Diffusion of Triplet Excitons in Pure Crystalline Naphthalene

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ABSTRACT

The diffusion of triplet excitons in pure crystalline naphthalene is investigated using delayed fluorescence, arising from the annihilation of two triplet excitons producing a fluorescing singlet exciton, as a probe. Insufficient lab time prevented any numerical evaluation of the diffusion constant. As previously reported,[1] the lifetime for the triplet exciton, determined from the first-order components of the phosphorescence and delayed fluorescence decay curves, is 130 ± 20 msec. Impurities and exposure of the sample to the atmosphere were found to have significant effects upon the spectral characteristics of the samples.

I. INTRODUCTION

Recently, considerable work has been done on the dynamics of the triplet state in anthracene. A similar study in naphthalene is more suitable because impurities in naphthalene can be reduced to as low as one part in 10^7 by a previously reported purification scheme which involves reaction over potassium and zone refining. Thus, in naphthalene a controlled study of the effects of impurities is possible. The purity of the samples used here was checked spectroscopically, a method by which the most common impurity, β-methyl-naphthalene, is easily detected if present.

Several experimental methods have been used in the past for anthracene. Two of these techniques were attempted with the naphthalene in the present work. Considerable disagreement currently exists with respect to diffusion of triplet excitons in anthracene, both on the experimental results and theoretical calculations. Two distinct categories of experimental results have appeared, with the results for the diffusion length of

the exciton differing by a factor of ten.[2-4] Theoretical calculations have been based upon both band models and hopping models for the diffusion process.[4] The purpose of this paper is to report the results of preliminary work on the experimental determination of the diffusion characteristics of triplet excitons in naphthalene.

II. THEORETICAL BACKGROUND

A derivation of the energy levels that arise due to interactions between the molecules of a molecular crystal will show how the energy states of the free molecules are changed by the formation of a crystal, and what physical properties the crystal will have when interacting with an electromagnetic field.

In order to avoid the complications arising from the interaction of the exciton states with the vibrational motion of the molecules in the crystal lattice, in this simple calculation the molecules are considered to be rigidly fixed in equilibrium positions. For simplicity also assume that there is only one molecule per unit cell of the crystal, and that the overlap functions of adjacent molecules (in the ground and first few excited states) in the solid are negligible.

If the Hamiltonian for the free molecule is $\mathcal{H}_n$ and the interaction energy operator between two molecules at lattice points n and m is V_{nm}, the total Hamiltonian for the crystal is

$$\mathcal{H} = \sum_n \mathcal{H}_n + \tfrac{1}{2} \sum_{\substack{n,\,m \\ n \neq m}} V_{nm} .$$

Momentarily neglecting the V_{nm}'s, the eigenvalues and eigenfunctions of $\mathcal{H}$ are found trivially. The ground-state energy of the crystal is $N\epsilon_0$, where ϵ_0 is the ground-state energy of the free molecule ($\mathcal{H}^0 \varphi^0 = \epsilon_0 \varphi^0$) and N is the number of molecules in the crystal. The crystal wave function is then $\psi^0 = \prod_n \varphi_n^0$ in the ground state. The $g^{\underline{th}}$ excited state of the crystal is N-fold degenerate, with energy $(N-1)\epsilon_0 + \epsilon_g$ and wave function (for excitation of molecule n) $\psi_n^g = \varphi_n^g \prod_m \varphi_m^0$. These degenerate wave functions can be used to form N orthonormalized functions Ψ_{kg},

$$\Psi_{kg} = \frac{1}{\sqrt{N}} \sum_n \psi_n^g \, e^{ikn},$$

where k is given by: $k = \sum_{i=1}^{3} \frac{2\pi}{N_i} V_i b_i$, $-\frac{N_i}{2} \leq V_i \leq \frac{N_i}{2}$, and where the b_i are reciprocal lattice basis vectors.

