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Absorption and Emission of Evanescent Photons*

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Experiments have been carried out to investigate the excitation of molecules by evanescent light, and the emission of evanescent light in the fluorescence of excited molecules. It is confirmed that the absorption proceeds at a rate proportional to the second-order (normally ordered) product of the complex field amplitude, whether the light field is homogeneous or evanescent, and that the emission process follows a reciprocity principle.

INDEX HEADINGS: Absorption; Emission; Surface waves.

Evanescent waves have long been familiar in optics and certain of their properties have been investigated at length, both experimentally¹⁻⁹ and theoretically.¹⁰⁻¹⁸ They play an essential role in interference filters based on the phenomenon of frustrated total internal reflection,¹⁹ and a technique of internal-reflection spectroscopy, based on the interaction between evanescent waves and a sample material, has been developed in recent years.²⁰ In these investigations the absorbing material is usually described by a refractive index, rather than in atomic terms. But the interaction at the microscopic level of evanescent waves with atomic dipoles has apparently received little attention. Whereas semiclassical methods of treating this problem have long been available, it appears that no quantized-field approach to the problem existed until recently, and that questions regarding the possible emission or absorption of an evanescent photon could not be answered. Indeed, it has been customary in quantum optics to expand the electromagnetic field in homogeneous plane-wave modes, from which possible evanescent components are explicitly discarded.

We have remedied this situation in a recent quantum treatment of the electromagnetic field,²¹ in which evanescent waves were included. Because these waves are always associated with surfaces, we considered an interface between a dielectric and vacuum and regarded

each triplet of incident, reflected, and transmitted waves as one fundamental mode of the system. We showed that photons, or discrete excitations, could be associated with these modes, so that a photon which is evanescent in one half-space may be homogeneous in the other. That formalism allowed us to study the interaction of a quantized electromagnetic field, having only evanescent components in one half-space, with a bound electron in that half-space, and to calculate the probability of photo-ionization or photo-excitation of an atom. The probability shows a pronounced peak at the critical angle, when plotted as a function of the angle of incidence of the wave in the dielectric. The result coincides with that obtained from a semiclassical calculation, in which the electromagnetic field is treated as a c -number perturbation on the atom. The excitation probability is found to be proportional to the square modulus of the complex field amplitude (usually known as the intensity in the literature of coherence theory).

The results of these calculations ought, of course, to be tested by experiment, and this is the purpose of the work reported here. We have studied the excitation probability of certain dye molecules by evanescent light, by measuring the resulting fluorescence. We have also investigated the inverse process, in which the excited molecules decay by emitting evanescent waves, or evanescent photons. In both cases, we find that the

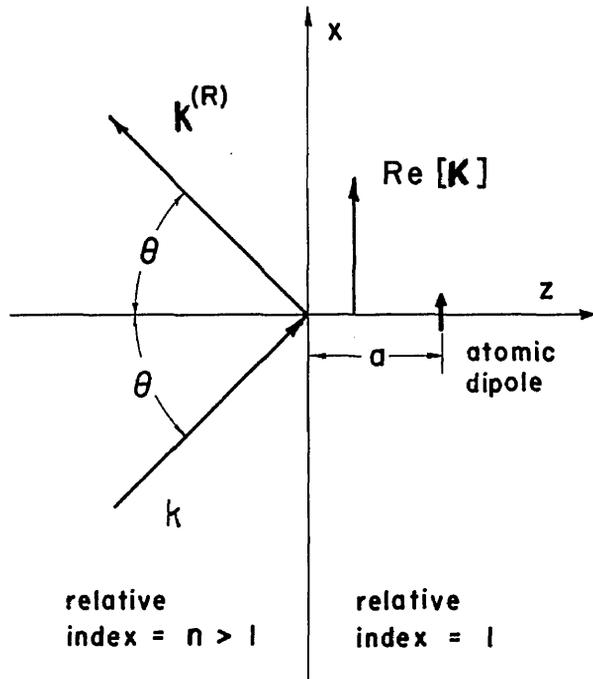


FIG. 1. Illustrating the principle whereby an atom or molecule is immersed in an evanescent optical field. A dipole excited by a T.E. wave would be perpendicular to the plane of the paper.

experimental results are in quantitative agreement with the theory, and that evanescent photons can be emitted and absorbed like homogeneous photons. Although some qualitative experiments on emission and absorption of evanescent light were carried out long ago,^{3,4} it is only since the development of the technique for depositing monomolecular dye layers⁶ that quantitative experiments on the interaction with single atoms or molecules became feasible. In this investigation we confirm that the absorption probabilities for evanescent and homogeneous photons are given by the same expression.

