INFLUENCE OF A DIELECTRIC INTERFACE
ON FLUORESCENCE DECAY TIME

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When a mirror is placed near a fluorescing molecule, not only the angular distribution of the fluorescence is affected, but also the decay time. This effect is considered for the case of the reflecting interface between two dielectrics of different refractive indices. The fluorescence decay time varies markedly due to the presence of such an interface. In case of fluorescing molecules placed directly at the interface between a medium of refractive index 1.54 and air, the decay time is lengthened by a factor of 1.08 if their transition moment is oriented parallel to the interface, and by a factor of 3.61 if the transition moment is oriented perpendicular to the interface. These considerations are compared with measurements on monomolecular layers of an europium dibenzoylmethane complex which were held at a variable, but well defined distance from the interface.

If one places an excited molecule (or atom) in front of a mirror, then the emission of radiation (fluorescence, phosphorescence) is influenced by the mirror. This comes about because part of the emitted light wave is reflected by the mirror and interferes with the non-reflected part. Let us consider the radiation of an oscillating electric dipole, which is emitted at a certain angle to the mirror normal (fig. 1, left). There the path difference between the direct and reflected beam is such that constructive interference occurs and therefore the molecule will radiate strongly in this direction. However, at a somewhat larger angle (fig. 1, right) the path difference is half a wavelength smaller so that the direct and reflected beam interfere destructively. If the reflectivity of the mirror equals 100%, the amplitude of the reflected wave is as large as the amplitude of the direct wave and therefore both cancel in this particular direction. The molecule will not radiate in this direction at all.

The angular distribution $P(\theta)$ of the fluorescence intensity, polarized perpendicular to the plane of incidence on the mirror is given[1−3] by:

$$P(\theta) = 1 + \rho_\perp^2(\theta) + 2\rho_\perp(\theta) \cos [(4\pi n d/\lambda) \cos \theta - \delta_\perp(\theta)], \qquad (1)$$

θ = angle between the direction of light emission and mirror normal;
d = distance between excited molecule and mirror; n = refractive index of

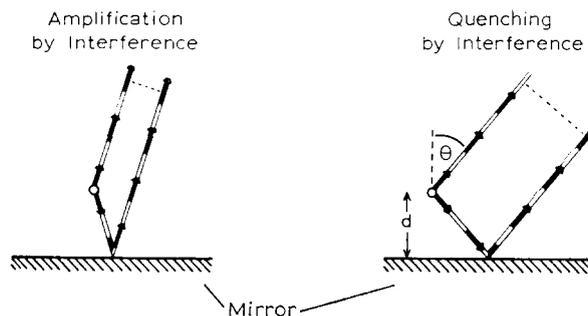* Present address: Eastman Kodak Research Laboratories, Rochester, New York, USA.

Fig. 1. Electric dipole radiation interacting with plane mirror.

the medium in front of the mirror; λ = vacuum wave length of the emitted light.

The reflection coefficient $\rho_\perp$ and the phase shift $\delta_\perp$ are in general dependent on the angle of incidence θ and can be calculated from Fresnel's formulae. As is seen from eq. (1) the fluorescence intensity in front of the mirror should exhibit a pattern well known from the emission of radio waves by antennas. The larger the distance d the more maxima and minima will occur.

We have investigated this effect on a europium-dibenzoylmethane complex, the molecules of which were placed at a well defined distance from the mirror[3]. The ligands of this complex absorb strongly in the ultraviolet. After intramolecular energy transfer to the central Eu^{3+}-ion this fluoresces with high quantum yield at about 612 nm. Fig. 2 shows the fluorescence of this compound placed at a distance of 6770 Å from a gold mirror. The measured angular distribution (full line) agrees very well with the calculation according to eq. (1) (dashed line).
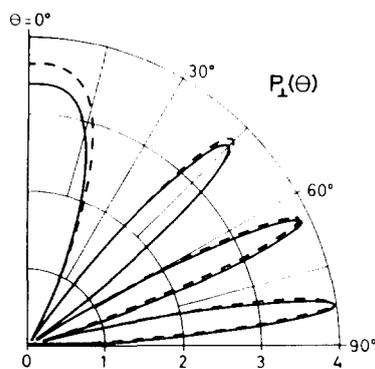

Fig. 2. Angular distribution of fluorescence of europium-dibenzoylmethane complex 6770 Å from gold mirror.