Now if the V_{nm} interaction term of the Hamiltonian is introduced as a perturbation on the wave function Ψ_{kg}, the degeneracy of the energies is removed. First-order perturbation theory gives

$$\epsilon_g = E_0 - E_g = \langle \psi^0 | \mathcal{H} | \psi^0 \rangle - \langle \Psi_{kg} | \mathcal{H} | \Psi_{kg} \rangle ,$$

where ϵ_g = excitation energy of crystal, E_0 = energy of ground state of crystal to first order, and E_g = energy of $g^{\underline{th}}$ excited state.

$$\epsilon_g = \Delta\epsilon_g^0 + \tfrac{1}{2} \left\langle \psi^0 \left| \sum_{\substack{n,m \\ n \neq m}} V_{nm} \right| \psi^0 \right\rangle - \tfrac{1}{2} \left\langle \Psi_{kg} \left| \sum_{\substack{n,m \\ n \neq m}} V_{nm} \right| \Psi_{kg} \right\rangle ,$$

where $\Delta\epsilon_g^0$ = excitation energy to $g^{\underline{th}}$ state of free molecule.

Now, the exciton states of the crystal have a wave function that might be written as

$$\Psi_{kg} = \frac{1}{\sqrt{N}} \sum_{n} \psi_n^g \exp\{i[kn - w_g(k)t]\} \ .$$

Such a wave function represents a plane wave spread over the entire crystal. A localized exciton state is represented by a linear combination (wave packet) of the Ψ_{kg}. The wave packet is characterized by a Δx and a Δk_x, related by the uncertainty principle. In organic crystals the Δx corresponds roughly to the wavelength of the exciting electromagnetic radiation, which is typically large compared to the lattice spacing. Thus, the Δk is rather small, and it is approximately correct to speak of the exciton with a definite k. Therefore, the wave packet can be thought of as moving through the crystal with a quasi-momentum $\hbar k = p$. From the particle point of view, the exciton is an electron-hole pair capable of transferring energy in the crystal and moving as a quasi-particle.

In organic crystals, study of the lowest-lying triplet exciton states is of importance because of their possible roles in energy transfer in photosynthetic processes. Moreover, several interesting features of the multiplet manifolds, such as intersystem crossing from the first excited singlet to the triplet, make exciton study in organic crystals interesting. Crystals of aromatic molecules such as naphthalene are convenient for the study of triplet exciton dynamics due to the long lifetime of the triplet, on the order of 100 msec.[1]

The particle current density for isotopic diffusion is $j = -D\nabla\cdot\rho$ where ρ is the particle density, or for anisotropic processes

$j_u = \sum_{\nu} D_{\mu\nu} \left(\frac{\partial \rho}{\partial x_\nu}\right)$, $\mu, \nu = 1, 2, 3$ are generalized orthogonal coordinates.

If there are generators and sinks, the continuity equation becomes:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot j = -\beta\rho - \gamma\rho^2 + S ,$$

where β^{-1} = exciton lifetime, γ = bimolecular rate constant, and S is the source generating the excitons. The diffusion and continuity equations give:

$$\frac{\partial \rho}{\partial t} = D\nabla^2\rho - \beta\rho - \gamma\rho^2 + S .$$

Analytical solutions to this equation are only possible in certain approximate cases and in certain geometrical symmetries. The purpose of this experiment was to attempt a determination of the diffusion coefficient D, which for anthracene has previously been reported as anywhere from 10^{-2} to 10^{-4} cm^2/sec.[4]

III. EXPERIMENTAL

Light from an Osram 6500-watt Xenon arc lamp was passed through a 5-cm quartz cell containing a $NiSO_4$-$CoSO_4$-water filter solution and the filtered light was used to excite the crystal, located at the center of a cylindrical phosphoroscope. The phosphoroscope was 20-cm in diameter and through reduction pulleys could be operated at several speeds from about 30 rpm to 1725 rpm with less than 2% drift in the frequency. The excitation and observation periods were of equal length and ranged from 0.9 sec at the lowest speed to 15.9 msec at the highest speed. Dead time between excitation and observation varied from 83 msec to 1.4 msec over

the range of phosphoroscope speeds. For spectral measurements the highest speed was used, whereas in the case of lifetime determinations the speed was chosen so as to give excitation and observation intervals equal to more than three lifetimes in all cases.

The crystal emission in the region from 2800 Å to 5400 Å was focused onto the slit of a Jarrell-Ash Model 82-000, 0.5-m Ebert scanning spectrometer. This instrument was equipped with a grating blazed at 5000 Å in first order, having a reciprocal linear dispersion of 16 Å/mm and effective aperture ratio of f/8.6. The slit width was set at 0.4-mm.

