambda_0 = 5860\ \text{Å},\quad \Delta\omega = 1.2 \times 10^{14}\ \text{s}^{-1},\quad C = 3.4 \times 10^{13}\ \text{s}^{-1},$$

and the theoretical Figs. 2, 3 and 4 have been calculated with this set of values. The experimental results are represented by circles.

These plots show that the main features of the experimental results are reproduced by the theoretical curves. Some differences, however, are obvious: The maxima in figures 2, 3 and 4 are located at $\lambda_0 = 5860$ Å which differs from the wavelength of the absorption maximum $\lambda = 5750$ Å. (Similar shifts of the absorption band have been observed with two other dyes.)

Further the peak values of R_{min} and of the half-width $\Delta\Theta$ differ of about 20% from the calculated values. The reason for this differences may be the simplification made in applying the classical model:

1. The assumption of an absorption curve of a single electron oscillator, whereas the absorption spectrum of the dye monolayer shows a broad absorption band at shorter wavelength with respect to the main absorption band;
2. The neglection of the influence of the silver film in the proximity of the dye monolayer on the absorption of the dye.

Therefore, further work is needed to improve the theoretical model.

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