The mirror not only influences the angular distribution of the fluorescence intensity, but also the fluorescence decay time. To understand this effect let us consider an excited molecule in the very center of a spherical mirror (fig. 3). If the radius of the mirror is for instance 1.75 λ (fig. 3, upper case),

Amplification by interference:
dipole radiates twice the power
as without the mirror $(\tau_M = \frac{1}{2}\tau)$

Radius 1.75 λ

Quenching by interference:
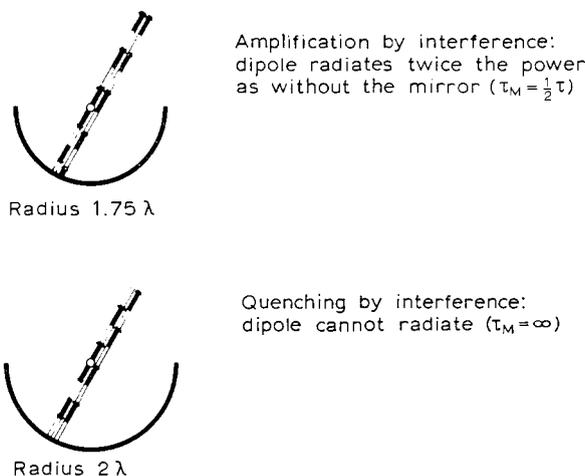dipole cannot radiate $(\tau_M = \infty)$

Radius 2 λ

Fig. 3. Radiation from excited molecule in center of spherical mirror.

constructive interference of the direct and reflected beam will occur in all directions of the upper half space. Since the radiated intensity is proportional to the square of the amplitude, the probability for radiation is four times as large as without the mirror. Into the lower half space there is no radiation due to the mirror. Therefore the integrated probability for radiation will be twice as large as without the mirror. This means the decay time of the molecule in the center of the mirror will be half the decay time of the molecule in free space (assuming there are no competing radiationless deactivation processes). On the other hand, if the radius of the spherical mirror is for instance 2λ (fig. 3, lower case), the direct and reflected beam interfere destructively and thus the excited molecule cannot radiate at all. Under the same assumptions as above it will stay high forever (decay time infinite).

In the same way as shown for a spherical mirror the fluorescence decay time is affected by a plane mirror. We again integrate the intensity above the mirror and find for the decay time τ_x of an excited molecule[1]:

a. axis of electric dipole oscillator perpendicular to the mirror

$$\tau_x/\tau_\infty = \left[1 - \frac{3}{2} \int_0^1 \rho_{||}(u)\,(1 - u^2)\cos{(xu - \delta_{||}(u))}\,du\right]^{-1} ; \qquad (2)$$

b. axis of electric dipole oscillator parallel to the mirror

$$
\tau_x/\tau_\infty = \left[1 + \tfrac{3}{4} \int_0^1 \rho_{||}(u)u^2 \cos(xu - \delta_{||}(u))du \right.
$$

$$
\left. + \tfrac{3}{4} \int_0^1 \rho_\perp(u) \cos(xu - \delta_\perp(u))du \right]^{-1} , \quad (3)
$$

$x = 4\pi nd/\lambda$; $u = \cos \theta$; $\rho_{||}(u)$, $\rho_\perp(u)$ reflection coefficients of the mirror, $\delta_{||}(u)$, $\delta_\perp(u)$ phaseshifts on reflection by the mirror.

In the case of an idealized mirror with $\rho_{||} = \rho_\perp = 1$ and $\delta_{||} = \delta_\perp = \pi$, independent of angle θ, the integrals in eqs. (2) and (3) can be easily solved and one gets:

Case a.

$$
\frac{\tau_x}{\tau_\infty} = \left[1 - \frac{3 \cos x}{x^2} + \frac{3 \sin x}{x^3} \right]^{-1} ; \quad (4)
$$

Case b.

$$
\frac{\tau_x}{\tau_\infty} = \left[1 - \frac{3 \sin x}{2x} - \frac{3 \cos x}{2x^2} + \frac{3 \sin x}{2x^3} \right]^{-1} . \quad (5)
$$

However, in all practical cases the reflection coefficients and phaseshifts depend in a complicated manner on the angle of incidence and on the polarization of the light.

We have measured the influence of a mirror on the fluorescence decay time for the first time using the above mentioned europium complex whose fluorescence decay time is roughly 1 msec [1]). The environment of the emitting Eu^{3+}-ion can be considered isotropic. Thus neither one of the particular orientations considered above is applicable to this case. The probability of light emission is rather found by averaging over the probability of case a. plus twice the probability of case b. In this way the fluorescence decay time in front of a silver mirror was calculated (fig. 4, full line). As can be seen from this figure the fluorescence decay time should be lengthened or shortened dependent on the distance d from the mirror.

