Quantum beats in the fluorescence decay of tetracene crystals

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In honor of Emanuel Mooser's 60th birthday

Abstract. The fluorescence decay of tetracene crystals excited by 5-ps-pulses of a dyelaser has been measured. It is nonexponential and has superimposed magnetic field dependent quantum beats. The spontanous fission of singlet excitons into two triplet excitons is responsible for the fast initial decay and the subsequent geminate re-fusion of these excitons accounts for both the nonexponential slow decay and the quantum beats. A two-dimensional random walk model for the triplet motion and fusion yields an excellent fit to the data. The resulting fit parameters are: hopping rate and fission rate: 13.1 and 5.8×10^9/sec respectively, triplet diffusion constant: 5.3×10^{-5} cm^2/sec and the ratio of out-of-plane to in-plane hopping rate: 0.0005.

1. Introduction

Molecular crystals such as naphthalene, anthracene and tetracene are ideal systems for the study of the transfer and the mutual interaction of Frenkel excitons. These mobile molecular states are characterised by a rather long lifetime even at room temperatures (nsec for singlets, msec for triplets). Exciton–exciton interactions are thus important even at low exciton densities. It is known for almost twenty years [1] that certain exciton reactions in molecular crystals are sensitive to external magnetic fields. The best studied bimolecular reaction is the fusion of two triplet excitons into a singlet exciton, as well as the reverse process, the fission of a vibrationally excited or relaxed singlet exciton into two triplets.

These exciton reactions are usually studied in steady-state experiments, i.e. the observed quantity (e.g. delayed fluorescence resulting from triplet–triplet fusion) is monitored as a function of the strength and the direction of an external magnetic field on the timescale of seconds or longer. However, the established theory for the magnetic field effect on the annihilation of two triplets, developed by Johnson and Merrifield [2] and expanded by Suna [3], is clearly a dynamical theory. So far, its results had to be time-averaged in order to allow a comparison with the usual steadystate experiments. As in the fusion, in the fission of a singlet exciton into two triplet excitons the crucial point of these theories is a dynamical equilibrium between the separation of the two triplets by diffusion and their geminate re-fusion, which in turn is modified by a magnetic field dependent quantum beat phenomenon. In an earlier paper [4] we have for the first time

confirmed experimentally the existence of such beats. In this paper the dynamics of the exciton fission and re-fusion process is analysed quantitatively on a timescale of the beat frequencies (a fraction of a nanosecond).

2. Experimental

All experiments have been performed with tetracene crystals. This material is especially well suited for our task, because its singlet energy is almost twice its triplet energy. At room temperature, thermal excitation suffices to induce a fission process [5, 6]. Note that this fission is also responsible for the low quantum yield of tetracene crystals at room temperature.

The experimental set up used is based on that presented in [7] and will be described elsewhere [10]. Its most important features are summarised as follows:

(i) The singlet excitons are excited with a synchronously pumped, mode-locked dye laser operating with rhodamin 6G. The pulse-repetition rate can be adjusted with a cavity dumper, usually at 4 MHz. The output of the dye laser is frequency doubled, which results in 5-ps-pulses of 2.5 pJ at 300 nm.

