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MEASUREMENT OF SINGLET EXCITON DIFFUSION COEFFICIENT IN THE c'-DIRECTION IN CRYSTALLINE NAPHTHALENE

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ABSTRACT : The diffusion coefficient of singlet excitons in the c' direction in crystalline naphthalene has been deduced from the temporal analysis of fluorescence quenching at the surface by an Al layer. $D_{c'} = 5 \times 10^{-5}$ cm^2 s^{-1}, corresponding to a diffusion length $\Lambda_{c'} = 230$ Å.

Several investigations have been concerned with energy transfer across crystalline anthracene-metal surface[1-3]. Recently, Kurczewska and Baessler[3] have shown experimentally, under stationary excitation conditions, that the quenching rate constant of the singlet excitons is a decreasing function of the distance separating gold and crystal surfaces. Moreover they pointed out that a gold layer deposited on the crystal surface acts as a perfect exciton sink. Here we report on the effect of the singlet exciton annihilation at the aluminium-naphthalene crystal interface on the time decay of naphthalene fluorescence.

Under pulsed excitation conditions and with the beam normally incident onto the crystal through the metallized surface, the rate equation governing the singlet concentration n at a given distance z from the Al-naphthalene inter-

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face is given by

$$\frac{\partial}{\partial t} n(z,t) = D_{c'} \frac{\partial^2}{\partial z^2} n(z,t) - \beta n(z,t) + N_0 \, \varepsilon \, e^{-\varepsilon z} U(z) \, \delta(t) \tag{1}$$

where $U(z)$ and $\delta(t)$ are respectively the Heaviside and Dirac function. N_0 is the total number of photons per excitation pulse, ε the absorption coefficient of crystalline naphthalene, β^{-1} the monomolecular lifetime of the singlet excitons and $D_{c'}$ their diffusion coefficient in a direction perpendicular to the crystal-Al interface.

Assuming perfect exciton quenching at the Al surface, Eq.1 can be solved with the following boundary conditions $n(\infty,t) = 0$ and $n(0,t) = 0$, and the time dependence $i(t)$ of the fluorescence emission is given by

$$i(t) = k_f N_0 \, e^{-\beta t} \, e^{\varepsilon^2 D_{c'} t} \operatorname{erfc} \varepsilon \sqrt{D_{c'} t} \tag{2}$$

where k_f is the rate constant of the radiative deexcitation.

The naphthalene crystals used in these experiments, were grown by the Bridgman method from zone-refined naphthalene. Four samples with well-developed cleaved non polished ab planes (dimensions : 4x8 mm^2) were selected. Aluminium layers 120 to 200 Å thick were evaporated on an area of about 12 mm^2.

The excitation light source was an actively mode-locked Argon-Ion laser associated with an electro-optical shutter (KDP) and a second-harmonic generator (Lithium Formiate) delivering linearly polarized 257.2 nm pulses of 0.13 ns duration with a repetition rate of 3.5 kHz. The incident UV beam was normal to ab plane of the naphthalene crystal : translation of the crystal allowed illumination of either the free or the Al-covered area ; rotation of the crystal enabled polarized excitation respectively parallel to the a and b axis. The time-dependent fluorescence emission emerging from the backside of the crystal was analyzed by means of a single photoelectron timing system[4] whose instrumental response function is better than 1 ns.

Fig. 1 shows experimental results (dots) obtained at room temperature : A corresponds to a clean surface excitation ; B and C are obtained with the incident beam falling onto the crystal surface through the Al layer, and polarized respectively parallel to the b and a axis. The solid lines are calculated curves : A shows the unimolecular decay of crystalline naphthalene ($\beta^{-1} = 109$ ns) ; B and C show the time evolution of the fluorescence calculated using Eq.2. The fit B has been obtained by chosing the coefficient $\varepsilon^2 D_{c'}$ equal to 3×10^{5} s^{-1} ; the experimental data could not be adjusted if $\varepsilon^2 D_{c'}$ was varied by more than 30% from this value. Taking for the absorption coefficient for light polarized parallel to the b crystallographic axis $\varepsilon_b = 8\times10^{4}$ cm^{-1}[5], the diffusion coefficient $D_{c'}$ of the singlet exciton in the c' direction is found to be 5×10^{-5} $cm^2 s^{-1}$. The solid line C corresponds to the case where $\varepsilon_a^2 \times D_{c'} = 8\times10^{4}$ s^{-1} ($\varepsilon_a \approx 4\times10^{4}$ cm^{-1}[5]). The calculated and experimental curves C do not differ from the exponential decay A : indeed, the greater the penetration depth of the excitation light, the smaller the number of excitons reaching the quenching surface.