I. THEORY OF THE ABSORPTION EXPERIMENT

Consider the situation illustrated in Fig. 1, in which a plane wave incident from the left within a transparent dielectric falls on an interface between the dielectric and air, or some other lower-index dielectric. If the angle of incidence exceeds the critical angle, the wave is totally reflected and an evanescent wave appears in the right half-space, whose amplitude decays exponentially with distance from the interface. The complex amplitudes of the incident (I), reflected (R), and transmitted (T) waves are connected by the Fresnel relations.²² If the waves are transverse electric (T.E.), and if the electric vector of the incident wave is given by

$$E^{(I)}(\mathbf{r}, t) = u(\mathbf{k})\boldsymbol{\epsilon} \exp i(\mathbf{k} \cdot \mathbf{r} - Kt) + \text{c.c.}, \quad (1)$$

then the reflected and transmitted waves are given,

respectively, by

$$E^{(R)}(\mathbf{r}, t) = u(\mathbf{k})\boldsymbol{\epsilon} \left[\frac{k_3 - K_3}{k_3 + K_3} \right] \times \exp i(\mathbf{k}^{(R)} \cdot \mathbf{r} - Kt) + \text{c.c.}, \quad (2)$$

$$E^{(T)}(\mathbf{r}, t) = u(\mathbf{k})\boldsymbol{\epsilon} \left[\frac{2k_3}{k_3 + K_3} \right] \times \exp i(\mathbf{K} \cdot \mathbf{r} - Kt) + \text{c.c.} \quad (3)$$

Here \mathbf{k} , \mathbf{K} are the wave vectors, with components k_1 , k_2 , k_3 and K_1 , K_2 , K_3 in the left and right half-spaces, respectively. They are related by

$$K_1 = k_1, \quad K_2 = k_2, \quad (4)$$

$$K_1^2 + K_2^2 + K_3^2 = K^2, \quad (5)$$

$$k_1^2 + k_2^2 + k_3^2 = n^2 K^2, \quad (6)$$

where n is the ratio of refractive indices in the two half-spaces.²³ We have chosen units in which the vacuum velocity of light $c = 1$, so that K is also the angular frequency of the light. $\mathbf{k}^{(R)}$ is the wave vector with components k_1 , k_2 , $-k_3$ of the reflected wave, $u(\mathbf{k})$ is some complex amplitude, and $\boldsymbol{\epsilon}$ is a unit polarization vector that is orthogonal to both \mathbf{k} and \mathbf{K} , and parallel to the interface.

From Eq. (6) we see that

$$k_3 = nK \cos \theta, \quad (7)$$

where θ is the angle of incidence from the left, so that, from Eq. (5),

$$K_3 = K \sqrt{1 - n^2 \sin^2 \theta}. \quad (8)$$

Evidently K_3 is real or imaginary according as the angle of incidence is less than or greater than the critical angle θ_c , for which $\sin \theta_c = 1/n$. It follows from Eqs. (3), (7), and (8) that the square modulus of the transmitted complex field amplitude $I(\theta, a)$ (usually known as the intensity in the literature on optical coherence), at a distance a beyond the interface, is given by

$$I(\theta, a) = |u(\mathbf{k})|^2 \left[\frac{4k_3^2}{(k_3 + K_3)^2} \right] = |u(\mathbf{k})|^2 4 \left[1 + \sqrt{1 - n^2 \sin^2 \theta} / n \cos \theta \right]^{-2} \quad (9a)$$

for $\theta < \theta_c$, and

$$I(\theta, a) = |u(\mathbf{k})|^2 \left[\frac{4k_3^2}{(k_3^2 + |K_3|^2)} \right] \times \exp(-2|K_3|a) = |u(\mathbf{k})|^2 4 \left[n^2 \cos^2 \theta / (n^2 - 1) \right] \times \exp[-2aK\sqrt{(n^2 \sin^2 \theta - 1)}] \quad (9b)$$

for $\theta > \theta_c$.

If the electromagnetic field is treated as a classical c -number perturbation acting on an atom, it can be shown²⁴ that the probability of photoelectric emission

or photo-excitation is proportional to $I(\theta, a)$, regardless of whether the wave is homogeneous or evanescent. It follows that an atom of some fluorescent material that is located in an evanescent field at a distance a from the interface should fluoresce at a rate given by Eq. (9b). The expected rate of fluorescence is plotted in Fig. 2 as a function of the angle of incidence θ of the incident plane wave, for angles θ both above and below the critical angle, and for several different ratios a/λ . We have chosen a refractive index $n=1.09$ corresponding to that used in the experiment, for which the critical angle $\theta_c \approx 66.5^\circ$. The rate of fluorescence is expected to be greatest at the critical angle, and to fall off with increasing angle at a rate depending on the depth a . Similar relations are readily derived also for waves polarized in the transverse magnetic (T.M.) direction, but our experiments were limited to T.E. waves.

