FISSION RATE OF SINGLET EXCITONS IN A TETRACENE CRYSTAL MEASURED WITH PICOSECOND LASER PULSES

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The fluorescenve lifetime of a tetracene crystal at room temperature was measured directly using picosecond techniques. The value obtained was 145 ± 50 psec. The risetime of the fluorescence was < 10^{-11} sec. The singlet exciton fission rate at infinite temperature is ~ 10^{13} sec^{-1} and is attributed to the hopping rate of triplet excitons in the crystal.

It is well known that the singlet exciton in tetracene crystal undergoes homofission into two triplet excitons at room temperature. This process is spin-allowed, has an activation energy [1] of about 1600 cm^{-1} and reduces the fluorescence lifetime to about 200 psec [1]. This lifetime was first arrived at by extrapolation of lifetime measurements from lower temperatures (160 K), where the rates were accessible to nanosecond technology. Subsequently, a lifetime of about 300 psec was measured at room temperature [2*] by deconvoluting the equipment response time of ~ 0.5 nsec from the fluorescence signal. We report here the direct measurement of the temporal dependence of the fluorescence at room temperature of a tetracene crystal following its excitation by a psec pulse using an ultrafast Kerr optical gate to yield new information on the physical mechanism of the fission.

process. The Kerr optical gate [3,4] has previously been used [5] to determine the onset of stimulated emission [5], to measure fluorescence lifetime [4,6,7], and to measure the vibrational decay time in the excited electronic state of a dye molecule [6,7].

In our experiment a mode locked Nd: glass laser emits 1.06 μ pulses of pulse width 6 psec as measured by two-photon fluorescence. These pulses are used to generate the second harmonic pulses at 0.53 μ of 4 psec duration upon passage through a KDP crystal. The experimental arrangement is shown in fig. 1. A dielectric mirror M_1 which reflects at 0.53 μ and transmits at 1.06 μ directs the different wavelength pulses along separate delay paths. The sample of tetracene is placed in the 0.53 μ beam which has been circularly polarized with a quarter wave plate. The 0.53 μ beam is reduced in size to ~ 0.5 cm at the tetracene samples position. The fluorescence from the tetracene samples is collected and collimated through the optical gate, a system of two crossed polaroids oriented at 45° to polarization direction of 1.06 μ beam with a cell of carbon disulfide placed in between.
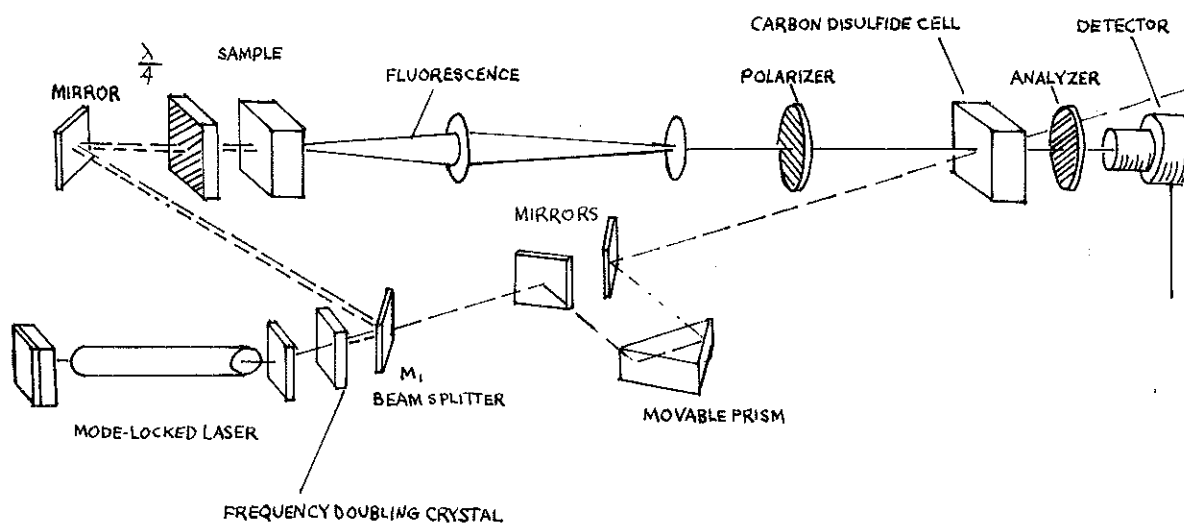
Fig. 1. Schematic of an optical Kerr gate.