(ii) The fluorescence of the crystal is focused onto the entrance slit of a double monochromator, and the fluorescence decay is monitored with a photo-multiplier using the single-photon counting technique. This technique has an excellent time resolution (rise time: 70 ps) and an enormous dynamical range (over 5 decades). Both these characteristics are essential for our experiments, as is illustrated in Fig. 1, where we compare the response to the excitation pulse to the fluorescence decay.
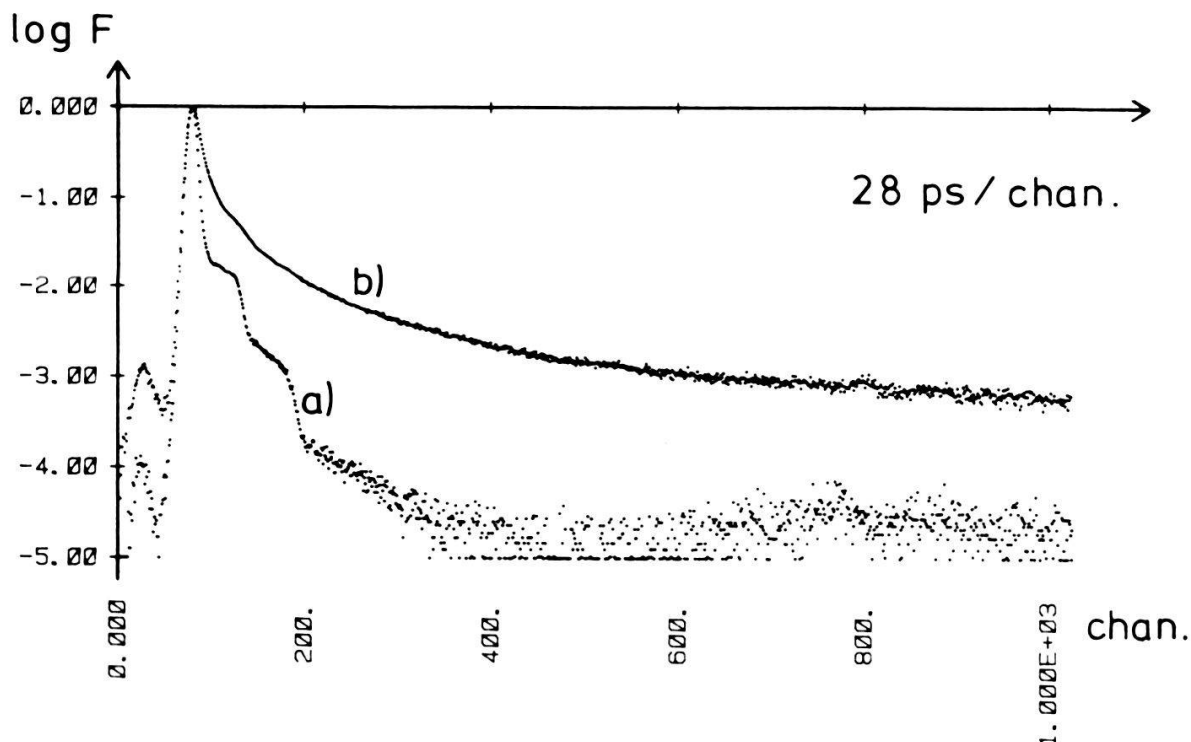

Figure 1
(a) Response of our measuring system to 5-ps-pulses of the dye laser. (b) Fluorescence decay of a tetracene crystal with a magnetic field of $0.5T$ in the direction of the a-axis (off resonance). Excitation at 300 nm, observation at 546 nm, temperature: 62°C.
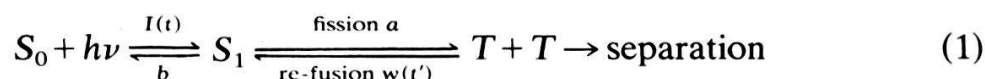
(iii) The tetracene single crystal, a sublimation flake, is mounted on a rotatable rod inside the poles of a small electromagnet, with the field in the crystallographic a, b-plane. The precise orientation of the crystal is determined from the known [1] resonance positions of the magnetic field effect on the steady-state fluorescence. For most of the experiments, the temperature was 62°C.

(iv) The experiment is controlled by a LSI11/23 computer, and the data (fluorescence decays) are stored on discs for further data handling.

3. Theory

3.1. The kinetic scheme of the singlet exciton fission

The exact description of the time evolution of the triplet pairs after its creation by a fission process leads to very complicated equations. We will thus use here a simplified description that is in line with the approach of Johnson and Merrifield [2] in their theory of fusion of triplets. The starting points is the following kinetic scheme:

$$S_0 + h\nu \underset{b}{\overset{I(t)}{\rightleftharpoons}} S_1 \underset{\text{re-fusion } w(t')}{\overset{\text{fission } a}{\rightleftharpoons}} T + T \rightarrow \text{separation} \tag{1}$$

A lightpulse $I(t)$ excites the singlet exciton S_1, which decays either radiatively (rate constant b, leading to the observed fluorescence) or by nonradiative fisson into a triplet pair (rate constant a). After the fission process, the triplets separate by diffusion and move through the crystal. Since the lifetime of triplet excitons in molecular crystals is in the millisecond range, they may meet again and even re-annihilate. After such a re-annihilation, the singlet can undergo fission again and the diffusion starts anew. To take this possibility into account, the re-annihilation rate in the reaction scheme (1) is denoted by $w(t')$, where t' is the time elapsed since the last fisson process. $w(t')$ contains all the dynamical information about the triplets. As can be seen from equation (1), it influences the fluorescence decay and will ultimately be determined from experiment.