In the above consideration we omitted possible radiationless deactivation processes, which are not affected by the mirror. If we take them into account, we find for the true decay time τ'_x

$$
\frac{\tau'_x}{\tau'_\infty} = \frac{1}{1 + \eta_\infty (\tau_x/\tau_\infty - 1)} , \quad (6)
$$

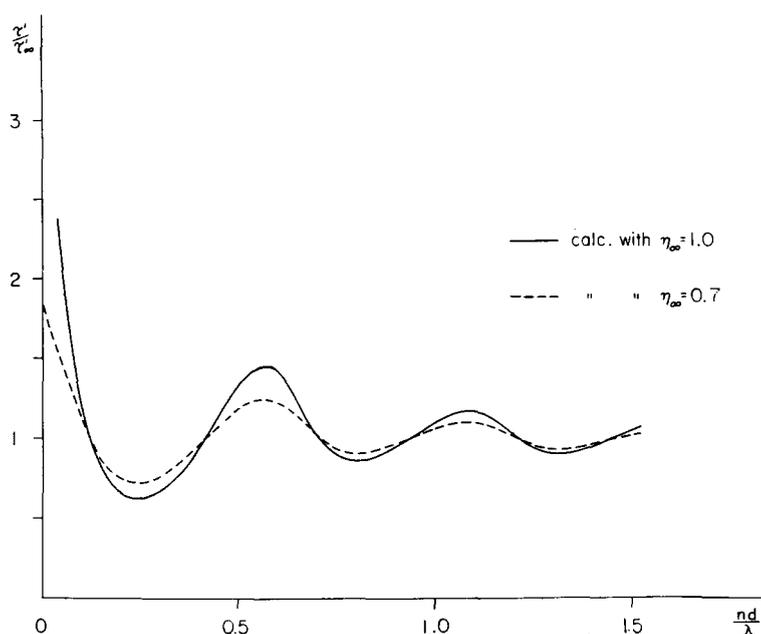where η_∞ is the quantum yield of the emitting state, which we must carefully

Fig. 4. Fluorescent decay time of Eu^{3+} in front of silver mirror.

distinguish from the quantum yield α_∞ defined as the ratio between the amounts of emitted and absorbed quanta. A quantum yield $\eta_\infty < 1$ leads to a less pronounced variation of the fluorescence decay time in front of the mirror, because in this case the radiationless deactivation processes which are not affected by the mirror, have an influence on the decay time. This is shown in fig. 4 for a quantum yield $\eta_\infty = 0.7$ (dashed line).

By comparing the curves τ_x'/τ_∞', calculated with different values η_∞, with the experimental data one is able to determine directly the quantum yield of the emitting state η_∞, an otherwise hardly accessible quantity. In case of the europium complex it was found: $\eta_\infty = 0.7$ (fig. 5). The experimental values of τ_x', measured by varying the distance d stepwise 52.8 Å [1]), agree very well with the theory outlined above. The disagreement at very small distances is due to energy transfer from the excited molecules to the silver mirror, which shall not be considered here.

As the mirror influences selectively the light emission, but not the competing radiationless deactivation processes, the quantum yield η_x varies with the distance from the mirror too. It follows quantitatively:

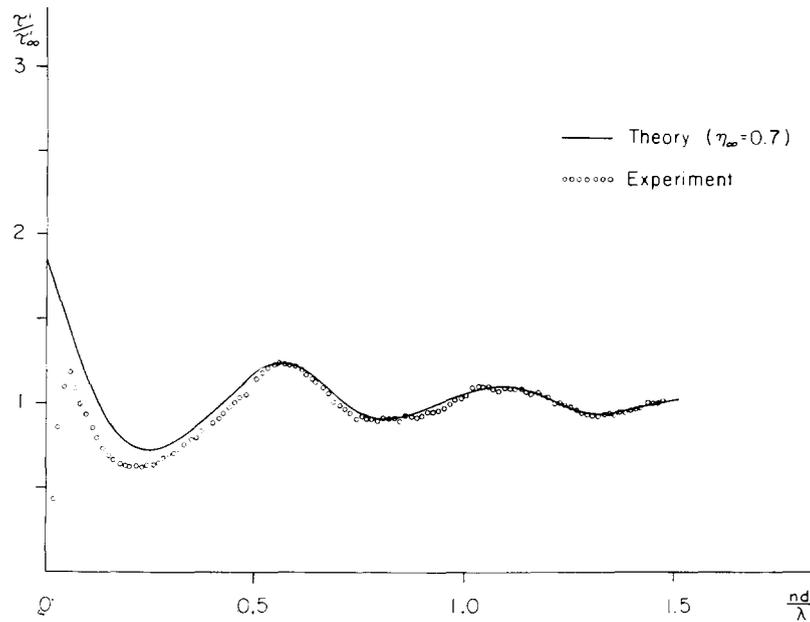$$\eta_x = \left[1 + \frac{\tau_x}{\tau_\infty} \left(\frac{1}{\eta_\infty} - 1 \right) \right]^{-1}. \tag{7}$$

Fig. 5. Comparison of theory and experiment for decay time of Eu³⁺ in front of silver mirror.