Light emerging from the exit slit of the spectrometer was collected on the cathode of a dry-ice cooled EMI 6256 SA photomultiplier by means of appropriate condensing optics. The photomultiplier output was fed into a Victoreen Model VTE-1 electrometer where it was amplified and the spectrum was recorded on a strip-chart recorder.

In determining the lifetime of the emission at a given wavelength, the photomultiplier signal was first amplified to about 1 volt and then fed into the time base unit of a Nuclear Data Model ND180 multichannel analyzer system operated in the averaging mode. This unit was triggered synchronously with the phosphoroscope by means of the output from a photodiode activated once per revolution at the beginning of the observation period. After averaging the raw signal over 10^5 counts, the resulting almost noise-free decay curve was plotted on a Hewlett-Packard Model 7590 C X-Y recorder. See Fig. 1.

Great care had to be taken in all experiments to minimize scattered light. To this end the phosphoroscope, spectrometer and photomultiplier were enclosed in a light-tight box to eliminate scattered light from around

the room. Moreover, within the light-tight box, both the excitation light and the emitted light were confined inside metal tubes that also housed the required optics. The following independent checks for scattered light were made both in the presence and absence of the Corning glass filters C.S. 3-72 and C.S. 3-73 to ensure that the precautions taken were sufficient to permit detection of the weak signals. For these checks, an empty sample cell was substituted for the sample in order to stimulate the actual experimental conditions as closely as possible.

1. Kodak 103a-0 plates, taken using the second order of a 600 line/mm Bausch and Lomb grating in a 2-m Czerny-Turner mount (effective aperture ratio f/11) showed no darkening on exposures up to 1 h.
2. Not even a dc level was evident when 10^6 counts were made with the multichannel analyzer.
3. Spectrometer traces made by scanning the 0.5-m spectrometer through the spectral region of interest exhibited only a straight base line.

The crystals were melt-grown from naphthalene that had been purified by a process developed in our laboratory and described elsewhere.[5] Crystals from three independent purification lots all exhibited similar lifetime and spectral characteristics.

IV. RESULTS

The lifetime of the triplet exciton obtained by this technique has been reported elsewhere[1] as 130 ± 20 msec. Unfortunately, much more experimental work is necessary before an accurate evaluation of the diffusion coefficient is possible. There are several difficulties that present themselves. First, with the phosphoroscope in such a position that the sample is being irradiated, the steady state spatial distribution of excitons can be given by:

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} - \beta \rho - \gamma \rho^2 + m\alpha I e^{-\alpha x} = 0 ,$$

where the source term is given by $m\alpha I e^{-\alpha x}$ and m is determined by the quantum yield for the photons → triplets transition, α is the absorption coefficient (at the irradiating wavelength) of naphthalene, and I is the intensity of irradiation. The solutions (neglecting $\gamma \rho^2$ term) have the form[2]:

$$\rho(x) = \frac{mI\alpha}{(\beta - D\alpha^2)} \left[e^{-\alpha x} - e^{-\sqrt{2}\, x/\ell_D} \right] , \qquad D\alpha^2 \neq \beta$$

$$\rho(x) = I\alpha mx e^{-\sqrt{2}\, x/\ell_D} , \qquad D\alpha^2 = \beta ,$$

where ℓ_D is the diffusion length of the exciton.

Now, when the phosphoroscope rotates so as to open the sample to the photomultiplier and turn off the exciting light, the exciton density is given by

$$\frac{\partial \rho}{\partial t} = -\beta \rho + D \frac{\partial^2 \rho}{\partial x^2} .$$

But now the boundary conditions on $\rho(x, t = 0)$ created by the steady-state irradiation must be applied. The result is extreme complication. Consider in addition that the model used here is only one-dimensional, and moreover that the diffusion "constant" is really a second-rank tensor due to anisotropic diffusion, and the immensity of any accurate experimental work becomes apparent.