The foregoing brief analysis was based entirely on a classical description of the electromagnetic field. However, we have recently shown²¹ that a similar result is also obtained from a fully quantum-mechanical treatment, if the initial state of the field is a coherent state.²⁵ The quantum-mechanical calculation will not be repeated here, but a brief outline of the procedure may be of interest to the reader.

We regard the triplet of incident, reflected, and transmitted waves associated with a particular incident wave vector, and a particular polarization, as one fundamental mode of the electromagnetic field. The different modes are found to be orthogonal, and may be used for the representation of an arbitrary free field satisfying the homogeneous Helmholtz equation. The energy of the field reduces to quadratures when expressed in terms of these modes. The field may then be quantized by associating Hilbert-space annihilation and creation operators with the complex amplitudes of the triplet-wave modes. If we identify the excitations of this quantized field with photons in the usual way, we are led to the concept of photons that, for certain wave vectors, are evanescent in one half-space. Having introduced the evanescent photons, we may investigate the interaction of these photons with atoms by making use of the usual electromagnetic interaction hamiltonian to couple the two quantized systems of atom and field. A first-order perturbation calculation of the probability of photo-excitation of the atom, when the field is in a coherent state, then leads directly to a term proportional to $I(\theta, a)$ given by Eqs. (9), in which $u(\mathbf{k})$ is the eigenvalue of the photon-annihilation operator belonging to the initial coherent state. Now the state of the optical field produced by a laser can be characterized approximately by a coherent state, so far as its interaction with the photodetector is concerned. It follows that quantum electrodynamics also leads us to predict the response shown in Fig. 2 for photo-excitation of molecules by laser beams.

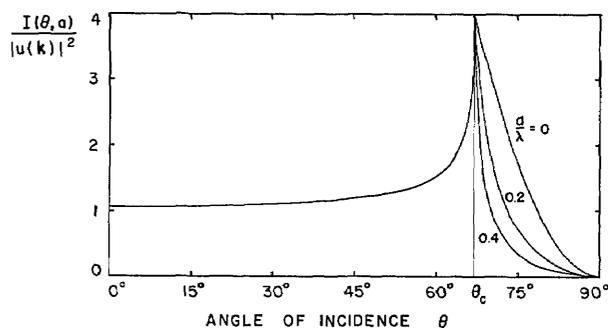


FIG. 2. Illustrating the predicted variations of $I(\theta, a)$, which is proportional to the molecular absorption probability, with angle of incidence θ , for several different ratios of distance a of molecule from interface to wavelength λ . The curves refer to T.E. polarization and to a refractive index $n=1.09$.

II. ABSORPTION EXPERIMENTS

Our method of studying the absorption of evanescent waves leans heavily on a technique developed previously⁶ for depositing monomolecular layers of a fatty acid (e.g., arachidic acid $C_{20}H_{40}O_2$), in which fluorescent dyes may be incorporated, on a glass surface. Five of these 26.4-Å-thick arachidic acid layers were deposited on a glass microscope slide to form a base. Two layers incorporating dye molecules that fluoresce in the yellow were then placed on these, and 16 additional, nonfluorescent arachidic acid layers were deposited on top. The resulting slide then contained a number of light absorbing, fluorescent molecules about 450 Å below the surface, but the number was small enough to limit the light absorption to less than 1%.²⁶

For total reflection to occur at the surface of the layers, it was necessary to immerse the slides in a liquid of refractive index higher than the index of the layers. High-index oils are not suitable because they attack the layer system, and therefore a high-index aqueous solution called Clerici solution was used.⁶ This consists of a 1:1 mixture of thallos formate and thallos malonate in water. A saturated solution at room temperature has an index of refraction of about 1.65 and a density of 4.5 gm/cc. The purest salts available were used in preparing the solution, and it was filtered through a fritted glass filter to remove most scattering impurities. The solution still contained some chemical impurities, however, as evidenced by the fact that it showed a weak fluorescence. The fluorescence was Stokes shifted by about 1000 Å from the wavelength of the exciting light and was several hundred angstroms wide. This was the major source of background light in the experiment.