$w(t')$ depends on the spin evolution of the pair as well as on its diffusion properties (e.g. the dimensionality of the exciton motion in the crystal). If we regard these two processes as independent, we can factorize $w(t')$:

$$w(t') = w_0 * s(t') * d(t') \tag{2}$$

where $s(t')$ depends only on the spin of the triplets and $d(t')$ only on the spacial position of the triplets at time t'. w_0 is proportional to the probability of annihilation if the two excitons are on neighbouring lattice sites. A coupling between the spin and the spatial motion would, to a first approximation, lead to a spin relaxation. Our experiments will show that spin relaxation rates are negligible on the time scale of the experiment and that equation (2) can be regarded as a good approximation.

3.2 *The spin evolution of a triplet pair*

The time evolution $s(t')$ of the spin of a triplet pair after its creation by a fission process has been treated by several authors [1, 4, 8], and all descriptions are based on Merrifields [2] theory. We will only recall the results in the two most interesting cases:

– zero magnetic field:

$$s(t') = (1/3) + (2/9) * (\cos(\omega_1 t') + \cos(\omega_2 t') + \cos(\omega_3 t'))   \quad (3)$$

where $(\omega_{1,2,3}/2\pi) = 2.97$, 1.86 and 1.12 GHz respectively.

– high magnetic field:

$$s(t') = (5/9) + (4/9) * \cos(\omega t')   \quad (4)$$

where ω depends only on the molecular data and the angle of the magnetic field with respect to the crystal axis, but not on the strength of the field. Rotation of the field in the a, b-plane results in a variation of $(\omega/2\pi)$ from zero (on resonance) to 2.10 GHz (off resonance, direction of the a' axis). $s(t')$ should thus exhibit quantum beats with frequencies that depend on the strength and direction of the applied magnetic field.

3.3 *Diffusion of triplet excitons*

The spatial motion of triplet excitons at room temperature is best described by a model of random hopping from site to site. The quantity that has the most direct influence on the kinetic of the exciton pair (i.e. on the function $d(t')$ in equation 2) is the dimensionality of the hopping process. Suna [3] has shown that a two-dimensional movement is a prerequisite for a large magnetic field effect on triplet exciton fusion. The same conclusion results from a fit of computer simulations of a two-dimensional random walk to our data. These calculations are presented in Section 5.

4. Results

Figure 2 shows two tetracene fluorescence decays, one for the magnetic field in off resonance direction (curve a, no detectable beats) and one with the field slightly shifted from the resonance direction (curve c, with pronounced beats). From such curves we find that beats are only observed, if the beat frequency is lower than 2 GHz, at higher frequencies the amplitude of the beats is strongly reduced. Note that this is not due to the time resolution of our measuring system, but a consequence of the repeated fission and fusion processes of the triplet pairs. The time spent in the S_1 state between fusion and subsequent fission processes tends to destroy the mutual spin coherence of different triplet pairs that has been established by the excitation process. For high beat frequencies, this time becomes comparable to a beat period and the phase-memory of the pair is lost. Also shown in Fig. 2(b) is the result of the model-calculation described in Section 4.

