Diffusion anisotropy of triplet excitons in stilbene single crystals

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It is suggested that the kinetic curves for the damping of scintillations, which are caused by α particles striking the sample parallel to different crystallographic axes, must be measured to determine the components of the diffusion tensor of triplet excitons in molecular crystals.

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The diffusion anisotropy of triplet excitons (henceforth called T excitons) in molecular crystals was investigated previously by means of optical excitation. In particular, the two-dimensional nature of their motion in anthracene was reliably established both theoretically [1] and experimentally.[2] However, a relatively low spatial gradient of T-exciton concentration was achieved by using optical excitation. This is apparently attributable to the large spread in the values obtained for the diffusion-tensor components (for anthracene, for example, by several orders of magnitude: from 10^{-2} (Ref. 3) to 10^{-7} cm^2. sec^{-1} Ref. 4).

The goal of this work is to investigate experimentally the diffusion anisotropy of T excitons in stilbene single crystals and to determine the components of the diffusion tensor. Knowledge of these parameters is essential for describing the dynamics of T excitons in molecular crystals, as well as in applications in fast-neutron spectroscopy.[5]

The experiment was as follows. A stilbene single crystal was bombarded with a collimated ($\theta \sim 15°$) beam of α particles. The track of an α particle can be regarded as

a cylinder (diameter $a_0 \sim 10$ nm and length $l \sim 30$ μm) in which a high[6] (10^{19} cm^{-3}) density of T excitons is achieved. The diffusive spread and the accompanying decrease of the T-exciton density $c(r, t)$ are determined by the diffusion coefficients in perpendicular directions to the track. The luminance of the "slow" component of scintillation—the luminescence resulting from annihilation of T excitons—is proportional to $c^2(r, t)$.

A recording of the decrease of luminescence intensity with time makes it possible to determine at what rate the diffusion proceeds and to calculate the diffusion coefficients along two mutually perpendicular axes that are prependicular to the track. By orienting the crystal in such a way that the α particles enter it along the a, b, c' crystallographic axes, we can obtain three pairs of diffusion coefficients D_a and D_b, D_b and $D_{c'}$, and $D_{c'}$ and D_a that form three matched pairs. Such an arrangement has the following advantages over the optical excitation: 1) because of the absence of spin forbiddenness, a high density gradient of T excitons $\nabla c(r, t)$ is achieved (within the track limits $c \sim 10^{19}$ cm^{-3} and outside of it $c \sim 0$), and 2) the transverse dimensions of the excitation zone are much smaller than the longitudinal dimensions $l/a_0 \sim 10^3$, which makes it possible to regard the diffusion as two-dimensional.

The equation describing the behavior of T excitons is

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} - \frac{1}{\tau} c - \gamma_T T c^2 - \gamma_R c_R c, \tag{1}$$

where $\tau \sim 10^{-2}$ sec is the lifetime, D_x and D_y are the diffusion coefficients in the perpendicular plane to the direction of the α-particle track, γ_{TT} is the rate constant of the triplet-triplet annihilation, c_R is the density of quenching centers, which are primarily radicals with a long lifetime, and γ_R is the quenching rate constant. The initial distribution was assumed to be Gaussian. Track bending due to scattering and the nonuniform energy release were ignored. They become noticeable only in the last portion of the track $\sim 0.1l$. The investigated intensity of the delayed fluorescence is determined by the expression

$$I(t) = \int_v \gamma_{TT} c^2 dv. \tag{2}$$

Figure 1 shows the damping curves calculated from Eq. (1) for the "slow" component of the scintillations for strong anisotropy $D_a \approx D_b \gg D_{c'}$, where a, b, and c' are the crystallographic axes; c' is perpendicular to the a plane (this is realized, for example, for anthracene). We can see that the kinetics are strongly dependent on the excitation direction. Quenching by radicals has practically no effect on the damping kinetics even when $\gamma_R c_{R_0} \sim 10^7$ sec^{-1}.[6]

The inverse problem of determining the components of the diffusion tensor from the kinetics of delayed fluorescence was solved experimentally.

The damping curves for the delayed fluorescence of stilbene single crystals were measured by using the "one-photon" method[7] on an apparatus with a time resolution of ~ 6 nsec for excitation along the principal crystallographic directions a, b, c'. The recording was done on a pulse analyzer after the entry of data into a computer. The

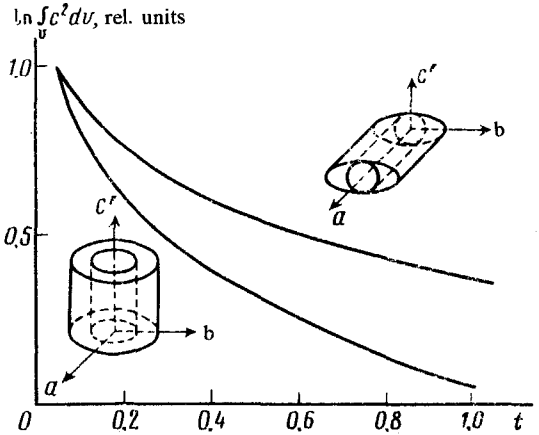

FIG. 1. Influence of anisotropy of T-exciton diffusion on the kinetics of the "slow" component of scintillations. The upper curve represents the track along the a axis ($D_b \gg D_{c'}$). The lower curve represents the track along the c' axis ($D_a + D_b$). The time is in units of $t_{\text{dif}} = a_0^2/D_a$.