V. SUGGESTIONS FOR FURTHER WORK

If cleaved crystals are used instead of whole crystals, the anisotropy of the diffusion tensor will no longer be an experimental problem. However, the problem of aligning cleaved crystals in a Dewar and preventing the crystals from being exposed to the air presents experimental difficulties. Moreover, neither of the previously reported methods of determining the diffusion constant[2, 3] are completely satisfactory, and some new approach to the problem is needed.

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FIG. 1. Diagram of experimental apparatus.

Diagram of Experimental Apparatus

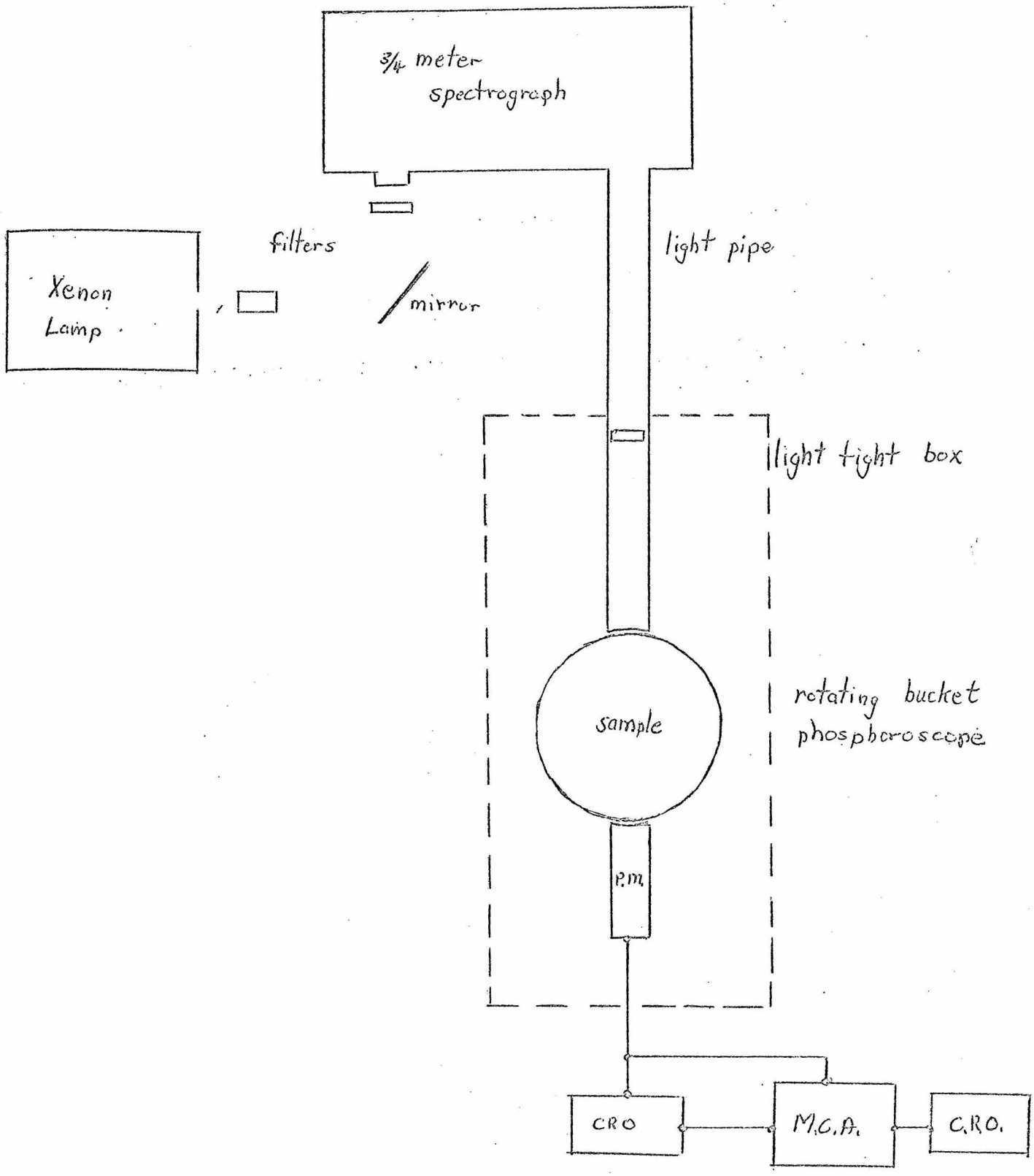


FIG. 2. Decay curve of the delayed fluorescence emission at 3500 Å from pure crystalline naphthalene at room temperature.