The time decay of the fluorescence is influenced, in fact dominated, by the
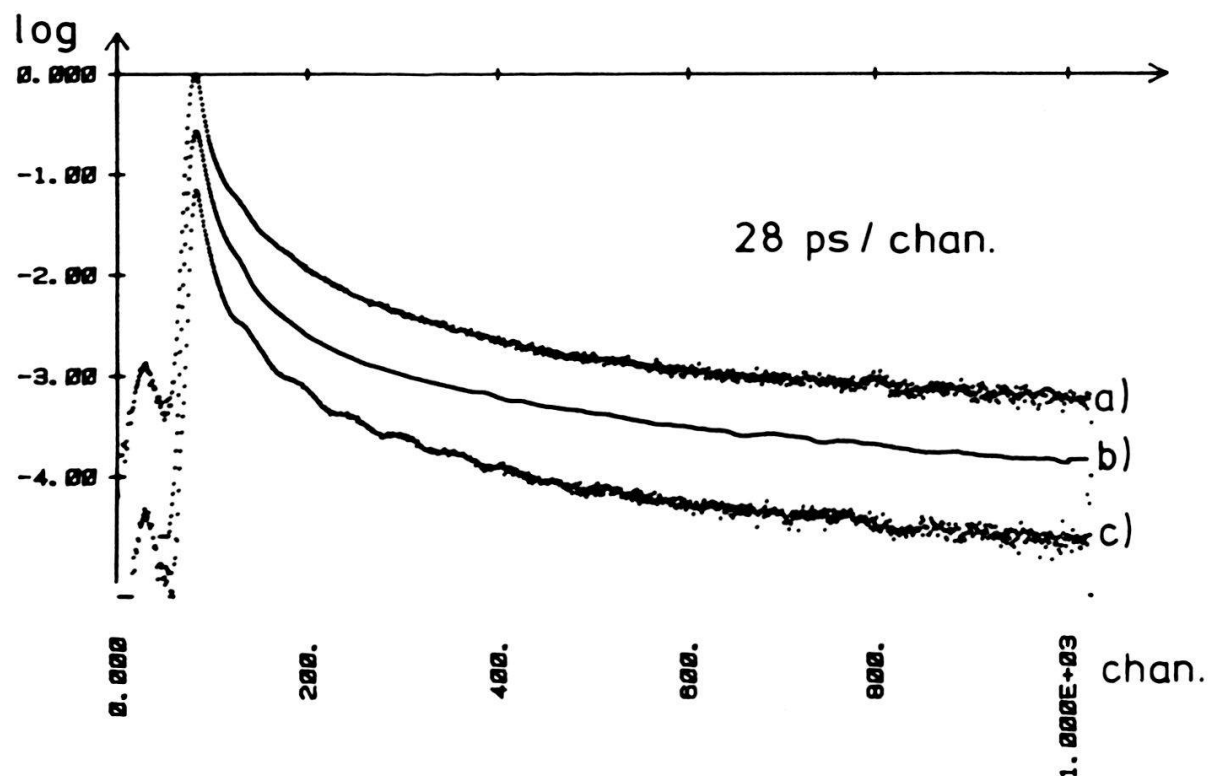
Figure 2
(a) and (c): Fluorescence decay of a tetracene crystal with a magnetic field of $0.5T$ in the a-direction (a) and 16° off the resonance direction (c). Excitation at 300 nm, observation at 546 nm, temperature: 62°C. Curve (b) is the fit to curve (a) with the parameters given in the text. The rms deviation between the two logarithms, calculated over the whole decay, is 0.05.
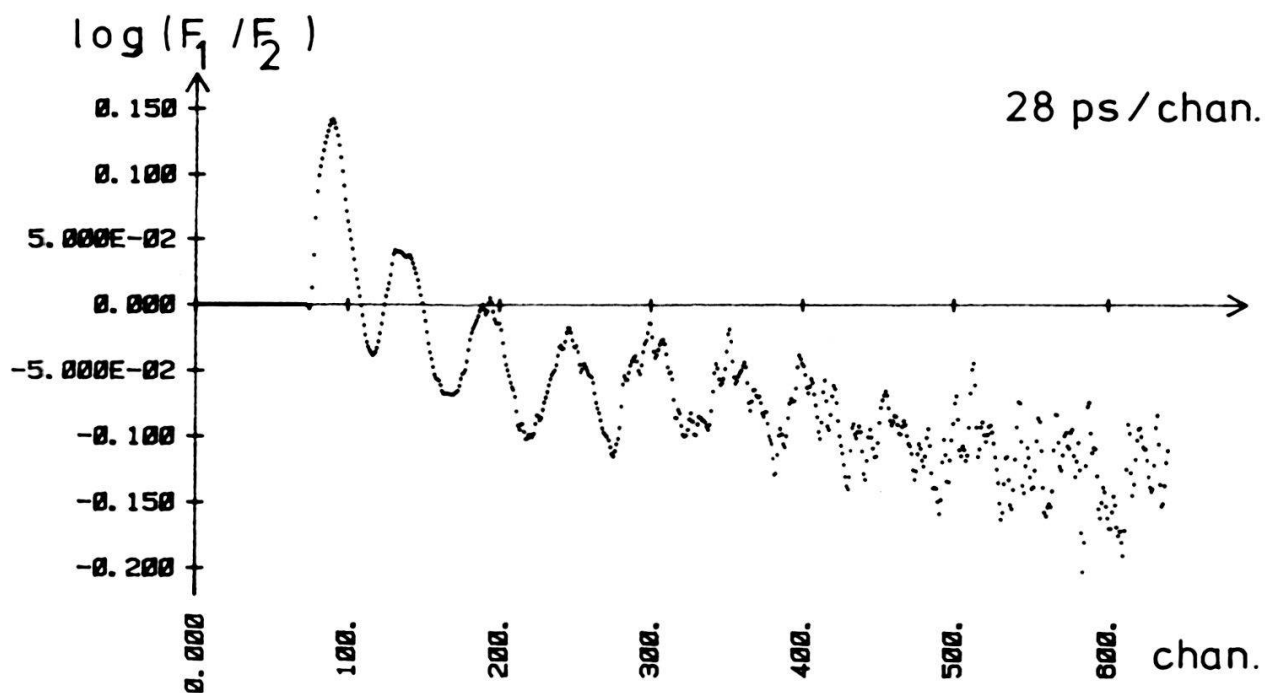