The container was made of black glass, except for the windows. Top and cut-away side views of the container are shown in Fig. 3. The window for the incident beam is glass with surfaces flat to a quarter wavelength. The cylindrical window, through which the fluorescence

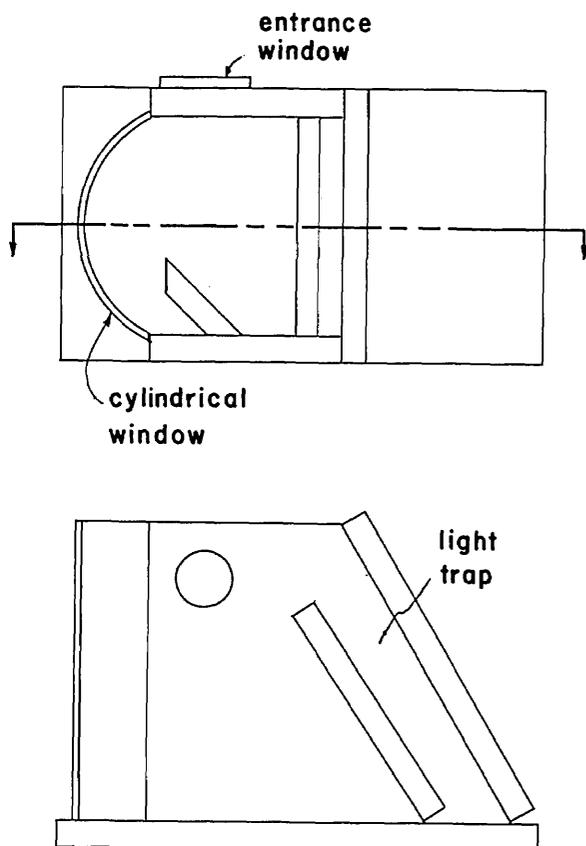


FIG. 3. Top and side views of the vessel holding the Clerici solution, in which the slide with monomolecular layers is immersed.

was viewed, was cut from a piece of glass tubing, and was of relatively poor optical quality. The shape of the container was chosen so that the light reflected from and transmitted by the microscope slide was trapped inside. The black glass of the container fluoresced slightly in the argon-laser beam used for the excitation, so some care had to be taken in positioning the container relative to the incident light beam and the detector.

The container was placed on a spectrometer table and the microscope slide was attached to a mount that could be rotated concentrically with the cylindrical window. The experimental setup is shown schematically in Fig. 4. The photomultiplier and associated optical components were mounted on one of the arms of the spectrometer table, and could be rotated while the Clerici-solution container remained fixed. The microscope-slide mount was coupled to the photomultiplier arm so that both rotated together. Thus the angle between the microscope slide and the detector remained fixed, while the angle between the exciting light beam and the microscope slide was changed.

The angle of incidence of the light beam was recorded with the help of an accurate potentiometer (Helipot), that was coupled by a friction drive to the

rotating spectrometer arm. When a current was passed through the Helipot, the potential at the sliding contact was a measure of the angle of rotation of the spectrometer arm, and this was fed to the x input of an xy recorder.

An argon laser was used as exciting light source for the experiment and the 4766-Å line was isolated. The light beam was expanded and collimated, and two sheets of Polaroid film were inserted to select T.E. polarization to an accuracy of about 2° . The transmittance of the orthogonal polarization by the polarizers was estimated to be several orders of magnitude smaller.

The fluorescent light collected by a large-aperture lens was registered by a IP28a photomultiplier, housed in a light-tight box with a slit about 3 mm wide in front of the photocathode. The signal from the phototube was fed into a Keithly picoammeter, whose output, in turn, was fed into the y input of the xy recorder. A Schott OG-2 filter was placed in front of the phototube to discriminate against scattered light from the argon laser and fluorescence of the Clerici solution.

III. RESULTS OF ABSORPTION MEASUREMENTS

The experimental results are shown in Fig. 5, together with the corresponding theoretical curve calculated from Eqs. (9), with $aK = 0.905$, corresponding to $a = 450 \text{ \AA}$, $n = 1.10$. Although the effect of the background light was almost negligible, we took account of any background contribution by taking readings from

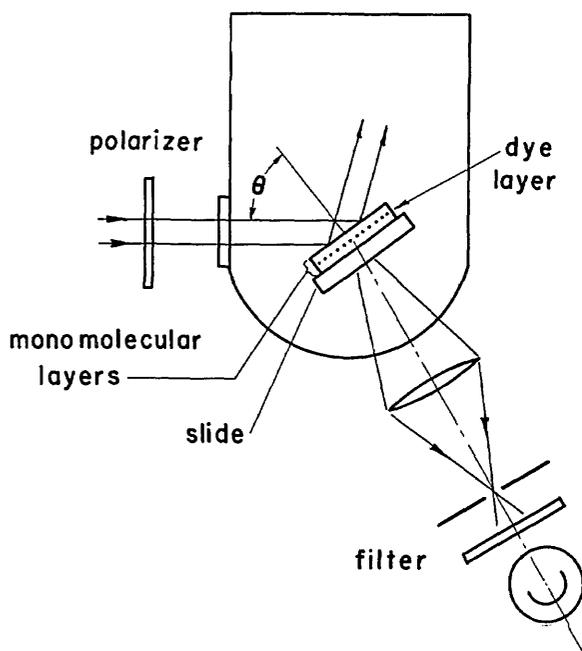


FIG. 4. The experimental setup for the absorption experiment. The slide and the detector assembly are coupled so as to rotate together about the axis of the cylindrical window.

a portion of the slide that contained no dye molecules, and used these readings to correct the data.