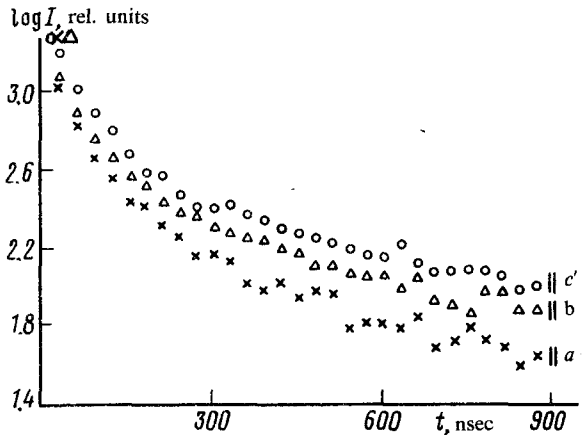

FIG. 2. Experimental data for the kinetics of the "slow" component for different excitation directions.

track diameter increased to $\sim 6\ a_0$ during the measurements ($\sim 1\ \mu$sec) because of diffusion. The experimental photoreadings y_i obeyed a Poisson distribution (Fig. 2) (rms deviation of $\sqrt{y_i}$). The approximate formula

$$I(\tilde{t})/I(0) = ((D_1\tilde{t} + 1)(D_2\tilde{t} + 1))^{-1/2} \tag{3}$$

which describes the kinetics of the delayed fluorescence, was obtained for the analysis of the results. Here $D_1 = 4\ D_x a_0^{-2}\Delta t$, $D_2 = 4\ D_y b_0^{-2}\Delta t$, a_0 and b_0 are the track dimensions on the x and y axes at the moment of completion of the "fast" component, Δt is the measurement interval, and $\tilde{t} = t/\Delta t$. The formula (3), which was obtained on the assumption that the distribution of T-exciton density has a Gaussian profile, ap-

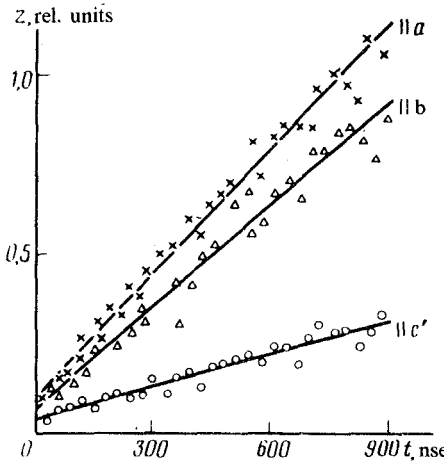

FIG. 3. Experimental data for the kinetics of the "slow" component for different excitation directions after a linearizing replacement of variables.

proximates well the results for both the numerical and full-scale experiment, if the "rate" of diffusion spreading is greater than the "rate" of triplet-triplet annihilation. Similar assumptions were made in Ref. 8.

For the subsequent analysis, the experimental data were subjected to nonlinear transformation $z_i = t^{-1}(y_i^{-2} - 1)$ by means of which Eq. (3) was reduced to $z_i = Bt_i + A$, where $B = D_1D_2$ and $A = D_1 + D_2$. The coefficients were determined by using the least-squares method with allowance for the statistical weights of the photoreadings. Figure 3 shows the straight lines that best fit the corresponding date (typical correlation coefficients are ~ 0.98).

As a result of computer analysis of several experimental curves and averaging, we have calculated three pairs of dimensionless diffusion coefficients D_1 and D_2 for irradiation along a, b, and c'. It is important that these three pairs of diffusion coefficients coincide. The following component ratios were obtained: $D_a:D_b:D_{c'} = 1:1, 8:2.6$; this indicates a relatively weak anisotropy of T-exciton diffusion in stilbene compared with the singlet exciton.[9]

The absolute values of diffusion coefficients were determined on the assumption that the initial density distribution is Gaussian: $D_a = (0.9 \pm 0.2) \times 10^{-5}$, $D_b = (2.4 \pm 0.5) \times 10^{-5}$, and $D_{c'} = (4.2 \pm 0.9) \times 10^{-5}$ cm^2·sec^{-1} (rms errors).

The obtained results are in agreement to within an order of magnitude with the data of Ref. 10, where the measurements for stilbene were made by using the optical method only in the ab plane.

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