OPTICAL-ENVIRONMENT-DEPENDENT EFFECTS ON THE FLUORESCENCE OF SUBMONOMOLECULAR DYE LAYERS ON INTERFACES

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We investigated laser-induced fluorescence of submonomolecular (spin coated) dye lasers, e.g., of rhodamine 6G and sulforhodamine 101, on glass surfaces. From angle-resolved emission and excitation spectra, we determine the orientation of the emission and absorption dipole moments relative to the surface. From the fluorescence depolarisation at low dye concentrations we determined the angle ψ between the absorption dipole moment and the emission dipole moment in rhodamine 6G to be $\psi \approx 13° \pm 3°$. We also measured the intensity quenching and the fluorescence depolarisation as a function of the dye concentration.

1. Introduction

We investigated the influence of the "optical environment" on the fluorescence lifetime of sulforhodamine 101. The lifetimes were found to depend on the refractive index of the glass substrates on which the dye was adsorbed. Reversible changes in lifetimes were observed when a second glass plate was pressed against the dye covered plate and was removed again. By a comparison of experiment and theory an estimate for the quantum efficiency of the adsorbed dye molecules was obtained.

We investigated the fluorescence of submonomolecular dye layers on glass surfaces. The main object was to study effects of the "optical environment" of the adsorbed molecules on the angular distribution of the fluorescence and on their fluorescence lifetimes.

2. Submonomolecular dye layers on glass surfaces

Submonomolecular dye layers were prepared with a spin coating technique as follows: A few drops of a dilute solution of the dye in methanol (with dye concentrations $c_{sol} \approx 10^{-4}$–10^{-6} mol/ℓ) were deposited on the (carefully cleaned) plane face of a hemi-cylindrical glass prism at low speed of rotation

(≈ 120 rpm). Then the speed of rotation was increased within two seconds to 3000 rpm for five seconds. After this time the solvent had evaporated completely.

Steady state fluorescence of the dye lasers was excited by a CW argon laser ($\lambda_e = 514$ nm). Fluorescence intensity measurements indicated that (i) the distribution of the adsorbed molecules is uniform, and (ii) that the surface coverage c_{sur} is linearly proportional to c_{sol}; it is reproducible to about 10% and is almost independent of the initial amount of dye solution deposited on the glass. By a comparison of the fluorescence intensities of an adsorbed layer with that of a dye solution of known concentration (which was in contact with the glass prism and was excited by an evanescent wave) we established the proportionality constant between c_{sur} and c_{sol}. With a dye concentration $c_{sol} = 1 \times 10^{-5}$ mol/ℓ we obtained a coverage $c_{sur} \approx 1 \times 10^{12}$ molecules/cm^2. We measured the fluorescence intensity I as a function of the dye concentration c_{sol} and found it to be approximately proportional to $c_{sol} \exp(-c_{sol}/c_{crit})$, with $c_{crit} = 1.8 \times 10^{-5}$ mol/ℓ for rhodamine 6G. This result expressed in terms of c_{sur} means, that for coverages $c_{sur} \approx 10^{11}$–10^{13} molecules/cm^2 (corresponding to intermolecular distances of 3–30 nm) $I \propto c_{sur} \exp(-c_{sur}/c'_{crit})$, where the critical surface coverage is $c'_{crit} = 1.8 \times 10^{12}$ molecules/cm^2. The intensity quenching at high coverages is probably caused by energy transfer from monomers to dimers acting as nonluminescent traps.

3. Angle-resolved measurements in emission and absorption

We measured the angular distribution of the steady state fluorescence intensity $P^{(s,p)}(\alpha)$ as a function of the angle of emission α for both s- and p-polarisation, while the angle of incidence α_e of the exciting argon laser beam ($\lambda_e = 514$ nm) was kept constant (see fig. 1). The experimental set-up was described by Fattinger [1].