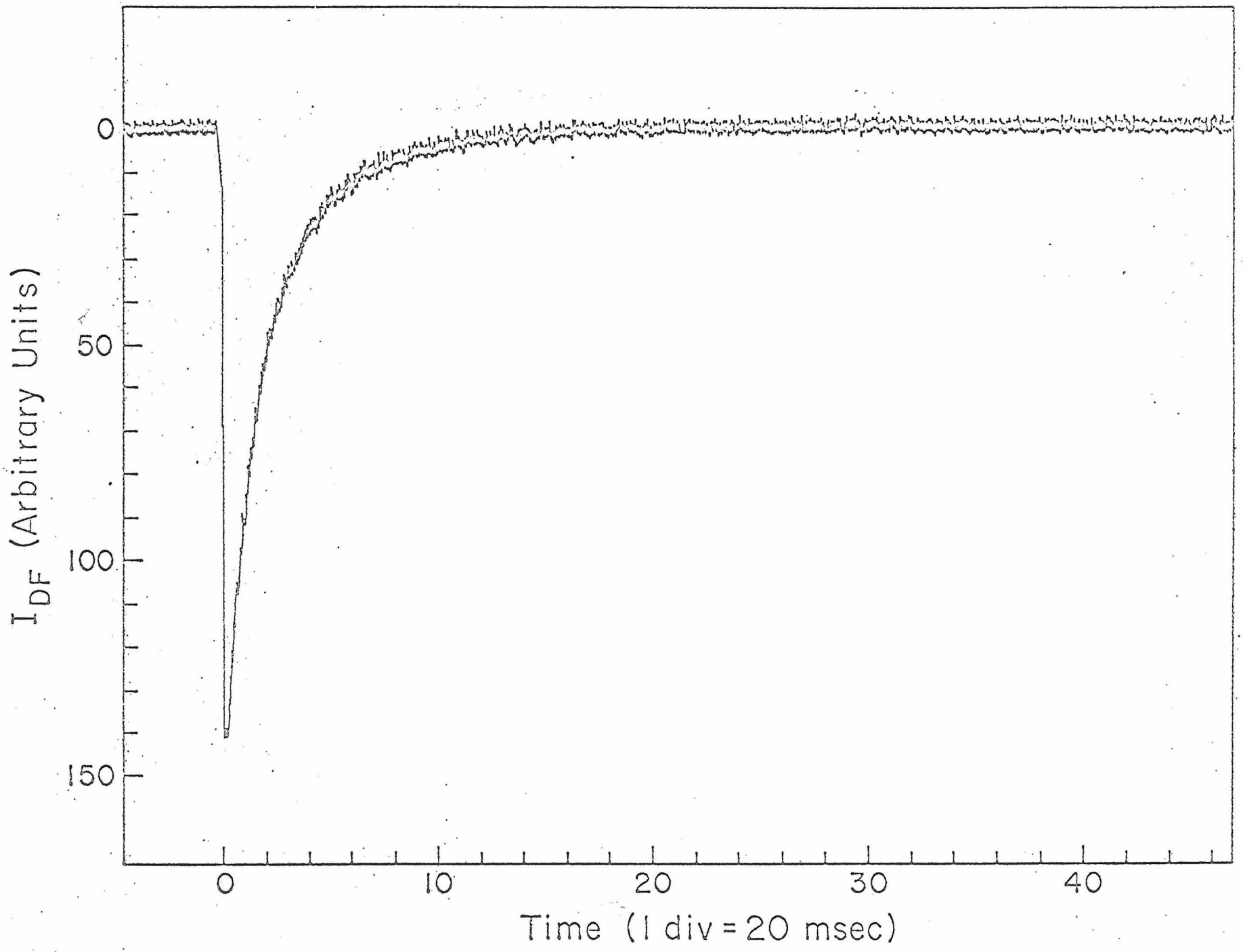
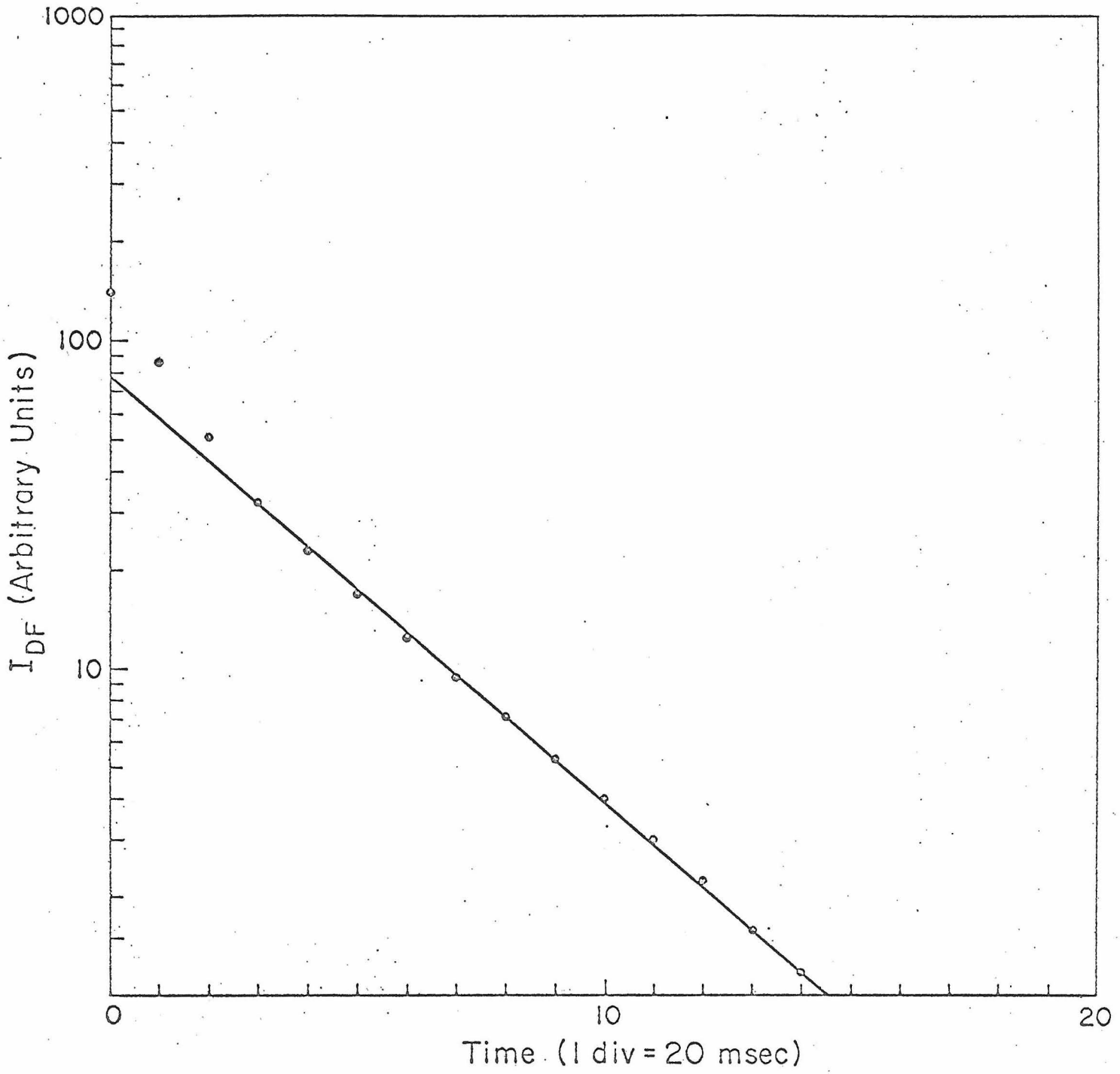

0
50
100
150
I_{DF} (Arbitrary Units)
0
10
20
30
40
Time (1 div = 20 msec)

FIG. 3. Plot of the logarithm of the emission intensity vs time for the delayed fluorescence decay curve shown in Fig. 2.


1000
100
10
I_{DF} (Arbitrary Units)
0
10
20
Time (1 div = 20 msec)