Whereas a silver mirror has a high reflectivity at all angles of incidence, the reflectivity of the interface between two media with different refractive index varies strongly with the angle of incidence θ, being very high only at large angles θ. However, by substituting the reflection coefficients and phase shifts of such an interface into eqs. (2) and (3) a pronounced influence on the fluorescence decay time is expected (fig. 6). Particularly in case of an electric dipole oscillator whose axis is oriented perpendicular to the interface the decay time is lengthened remarkably. If the ratio of the refractive indices is for instance 1.54, the decay time of an excited molecule near the interface will be lengthened by a factor of 3.61. If the ratio of the refractive indices is 2.00, the lengthening factor amounts to a value as large as 9.31.

The considered phenomenon is dependent on the nature of the fluorescent transition. The influence of a dielectric interface on a *magnetic* dipole oscillator is shown in fig. 7. It turns out that in this case the decay time near the mirror is also lengthened.

Experimental data on the europium complex are in fair agreement with the expected curve which was calculated using the value $\eta_x = 0.7$ and taking the average described above (fig. 8).

Finally, we want to mention that a reflector will affect the probability
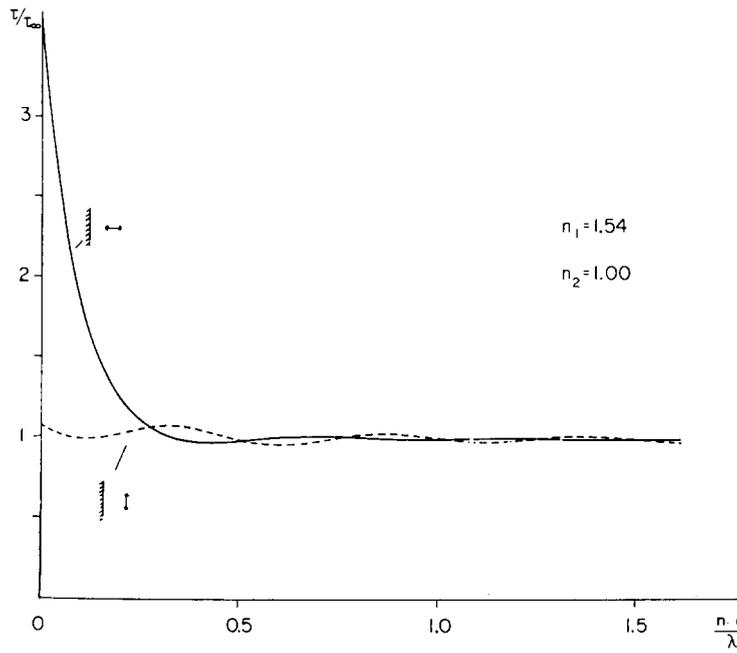
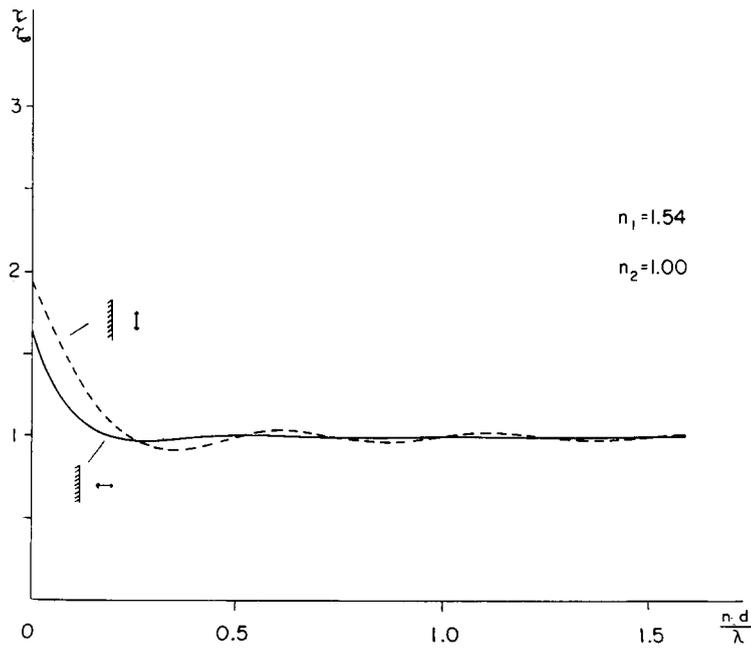Fig. 6. Decay time of electric dipole oscillator in front of a dielectric interface.