Figure 3
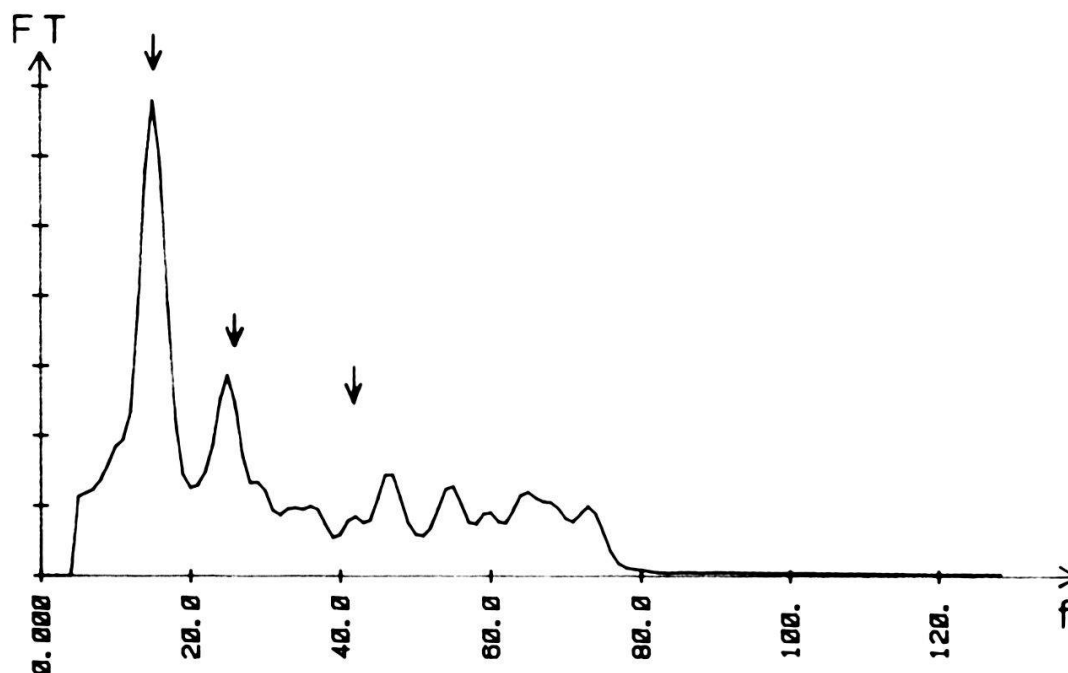Ratio of the decays of curve (c) and curve (a) of Fig. 2.

Figure 4

Fourier transform of a tetracene fluorescence decay with no applied magnetic field. Excitation at 300 nm, observation at 546 nm, temperature: 25°C. The frequency unit is 69 Mhz. The arrows indicate the theoretical beat frequencies calculated from the finestructure constants [1] of a free triplet exciton.

magnetic field independent exciton diffusion. The above beats are thus superimposed to the decay due to diffusion ($d(t')$ in equation 2), which is responsible for the non-exponential shape of the fluorescence decay. From the ratio between a measured decay with superimposed beats and a decay with unresolved beats we can eliminate the influence of the diffusion and study the decay of the beat signal itself. This is shown in Fig. 3. As can be seen, the beats disappear after about 15 ns in the noise, but their amplitude does not appreciably decrease during the whole decay period. This indicates, that spin relaxation processes can be neglected, and confirms the validity of equation 2.

Finally, Fig. 4 shows the Fourier-transform of a fluorescence decay in zero magnetic field. As can be seen, there are at least two beat frequencies present in the decay. These frequencies correspond well with the theoretical values (equation 3, indicated by arrows in Fig. 4). The highest frequency is buried in the noise.