The 1.06 μ beam follows a path which can be adjusted by a variable optical delay (τ_D) and is reduced in size to 1 mm upon passage through the 1 cm long carbon disulfide cell. The fluorescence after passing through the gate is focused into a monochromator (1/4-m Jarrell-Ash and RCA 7265 photomultiplier) so that the time dependence of the fluorescence can be recorded as a function of wavelength. The point when the two beams coincide in time and space in the carbon disulfide cell, was determined by timing the 0.53 μ pulses relative to the 1.06 μ pulse with slide of glass instead of a sample. This prompt curve was 8 psec wide with a peak to noise background of 10^3. The intensity of the 1.06 μ and the 0.53 μ beams, total fluorescent intensity, and fluorescent intensity signal through the gate at a particular wavelength were detected and displayed on a dual beam oscilloscope simultaneously using appropriate delay cables.

The single crystal of tetracene was grown from the vapor [#] and was about 0.25 mm thick and 3 X 4 mm^2 in cross-sectional area.

The experimental results showing the fluorescence intensity as function of time for tetracene at room temperature is plotted in fig. 2. Experimentally the fluorescence is detected at wavelength of 5800 Å; it

[#] Grown at the Radiation and Solid State Laboratory of New York University.

reaches a sharp peak at 15 psec after excitation with risetime of 12 psec; and it rapidly decays to the 1/e point in 145 ± 50 psec.

The ultrafast risetime of the fluorescence 12 psec indicates that vibrational relaxation within the singlet manifold is equal to or shorter than this time. Since the risetime is extremely fast, the measured fluorescence decay time of 145 psec gives a measure of the
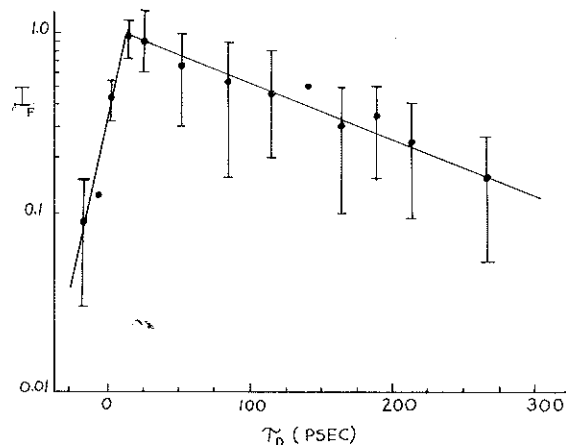

Fig. 2. Fluorescence from a tetracene crystal as a function of time measured at 5800 Å. The decay time is 145 psec, the risetime is 12 psec, and the mean induction time (time to reach the fluorescence peak after the time of excitation) is 15 psec.

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fluorescence decay rate which is equal to the sum of the radiative, nonradiative [‡], and fission rate ($K = K_R + K_{NR} + K_F$). To obtain the fission rate, the relaxation rates are assumed to be independent of temperatures except for the fission rate which is given by

$$K_F(T) = K_F(\infty) \exp(-E_D/kT) ,$$

where $E_D = 1600$ cm^{-1} is the energy difference between the triplet pair state (2T) and the singlet excitation level. Using the value [2[★]] $K_R + K_{NR} = 1.24 \times 10^9$ sec^{-1} and the measured fluorescence rise and decay time, one calculates K_F (300 K) = 5.7×10^9 sec^{-1} and $K_F(\infty) = 1.7 \times 10^{13}$ sec^{-1} is obtained. Hence, the fission time is $\sim 5.9 \times 10^{-12}$ sec.

The quantity $K_F(\infty)$ represents the infinite temperature fissioning rate and is determined by at least two processes — the rate at which the newly created triplet excitons avoid geminate recombination by moving away from each other, and the rate at which the triplet exciton pair loses the spin-correlation it possesses at the moment of creation. The exciton—pair spin-correlation time is not expected to be as short as 10^{-13} sec, in anthracene, it is estimated to be no less than 10^{-10} sec [8] and a similar situation is expected in tetracene [9].