The experimental radiation patterns $P^{(s,p)}(\alpha)$ of the adsorbed dye layers were compared with the radiation patterns of an ensemble of incoherently radiating electric dipoles located in a medium of refractive index $n_2 = 1$ on the interface to a homogeneous, isotropic, loss-free, dielectric medium of index n_1 (see refs. [2,3]). We described the radiation pattern of the ensemble as a weighted sum of the radiation patterns of dipoles oriented along the x, y, and z directions with weight factors g_x, g_y, and g_z, respectively, where $0 \le g_j \le 1$ with $j = x$, y, z and $g_x + g_y + g_z = 1$. The weight factors g_j depend not only on the orientation of the molecules, but also on the exciting electric field, i.e., on the angle α_e and the polarisation of the exciting beam, and on depolarisation caused by energy transfer.

In fig. 2 we show calculated radiation patterns of electric dipoles oriented along the x, y, and z direction for the case where $n_1 = 1.86$ and $n_2 = 1$. A
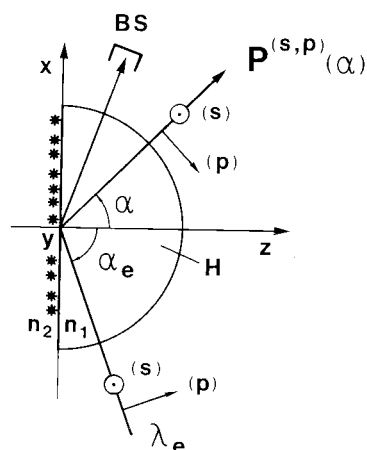
Fig. 1. Schematic of experimental configuration. $*$, fluorescent molecules; H, hemi-cylindrical prism of refractive index n_1 (silica with $n_1 = 1.46$ or Schott glass LaSF31 with $n_1 = 1.86$); $n_2 = 1$, air; α_e, angle of incidence of excitation wavelength λ_e; BS, beam stopper; α, emission angle; $P^{(s,p)}(\alpha)$, radiation patterns, i.e., angular distribution of s- and p-polarised emitted light intensity.

typical measured radiation pattern of rhodamine 6G on a LaSF31 prism is given in fig. 3. A fit of the theoretical to the experimental radiation patterns $P^{(p)}(\alpha)$ for p-polarisation permits to determine the ratio g_z/g_x; while the s-polarised curve $P^{(s)}(\alpha)$ served to check the reliability of the experimental data. Measurement of the ratio of the s- and p-polarised light intensities
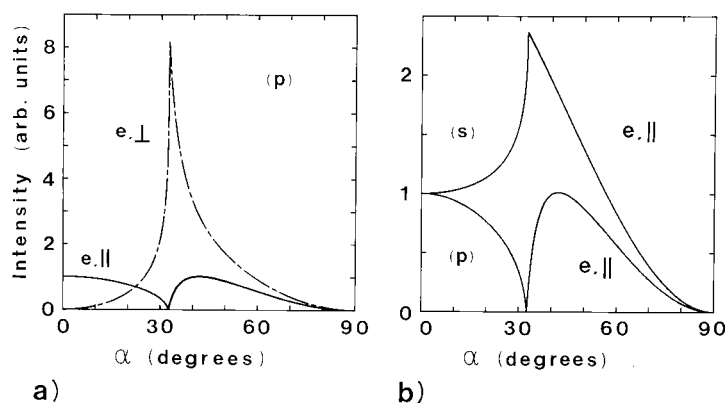