Fig. 7. Decay time of magnetic dipole oscillator in front of a dielectric interface.
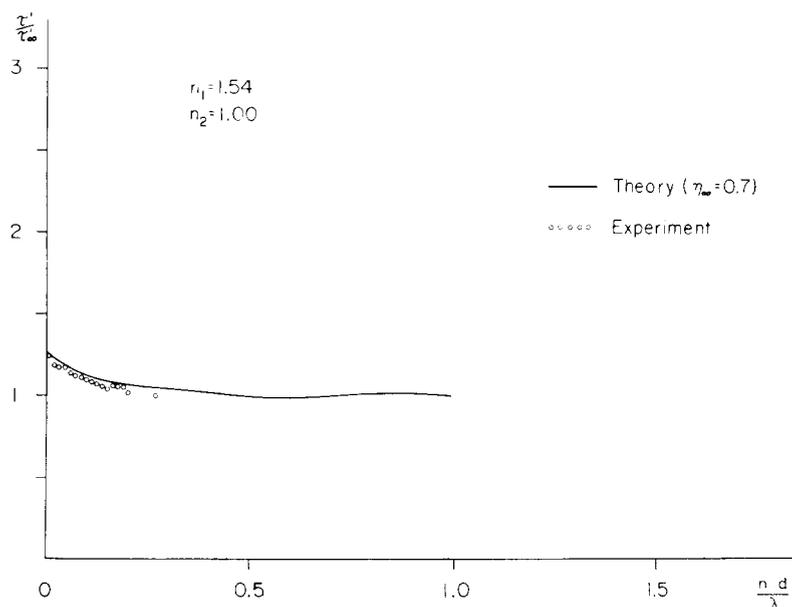
Fig. 8. Fluorescent decay time of Eu^{3+} in front of a dielectric interface.

of any emission process. It has long been known that the impedance of a radio antenna is changed by a reflector. In this paper it is shown that the probability of light emission is influenced by a mirror, which may be merely a dielectric interface. If we are allowed to extend our considerations to even shorter wavelengths, i.e. the emission of γ-quanta by nuclei, an interesting conclusion can be drawn: if we had a mirror for γ-rays, we would be able to influence the lifetime of radio-active nuclei.

References

1) K. H. Drexhage, Optische Untersuchungen an neuartigen monomolekularen Farb-stoffschichten (Habilitations-Schrift), Marburg (1966).
2) H. Bücher, K. H. Drexhage, M. Fleck, H. Kuhn, D. Möbius, F. P. Schäfer, J. Sonder-mann, W. Sperling, P. Tillmann and J. Wiegand, Mol. Cryst. 2 (1967) 199.
3) M. Fleck, Weitwinkelinterferenz und Multipolcharakter der Lumineszenz organischer Farbstoffe (Dissertation), Marburg (1969).

Discussion on paper I2

Question 1: W. Gebhardt

I wonder how you prepare the mirror and how you establish a distinct distance between the surface and the organic molecules?

Answer: K. H. Drexhage

The metal mirror is evaporated in vacuum. On top of the mirror a certain number of fatty acid layers are deposited using the technique founded by Langmuir and Blodgett. Finally a monomolecular layer of a fluorescent dye is deposited by means of the same technique.

Question 2: G. F. J. Garlick

I wonder if you are aware of some much earlier work by Selenyi, and I think, some later work by Freed and Weissman in which your effect was studied in thin acetate films containing dispersed fluorescent molecules. The study of angular dependence of polarization of the emission was used to distinguish the nature of the oscillators involved.

Answer: K. H. Drexhage

I am grateful for your comment. In fact, Selenyi's work has stimulated us to investigate the angular distribution of fluorescence with the much more sensitive monolayer technique.

Question 3: W. B. Fowler

For simple systems the absorption cross sections and the reciprocal decay time are related by the Einstein relation. Does an infinite decay time imply a zero absorption cross section?

Answer: K. H. Drexhage

The Einstein relation holds for molecules in free space. One can derive a corresponding relationship for molecules in front of a mirror.