The experimental results are seen to be in good agreement with the theory, both below and above the critical angle. In particular, there is no discontinuity of the excitation probability as the exciting light changes from homogeneous to evanescent, although the derivative with respect to angle is discontinuous. The predictions of both the classical and quantum theories of evanescent light are therefore well confirmed.

IV. THEORY OF EMISSION OF EVANESCENT WAVES BY EXCITED MOLECULES

After studying the excitation of molecules by evanescent waves, or the absorption of evanescent photons, we are naturally led to examine the inverse process also, and to ask whether excited atoms or molecules emit evanescent photons. The principle of reciprocity would lead us to expect that emission should take place also, and that an excited molecule, placed close to the dielectric-to-air interface in Fig. 1, should give rise to homogeneous light within the dielectric propagating in directions beyond the critical angle. Such large-angle emissions were already observed by Selenyi,³ who made use of the light emission from a drop of fluorescein solution placed on a prism, and by Fröhlich,⁴ who used secondary sources in the form of illuminated score marks on a glass surface. But in neither case was the emission process studied quantitatively.

Despite the fundamental symmetry of the elementary processes of emission and absorption, the emission problem cannot be treated in quantum electrodynamics in quite the same manner as the absorption problem that we outlined briefly in Sec. II. The reason is that the electromagnetic field produced by the atomic source cannot be represented in terms of the modes used in the quantum treatment of the free field.²¹ The source field of the atom differs in a fundamental manner from the free fields we have considered so far. A quantum treatment is possible, of course, but it would naturally follow the classical scheme in which the electromagnetic field is explicitly expressed in terms of its sources.

It is simplest therefore to adopt a classical point of view, and to regard the excited atom or molecule as an oscillating dipole that radiates an electromagnetic field. We may then examine the angular dependence of the light flux radiated in the dielectric, and see if it has the same form as $I(\theta, a)$ in Eqs. (9). In particular, any field in the dielectric propagating in a direction beyond the critical angle will imply the emission of an evanescent photon by the molecule.

Let us represent the excited molecule by a dipole parallel to the interface of amplitude \mathbf{P} oscillating at the frequency K . Then, if the dipole source is located at the point $(0,0,a)$ at a distance $z=a$ from the interface (see Fig. 1), the electric field $\mathbf{E}(x,y,0,t)$ at some point

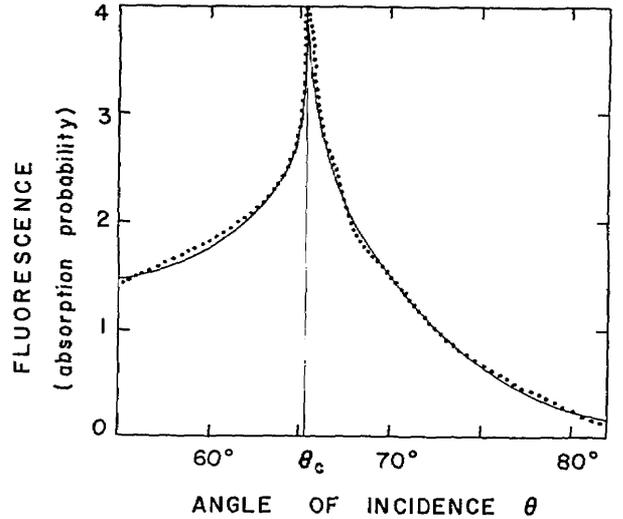


Fig. 5. Experimental results for the absorption of evanescent light by dye molecules located at a distance $a=450 \text{ \AA} = 0.14\lambda$ from the interface. The full curve is the theoretical value of $I(\theta, a)/|u(\mathbf{k})|^2$ and is based on Eqs. (9) with $n=1.10$. The experimental values have been scaled so as to agree with the theory at the peak.

on the interface (the plane $z=0$) can be given the angular-spectrum representation^{13,27}

$$\mathbf{E}(x,y,0,t) = \frac{-i}{2\pi} \int \int_{-\infty}^{\infty} dK_1 dK_2 \frac{\exp(iK_3 a)}{K_3} \times [(\mathbf{P} \cdot \mathbf{K})\mathbf{K} - K^2\mathbf{P}] \exp i(K_1 x + K_2 y - Kt) + c.c. \quad (10)$$