Fig. 2. Calculated radiation patterns $P^{(s,p)}(\alpha)$ versus emission angle α for fluorescent molecules on a glass surface (indices $n_1 = 1.86$, $n_2 = 1$). Electric dipole transitions with dipole moments parallel (e, ||) and perpendicular (e, $\perp$) to the interface. (a) p-polarized light emitted by an e, $\perp$ dipole and an e, || dipole oriented along the x direction, respectively (the latter curve is repeated in (b); (b) s-polarized light emitted by an e, || dipole oriented along the y direction.
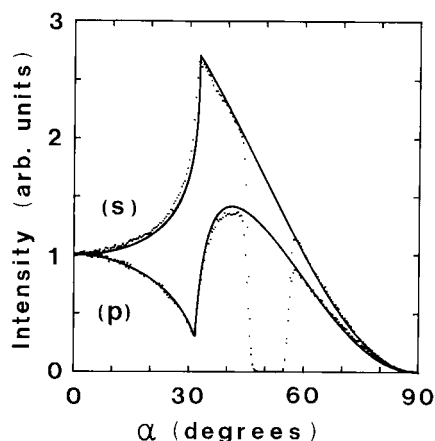
Fig. 3. Angular intensity distributions for s- and p-polarisation versus emission angle α. Radiation pattern $P^{(s,p)}(\alpha)$ versus α of dye rhodamine 6G on a Schott glass LaSF31 ($n_1 = 1.86$). Fit of the theoretical curves (solid line) to the experimental data permits to determine the orientation of electric dipole moments relative to the surface (see text).

$P^{(s,p)}_{exp}(\alpha)$ at emission angle $\alpha \approx 0$ permits to determine the ratio $g_y/g_x = P^{(s)}_{exp}(\alpha = 0)/P^{(p)}_{exp}(\alpha = 0)$.

For rhodamine 6G we found – for different coverages c_{sur} and excitation under different angles α_e – that always $g_z < 0.03$. This proves that the emission dipole moments are parallel to the surface. (Expressed more precisely, the angle θ between the dipole moments and the surface is $\theta < 10°$). We also found the absorption dipole moments in rhodamine 6G to lie flat on the glass surface. This result was obtained from measurements of the s- and p-polarized fluorescence intensities at a fixed emission angle $\alpha \approx 0$ as a function of the angle of incidence α_e of the exciting beam. These intensities are proportional to the absorbances $A^{(s,p)}(\alpha_e)$ of the dye layer as a function of α_e, which, according to the reciprocity theorem, are identical with $P^{(s,p)}(\alpha)$ (see ref. [4]). Therefore, in analogy to the emission case, the orientation of the absorption dipoles can be determined from a comparison of experimental and theoretical $A^{(s,p)}(\alpha_e)$ curves.

We determined the angle ψ between the absorption and the emission dipole moment in rhodamine 6G to be $\psi = 13° \pm 3°$. This determination is based on (i) the theoretical expression $g_x/g_y = (1 + 2 \sin^2\psi)/(1 + 2 \cos^2\psi)$, which holds if the dipole moments are parallel to the surface and have random orientations in that plane and (ii) the measurements of the ratio $g_x/g_y = P^{(p)}_{exp}(\alpha = 0)/P^{(s)}_{exp}(\alpha = 0)$ for s-polarised excitation, at lower dye coverages where depolarisation due to energy transfer is negligible. The measured ratios g_x/g_y increased with increasing c_{sur} to the value of ~ 1, due to higher energy

transfer at smaller intermolecular distances; the latter effect was also investigated by Garoff et al. [5].

4. Fluorescence lifetimes

The time decay of the fluorescence of sulforhodamine 101 was measured by time correlated single photon counting. The emission wavelength was $\lambda = 600$ nm. Excitation was by a synchronously pumped dye laser; $\lambda_e = 563$ nm. At the chosen dye coverage energy transfer is negligible, so that the measured lifetime represents the lifetime of an isolated molecule on the surface (see Leitner et al. [6] for measurements of coverage dependence of the lifetime of rhodamine 6G).