It therefore appears that $K_F(\infty)$ is determined by the triplet exciton incoherent hopping rate [‡]. According to Avakian and Suna [8] the fission and fusion processes are confined chiefly to the ab planes of anisotropic crystals like anthracene and tetracene. Furthermore, Avakian and Suna [8] estimate that in anthracene, a triplet exciton pair initially situated as nearest neighbors will recollide with each other an average of five times before either fusing to form a singlet exciton or moving apart from each other. It therefore appears that since $K_F(\infty)$ is an effective fissioning rate, it must include several geminate recollision processes. In other words, $K_F(\infty) = \alpha k_h$, where

k_h is the incoherent triplet exciton hopping rate in the ab plane and $\alpha \lesssim 1$.

Using the calculated value of $K_F(\infty)$, it follows that $k_h \gtrsim 10^{13}$ sec^{-1}. Using an average triplet exciton lifetime of about 100 μsec [10], and an average jump length [11] of 7 Å, one can estimate that the exciton makes 3.2×10^4 hops in a straight line during its lifetime, which is a diffusion length of $l = 22$ μ in the ab plane (the distance travelled by the triplet exciton in the C' direction in its lifetime is about 0.4 μ) [12,13].

From the expression $l = \sqrt{D_{ab}\tau}$, where l and D are the diffusion length and diffusion coefficient respectively of the triplet exciton in the ab plane, we obtain a lower limit for D: $D_{ab} \gtrsim 4.8 \times 10^{-2}$ cm^2 sec^{-1}. In the C' direction, $D_{C'} \simeq 2 \times 10^{-4}$ cm^2 sec^{-1} [13]. It thus appears that there is an anisotropy of a factor of about 100 in the triplet exciton diffusion tensor in tetracene. An anisotropy of this order of magnitude has been predicted [14] and found in anthracene [15].

A qualitative estimate of D_{ab} may be obtained by comparing the measured values of the total bimolecular triplet—triplet exciton fusion rate constants γ_{total} in anthracene and tetracene. This constant can be expressed as a product of a diffusion controlled collision term γ'_{total} and a probability of fusion f. The f term is not markedly different in anthracene and tetracene, so a comparison of γ_{total} is essentially a comparison of the diffusion controlled terms γ'_{total}, which in turn depend chiefly on D_{ab}. For anthracene [14], $\gamma_{total} = 2 \times 10^{-11}$ cm^3 sec^{-1}, while in tetracene [1] $\gamma_{total} \simeq 2 \times 10^{-9}$ cm^3 sec^{-1}. This is suggestive evidence that D_{ab} is considerably larger in tetracene than the value of $D_{ab} = 2 \times 10^{-4}$ cm^2 sec^{-1} found in anthracene [15] and tends to support the estimated value $D_{ab} \simeq 5 \times 10^{-2}$ obtained by considering the fission rate constant $K_F(\infty)$.

Summarizing, the room-temperature lifetime of the first excited singlet state in tetracene has been measured directly by psec techniques, and is 145 ± 50 psec. The risetime of the fluorescence is < 10 psec, so vibrational relaxation occurs in times shorter than 10^{-11} sec. Using the known activation energy for the singlet exciton fission rate, it is concluded that the triplet exciton hopping frequency in the ab plane of the crystal is $\gtrsim 10^{13}$ sec^{-1}, and that the triplet exciton diffusion coefficient $D_{ab} \gtrsim 10^{-2}$ cm^2 sec^{-1}.

Note: Experiments have been performed recently [16] from which D_{aa} (about $\sim D_{ab}$) was calculated

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[‡] This includes the rate k_{21} defined by ref. [2] between two states.

[★] The measurement equipment consists of a mode locked YAG laser, fast photomultiplier, and a sampling oscilloscope.

[⊞] The hopping can be in the ab plane or in the C' direction. Since the hopping rate in the C' direction is likely to be slower than in the ab plane, we will assume that the hopping is in the ab plane so that the value estimated for D_{ab} will either be close to or less than the true value for D_{ab}.

more directly; the value obtained was $D_{aa} \sim 10^{-2}$ $cm^2 \, sec^{-1}$.

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