In conclusion, we have measured the diffusion coefficient $D_{c'}$ of the singlet exciton in the c' direction of crystalline naphthalene. The fluorescence decay of the Al-crystal system is shortened if the penetration depth $1/\varepsilon$ is less than 5 times the diffusion length $\Lambda_{c'} = 230$ Å ($\Lambda_{c'} = \sqrt{D_{c'}\beta^{-1}}$). The absolute accuracy of the $D_{c'}$ value depends on that of the absorption coefficient, and on the validity of the assumption that the Al-crystal interface acts as a perfect exciton sink. The value $D_{c'} = 5\times10^{-5}$ cm^2 s^{-1} can be compared to the average diffusivities assuming isotropic three-dimensional diffusion of the excitons, inferred from sensitized fluorescence experiments in mixed crystals $D \approx 1.5\times10^{-4}$[6-7] and $D = 5\times10^{-5}$ cm^2 s^{-1}[8-9] and to that deduced from the singlet-singlet annihilation rate constant in crystalline naphthalene $D = 2\times10^{-4}$ cm^2 s^{-1}[10].

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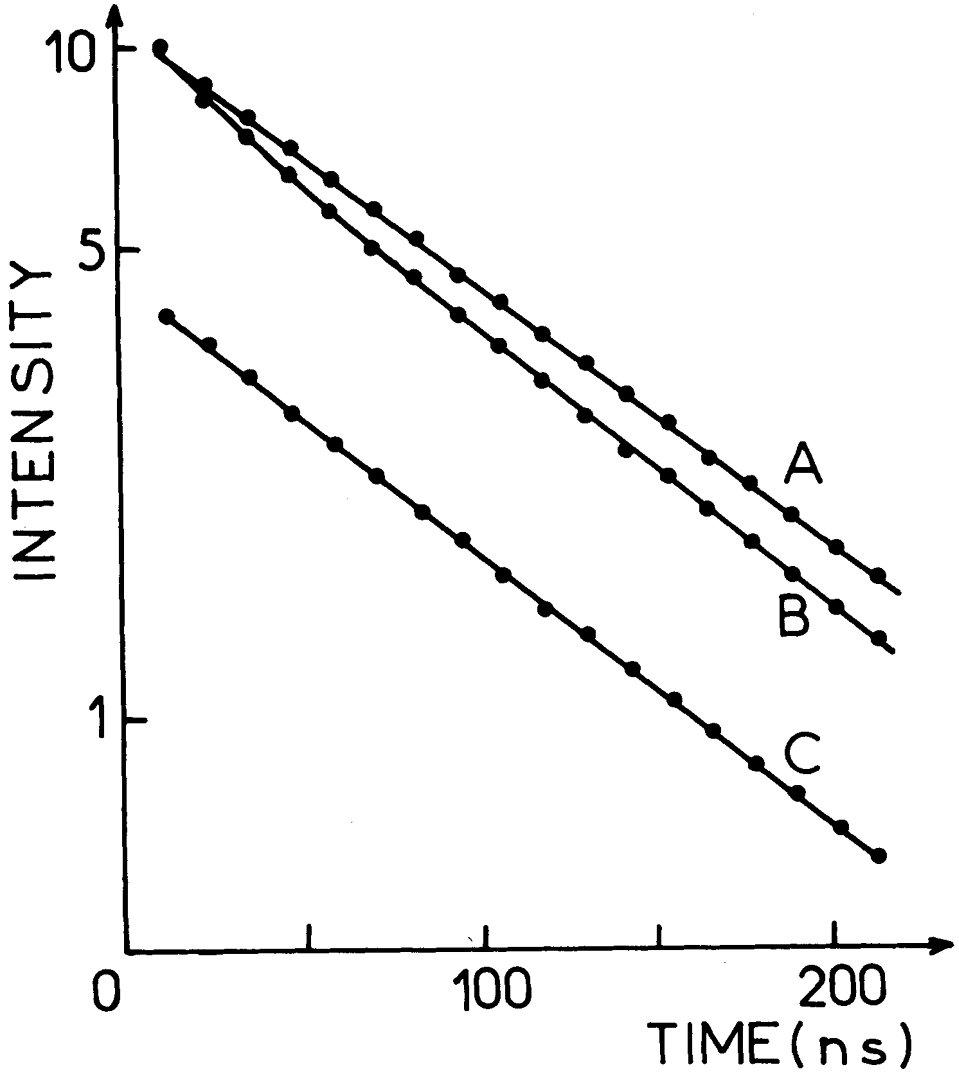

Figure 1. Fluorescence decay curves

REFERENCES :

1. H. Kallmann, G. Vaubel and H. Baessler, Phys. Stat. Sol. (b) 44, 813 (1971)

2. G. Vaubel, H. Baessler and D. Möbius, Chem. Phys. Lett. 10, 334 (1971)

3. H. Kurczewska and H. Baessler, Journ. Luminescence 15, 261 (1977)

4. B. Sipp, J.A. Miehé and R. Lopez-Delgado, Opt. Comm. 16 202 (1976)

5. A. Bree and T. Thirunamachandran, Mol. Phys. 5, 397 (1962)

6. C.L. Braun and G.M. Dobbs, J. Chem. Phys. 53, 2718 (1970)

7. V.L. Zima and A.N. Faidysh, Opt. Spectry. 20, 566 (1966)

8. K. Uchida and M. Tomura, J. Phys. Soc. Jpn. 36, 1358 (1974)

9. A. Hammer and H.C. Wolf, Mol. Cryst. 4, 191 (1968)

10. F. Heisel, J.A. Miehé, M. Schott and B, Sipp, Chem. Phys. Lett. (in press).