Here $K_3 = (K^2 - K_1^2 - K_2^2)^{1/2}$ as before.²³

In order to obtain the electric field transmitted into the high-index region in the left half-space, it is useful first to decompose the angular spectrum into its T.E. and T.M. components. The unit vector for the T.E. component, which is perpendicular to the wave vector \mathbf{K} and lies in the plane of the interface, is given by

$$\boldsymbol{\varepsilon} = (\mathbf{K} \times \mathbf{e}_3) / (K_1^2 + K_2^2)^{1/2} = (K_2 \mathbf{e}_1 - K_1 \mathbf{e}_2) / (K_1^2 + K_2^2)^{1/2}, \quad (11)$$

where $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ are unit vectors in the directions of the coordinate axes. The corresponding vector for the T.M. polarization is orthogonal to $\boldsymbol{\varepsilon}$ and \mathbf{K} and is given by

$$\mathbf{c} \times \boldsymbol{\varepsilon} = (K_3 \mathbf{K} - K^2 \mathbf{e}_3) / K(K_1^2 + K_2^2)^{1/2}, \quad (12)$$

where $\mathbf{c} \equiv \mathbf{K}/K$ is the unit vector in the direction of \mathbf{K} . The dipole field of Eq. (10) can then be expressed in terms of these unit vectors with the help of the expansion

$$(\mathbf{P} \cdot \mathbf{K})\mathbf{K} - K^2\mathbf{P} = P_0[\alpha \boldsymbol{\varepsilon} + \beta (\mathbf{c} \times \boldsymbol{\varepsilon})], \quad (13)$$

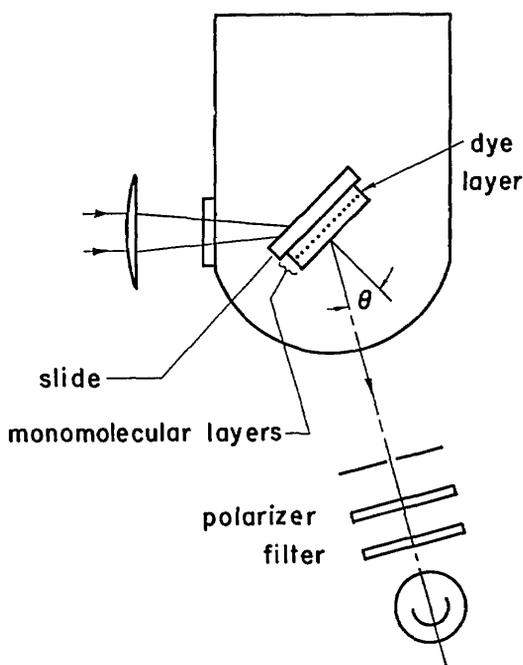


FIG. 6. The experimental setup for the emission experiment. The position of the slide remains fixed while the detector assembly rotates about the axis of the cylindrical window.

where α , β , and P_0 are given by

$$\alpha = K^2(K_1 \sin\psi - K_2 \cos\psi) / (K_1^2 + K_2^2)^{1/2}, \quad (14)$$

$$\beta = -KK_3(K_1 \cos\psi + K_2 \sin\psi) / (K_1^2 + K_2^2)^{1/2}, \quad (15)$$

$$\mathbf{P} = P_0(\mathbf{e}_1 \cos\psi + \mathbf{e}_2 \sin\psi), \quad (16)$$

and ψ is the angle between the dipole and the x axis.

The transmission of each homogeneous and evanescent wave component across the interface is described by the Fresnel formulas,²² and, with the help of Eqs. (10)–(16), the electric field in the left half-space is found to be

$$\begin{aligned} \mathbf{E}(\mathbf{r}, t) = & \frac{-iP_0}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dk_1 dk_2 \\ & \times \exp(iK_3 a) \left[\left(\frac{2\alpha}{k_3 + K_3} \right) \mathbf{e} + \left(\frac{2n\beta}{k_3 + n^2 K_3} \right) (\boldsymbol{\kappa} \times \mathbf{e}) \right] \\ & \times \exp i(\mathbf{k} \cdot \mathbf{r} - Kt) + \text{c.c.}, \quad (17) \end{aligned}$$

where k_3 is given by Eq. (6) and $\boldsymbol{\kappa}$ is the vector \mathbf{k}/k .

Because the light detector used in the experiment is located far from the interface, we are interested only in the asymptotic limit of $\mathbf{E}(\mathbf{r}, t)$ given by Eq. (17), for some point \mathbf{R} such that $kR \gg 1$. In this region the only significant contribution to the integral comes from values of k_1, k_2 such that \mathbf{k} is real and parallel to \mathbf{R} . The asymptotic limit of the angular spectrum representation has been investigated by several workers,^{18, 28, 29}

and $\mathbf{E}(\mathbf{R}, t)$ is found to be given by

$$\begin{aligned} \mathbf{E}(\mathbf{R}, t) = & \frac{-P_0}{R} \exp(iK_3' a) \left[\left(\frac{2\alpha' k_3'}{k_3' + K_3'} \right) \mathbf{e} \right. \\ & \left. + \frac{2n\beta' k_3'}{k_3' + n^2 K_3'} (\boldsymbol{\kappa}' \times \mathbf{e}) \right] \exp i(nKR - Kt) + \text{c.c.}, \quad (18) \end{aligned}$$

where \mathbf{k}' is the wave vector pointing in the direction of \mathbf{R} and \mathbf{K}' is the corresponding wave vector in the other half-space.