On different glass substrates we measured the following lifetimes: τ(silica) $= 3.5$ ns, τ(Pyrex) $= 4.0$ ns, τ(BK7) $= 2.9$ ns, τ(LaSF15) $= 2.5$ ns, and τ(LaSF31) $= 2.5$ ns. The data points in fig. 4 are the normalised lifetimes τ/τ_{vac}, with $\tau_{vac} = 5.6$ ns. The measured lifetimes decrease with increasing refractive index n_1 of the substrate. We interpret this result as an electrodynamical effect, i.e., as a dependence of the radiative lifetime τ_r on the optical environment of the molecule. The ratio of the radiative lifetimes in two different environments (denoted by a prime and no prime, respectively) is given by the ratio of the total powers L radiated by a classical electric dipole in the two environments $\tau_r'/\tau_r = (L'/L)^{-1}$ (see ref. [7]). The fluorescence lifetime is $\tau = \eta\tau_r$, where η is the quantum efficiency. Calculated normalised lifetimes $\tau/\tau_{vac} = \eta(L/L_{vac})^{-1}$ as a function of the substrate index n_1 are

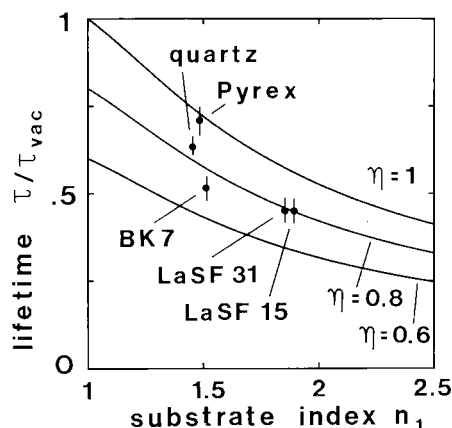Fig. 4. Normalised lifetimes τ/τ_{vac} of sulforhodamine 101 dye molecules on the surfaces of different substrates versus refractive index n_1 of substrate. Solid lines are calculated lifetimes τ/τ_{vac} for different quantum efficiencies η. $\tau_{vac} = 5.6$ ns.

shown in fig. 4 for different values of η. The subscript vac denotes the case where $n_1 = n_2 = 1$, i.e., vacuum. Comparison of these curves with the data points yield the quantum efficiencies η of the dye on different surfaces. These η values depend critically on the value τ_{vac} used to normalise the measured lifetimes. We obtained τ_{vac} as follows: We measured the lifetimes $\tau_{sol}(n)$ of the dye in solvents of different refractive index n. From $L = nL_{vac}$ we derive theoretically, assuming a quantum efficiency $\eta_{sol} = 1$, that $n\tau_{sol}(n) = \tau_{vac}$, where τ_{vac} is a constant independent of n. We found this relationship to be quite well satisfied in solvents with indices ranging from $n = 1.33$ (methanol) to $n = 1.54$ (benzylalcohol).

The quantum efficiency η of adsorbed dye molecules can also be determined by "optical contact experiments". The only previous experiments of this kind were performed with about 30 nm thick layers of an organic Eu^{3+} compound with luminescence lifetimes of about 0.5 ms [8]. The lifetime $\tau = 3.54$ ns of sulforhodamine101 on a silica substrate was reduced to $\tau' = 2.99$ ns when a LaSF15 glass plate was pressed against the dye layer coated silica plate until optical contact was established. With the assumption that the rate of non-radiative transitions remains the same in both optical environments, theory [7] predicts that $\tau/\tau' = 1 + \eta(L'/L - 1)$. With the calculated values $L/L_{vac} = 1.350$, $L'(d = 0)/L_{vac} = 1.747$, $L'(d = 1 \text{ nm})/L_{vac} = 1.722$ and $L'(d = 3 \text{ nm})/L_{vac} = 1.676$ for electric dipoles parallel to the surface, we find $\eta(d = 0) = 62\%$, $\eta(d = 1 \text{ nm}) = 66\%$ and $\eta(d = 3 \text{ nm}) = 76\%$ for sulforhodamine 101 on silica in air. The obtained values of the quantum efficiency η depend critically on the assumed median distance d between the glass plates in optical contact. This distance d has not yet been experimentally determined; we assume it to be of the order of magnitude of the surface roughnesses. We stress that the observed lifetime changes, i.e., the changes in spontaneous emission rates, are reversible, i.e., when the second plate is removed again the original lifetime is recovered.

Acknowledgement

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