5. Model calculations

Because of the term $w(t')$, which depends on the time t' elapsed since the last fission process, the kinetic scheme (1) has a very complicated structure. We therefore solve the rate equations that correspond to (1) numerically in two steps. First, we calculate with a computer experiment from a random walk model the probability $d(n)$ of a first encounter of the two excitons after n random steps. We use a two-dimensional square lattice and begin with the excitons sitting on neighbouring lattice sites. After one step, both excitons have equal probability of staying on its site or moving to one of the four next neighbours. An encounter is defined as a hop of the excitons onto the same lattice site. In a second step we

solve (1) by an iterative procedure:

$$S(n) = S(n-1)*(1-a-b) + \sum_{k=1}^{n-1} w(k)*P(n-1, k-1)$$

$$P(n, 0) = a*S(n-1)$$

$$P(n, k) = (1-w(k))*P(n-1, k-1) \quad \text{with} \quad k = 1, \ldots, n-1$$

using the starting conditions

$$S(0) = 1; \qquad P(0, 0) = 0$$

where $S(n)$ is the singlet density at step n, $P(n, k)$ is the density of triplet pairs at step n that are k steps old. $w(n)$ is the product of the return probability $d(n)$ and a quantum beat term of the form of equation (3) or (4) with $t' = n*t_0$, t_0 = hopping time.

The result of this procedure is a theoretical prediction for the impulse response of the fluorescence decay. After convolution with the experimental impulse-response we can compare it with the experimental data. We can then vary the three free parameters a, b and t_0 to get a best fit.

The most obvious experiment to fit is a fluorescence decay with the magnetic field in a off-resonance direction, since then the spin-dependent part of $w(n)$ is constant (=(5/9), equation (4); note that the beat frequency for this field is too large to be resolved). Using the above three parameters, a reasonable fit could be achieved. The introduction of a pair-lifetime (or out-of-plane hopping rate) greatly improved the quality of the fit, see Fig. 2. Our analysis of the fluorescence decay leads thus to a similar set of parameters as Suna's theory. The best parameters are, in units of 10^9 sec^{-1}: $a = 5.8$, $b = 0.032$, the in-plane hopping rate 13.1 and the out-of plane hopping rate 0.006. The two large values (hopping rate and fission rate) vary only slightly from fit to fit, the two smaller values are much more sensitive and may vary over a factor of 5.

In a next step, we turn on the beats, i.e. we allow for oscillations in $w(t')$ in the form of equations (2)–(4) with frequencies that can be calculated from the intensity and the direction of the applied magnetic field, so no new parameters are introduced. It turns out, that the predicted amplitude of the beats is about twice as large as the observed beats. No readjustments of the original four parameters could remove this discrepancy. A possible explanation for it is, that the crystal quality of our flakes is not perfect and contains distorted or twisted regions. An indication in this direction is the observation, that we could not reproduce the height of the resonances reported in the literature (we obtained a maximal magnetic field effect of 20% instead of 33%). Also, the amplitude of the beats varied slightly from sample to sample.

The rates for hopping, fission and fluorescence that result from our fit are model-dependent. If we choose a different hopping scheme, e.g. a statistical distribution of hopping times, we will get different hopping rates from a fit to the data. However, we can determine the triplet diffusion constant by a comparison of the long-time behaviour of a computer simulated diffusion, using our kinetic, with the result of a two-dimensional continuum diffusion model. This leads to a value for the diffusion constant D of $5.3 \times 10^{-5} \text{ cm}^2/\text{sec}$. This value, as well as the value for the hopping time, is a factor of 20 smaller than the values used by Klein [8] to fit data of Lopez-Delgado et al. [9], using a continuum model. However, he had to

fit data that were already a bi-exponential fit to the experimental data. Moreover, the time decay was measured only over 4 ns and with considerably less dynamic range than our data. From Figs. 1–3 it is easily seen that a bi-exponential fit for the first 4 ns will not accurately reproduce the whole decay.

Conclusion

The experiments have shown that the decay of the tetracene fluorescence is strongly nonexponential and has superimposed magnetic field dependent oscillations (quantum beats). The nonexponential decay is essentially due to the geminate re-fusion of triplet pairs generated by fission processes and the beats reflect the spin evolution of these pairs.

From the pattern of the beats, information on the dynamics of the spin evolution may be infered. From the nonexponential decay we can deduce quite detailed information on the triplet exciton motion in tetracene crystals: A two-dimensional random hopping yields an excellent fit to the data, especially if we allow for a small out-of-plane hopping rate. However, the deviation from pure two-dimensional motion turns out to be extremely small (0.0005). The hopping and fission rates deduced from the fit are 5.8 and 13.1×10^9/sec respectively.

In conclusion, we believe that the experiment presented, the direct observation of the spin and the spatial motion of the triplet excitons, is probably the most elegant and straightforward way to get insight into the dynamics of triplet exciton motion in molecular crystals.

Acknowledgement

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