It is convenient to re-express this result in terms of variables relating more directly to the experiment. Let χ be the angle between the wave vector \mathbf{k}' and the xz plane and let θ be the angle between the projection of \mathbf{k}' on the xz plane and the z axis. In terms of these angles

$$\begin{aligned} k_1' &= nK \sin\theta \cos\chi, \\ k_2' &= nK \sin\chi, \\ k_3' &= nK \cos\theta \cos\chi. \end{aligned} \quad (19)$$

If the point \mathbf{R} lies in the xz plane, $\chi = 0$, and we find with the help of Eqs. (12)–(16) that Eq. (18) becomes

$$\begin{aligned} \mathbf{E}(\mathbf{R}, t) = & \frac{-P_0}{R} \exp(iK_3' a) \left[\sin\psi \left(\frac{2K^2 k_3'}{k_3' + K_3'} \right) \mathbf{e} \right. \\ & \left. - \cos\psi \left(\frac{2nKK_3' k_3'}{k_3' + n^2 K_3'} \right) (\boldsymbol{\kappa}' \times \mathbf{e}) \right] \exp iK(nR - t) + \text{c.c.} \quad (20) \end{aligned}$$

If a polarizer is placed in front of the detector, so that only the T.E. component of the electric field contributes to the measured signal, we may restrict ourselves to the first vectorial term on the right of Eq. (20). The intensity $I(\theta, a)$ (i.e., the square modulus of the complex wave amplitude) of the T.E. component propagating in a direction θ , contributed by a dipole at distance a from the interface, is then found to be

$$(\text{T.E.}) I(\theta, a) = \frac{P_0^2 K^4}{R^2} \left| \frac{2k_3'}{k_3' + K_3'} \exp(iK_3' a) \right|^2 \sin^2\psi. \quad (21)$$

Because of the character of the monomolecular layers used in the experiment, the transition moments responsible for the fluorescence of the dye molecules incorporated in these layers lie in a plane parallel to the interface, but they are randomly oriented in this plane.²⁶ In order to take account of this random orientation we average $I(\theta, a)$ given by Eq. (21) over all angles ψ , and find

$$(\text{T.E.}) I(\theta, a) = \frac{P_0^2 K^4}{2R^2} \frac{4k_3'^2}{(k_3' + K_3')^2} \quad \text{for } \theta < \theta_c \quad (22a)$$

$$= \frac{P_0^2 K^4}{2R^2} \frac{4k_3'^2}{k_3'^2 + |K_3'|^2} \exp(-2|K_3'|a) \quad \text{for } \theta > \theta_c. \quad (22b)$$

Apart from a scaling factor, this result is identical with that obtained previously in Eqs. (9a) and (9b) for the intensity of the field on the low-index side, when a plane wave is incident from the left. The validity of the reciprocity principle in this situation is therefore confirmed. We conclude that the angular distribution of the light emerging on the high-index side of the interface, that has been emitted by excited dye molecules, should also follow the form of the curve shown in Fig. 2. Any light emerging beyond the critical angle must have its origin in the emission of evanescent photons by the source.

Finally, we may examine the effect of collecting the light emitted over a finite solid angle. Needless to say, the aperture placed in front of the detector in the experiment was finite and admitted a finite range of angles, from $\theta = \theta_0 - \frac{1}{2}\delta\theta$ to $\theta = \theta_0 + \frac{1}{2}\delta\theta$, and from $\chi = -\frac{1}{2}\delta\chi$ to $\chi = \frac{1}{2}\delta\chi$. The output from the detector is therefore expected to be of the form

Detector output

$$= \text{const} \times \int_{-\frac{1}{2}\delta\chi}^{\frac{1}{2}\delta\chi} d\chi \int_{\theta_0 - \frac{1}{2}\delta\theta}^{\theta_0 + \frac{1}{2}\delta\theta} d\theta \cos\chi I(\theta, \chi, a), \quad (23)$$

with $I(\theta, \chi, a)$ derived from the more general expression (18) and given by

$$I(\theta, \chi, a) = \frac{P_0^2}{R^2} \left| \frac{2k_3' \alpha'}{k_3' + K_3'} \exp(iK_3' a) \right|^2. \quad (24)$$

The effect of the integral is to lower the peak in the θ_0 dependence of the detector output.

V. EMISSION EXPERIMENTS

Whereas the incident light beam in the absorption experiments was required to be collimated, polarized, and monochromatic, these same conditions apply to the emitted light in the emission experiments. It was therefore necessary to introduce a small aperture, a polarizer, and a narrow-band filter in front of the photodetector, each of which substantially reduced the light flux detected.

The experimental setup is shown in Fig. 6. The microscope slide was mounted with the dye layer facing the photomultiplier, and the slide was maintained stationary while the detector was rotated. The laser beam was focused to a line on the microscope slide, at an angle of incidence well below the critical angle for the liquid-fatty-acid layer combination.³⁰ A polarizer and a Schott OG-2 spectral filter were placed in front of the photomultiplier, to select the T.E. polarization, and to limit the bandwidth of the detected light. With the filter in place, about 60% of the fluorescence reaching the photomultiplier had a wavelength between 5700 and 5900 Å. Thus the relative wavelength spread $\Delta\lambda/\lambda$ was about 1/30. We believe that the dispersion of the Clerici

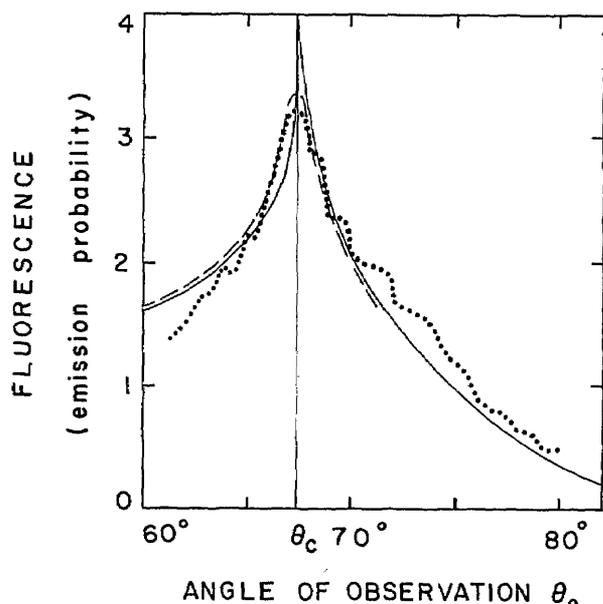


FIG. 7. Experimental results for the emission of evanescent light by excited dye molecules located at a distance $a = 450 \text{ \AA} = 0.14\lambda$ from the interface. The lightly drawn theoretical curve is based on Eqs. (22) with $n = 1.08$. The broken theoretical curve is based on Eq. (23), and takes the effect of finite aperture size into account. The units are arbitrary, and the experimental values have been scaled so as to agree with the theoretical values near the peak.

solution is low enough for the wavelength spread to have little effect on the results. A small aperture placed in front of the detector limited the field of view to an angle $\delta\theta$ of about 1° in the xz plane and to about 20° in the y direction ($-10^\circ < \chi < 10^\circ$). The finite size of the aperture has the effect of smoothing the results in the neighborhood of the critical angle, so that the height of the observed emission peak is reduced. The detector arm was rotated, and the outputs of the detector and of the Helipot measuring the angle of rotation were applied to the y input and the x input, respectively, of the xy recorder.

VI. RESULTS OF EMISSION MEASUREMENTS

The experimental results are presented in Fig. 7. It will be seen that light is observed beyond the critical angle, so that the emission of evanescent waves or photons by the excited molecules is thereby confirmed.³⁰

The agreement between the experimental curve and the theoretical curve given by Eqs. (22) is not impressive. However, when we take account of the finite detector aperture used in the experiment, corresponding to $\delta\chi \sim 20^\circ$ and $\delta\theta \sim 1^\circ$, and calculate the expected detector output from Eq. (23), we obtain the broken curve shown in Fig. 7, which is much closer to the experimental curve.

The waves in the observed curve are almost certainly due to imperfections in the curved wall of the vessel (see Fig. 3), through which the output beam had to

pass. As was mentioned earlier, this wall was cut from a large-bore glass tube, and was not of optical quality. The imperfections were unimportant in the absorption experiments described in Sec. III, because the detector was allowed to collect the light within a large solid angle. However, such imperfections became significant when measurements of emission within a small solid angle were made, as in this experiment. We have obtained a similar wavy response on observing a cylindrical, diverging light beam through the same vessel when empty.

It would obviously be desirable to use a vessel of good optical quality for the experiment, but as our results were substantially as predicted, we did not construct another vessel and repeat the experiment. Within the limitations of the apparatus, it appears that both the absorption and the emission of evanescent photons by molecules have been quantitatively confirmed.

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