

EXCITED STATE DYNAMICS IN PURE MOLECULAR CRYSTALS: PERYLENE AND THE EXCIMER PROBLEM

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Perylene excited state dynamics are examined using steady-state and time-resolved fluorescence spectroscopy as well as picosecond probe pulse and picosecond transient grating experiments. Relaxation of the initially prepared state into the excimer state is observed. The gerade Davydov components are approximately located. Measurements of excited state mobility at 298 K and 1.7 K are reported.

1. Introduction

Exciton states of pure molecular crystals arise from electronic excited state interactions between molecules arranged on a periodic lattice [1]. The interactions of excited states with the lattice make it necessary to consider the effect of the lattice degrees of freedom [1]. In the case that the exciton-phonon interactions are relatively weak, optical excitation results in an exciton clothed with phonons [2]. A band description is appropriate although the bandwidth is reduced from that of the bare exciton. Electronic excited state transport is accompanied by a lattice distortion associated with the phonon cloud. When the effect of the electronic excitation on the lattice is large, the lattice distortion can be sufficient to localize the excitation, i.e. the excitation is "self-trapped" [1,3]. A band picture is no longer appropriate although excited state transport may still occur via quasi-resonant interactions and phonon-induced level crossings [4].

Excimer formation is an extreme case of lattice distortion. Following excitation, a bound molecular pair can be formed if the lattice structure is appropriate [5]. Perylene molecular crystals, with four molecules per unit cell arranged as two molecular pairs, exhibit excimer formation [6,7]. Calculations indicate that upon excitation the change in intermolecular separation in a pair may be as great as 1 Å [8,9].

In this paper we present an experimental study of exciton and excimer dynamics in crystalline perylene. A variety of techniques were employed including time-dependent and steady-state fluorescence spectroscopy, picosecond probe pulse experiments and picosecond transient grating experiments [10,11]. The results presented below show that at room temperature excimers are relatively immobile, having a diffusion coefficient $D < 3 \times 10^{-3} \text{ cm}^2/\text{s}$. The two low-lying gerade Davydov components are approximately located. The relaxation of the initially prepared exciton state into the excimer is observed via time-dependent spectral changes. It is well-known that the excimer state moves to higher energy at low temperatures [6]. The low temperature state has been referred to as the "partially relaxed excimer" [9,12]. It is basically a self-trapped exciton arising from the ungerade Davydov components. Our picosecond experiments suggest that this state is mobile at 1.7 K. The gerade states are found to lie below this state and a rough estimate of their energy separation is a few tens of wavenumbers.

2. Experimental

Perylene (99%) was obtained from Aldrich and zone refined under argon for 200 passes. Material from the center sections of two zone refining tubes was combined and again zone refined. The purest material was used to grow crystals under vacuum by the Bridgman

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technique. By this method strain-free optically transparent samples approximately 2 mm X 2 mm X 1 mm could be obtained by cleaving along the ab plane.

Spectra were taken with a 1/2 m scanning monochromator and either an EMI 9658 photomultiplier or an RCA 1P28A photomultiplier for time resolved work. Time-resolved emission spectra were measured using a gated boxcar integrator. Fluorescence lifetimes were measured with a Tektronix R7912 transient digitizer interfaced to an on-line computer.

The pulsed excitation source was a high repetition rate, high power continuously pumped Nd:YAG laser which is acousto-optically *Q*-switched and mode-locked. The output consisted of single pulses at 200 Hz, 80 ps in duration, and 10^5 W peak power at 532 nm or 355 nm. The probe pulse experiments were conventional in nature. The transient grating method for measuring excited state mobility has been described recently [10]. A 100 W Hg arc lamp with an interference filter produced continuous radiation at 350 nm for steady-state fluorescence spectra.

3. Results and discussion

Fig. 1A displays room temperature perylene absorption spectra previously reported in the literature [13]. The observed polarization dependence is consistent with the symmetry assignments and state ordering reported for the four Davydov components. The absorption spectra in fig. 1A correspond to the two allowed ungerade Davydov states. Calculations indicate that the two gerade components should lie lower in energy and that their splitting should be less than the ungerade splitting [13]. Note that all of the intense absorption occurs to the blue of 500 nm.

Fig. 1B displays room temperature fluorescence spectra obtained using two different excitation sources. The evidence that this is excimer emission has been previously discussed [5-7], but briefly it is: (1) there is a large Stokes shift (1800 cm^{-1}) between the strong absorption and emission, (2) the emission is unstructured and very different from the absorption, (3) perylene excimer formation occurs in liquids, and (4) β -perylene crystals, which do not have paired molecules in the unit cell, exhibit exciton emission which is unshifted from the absorption [12]. The lower spectrum in fig. 1B was taken using an arc lamp filtered to excite

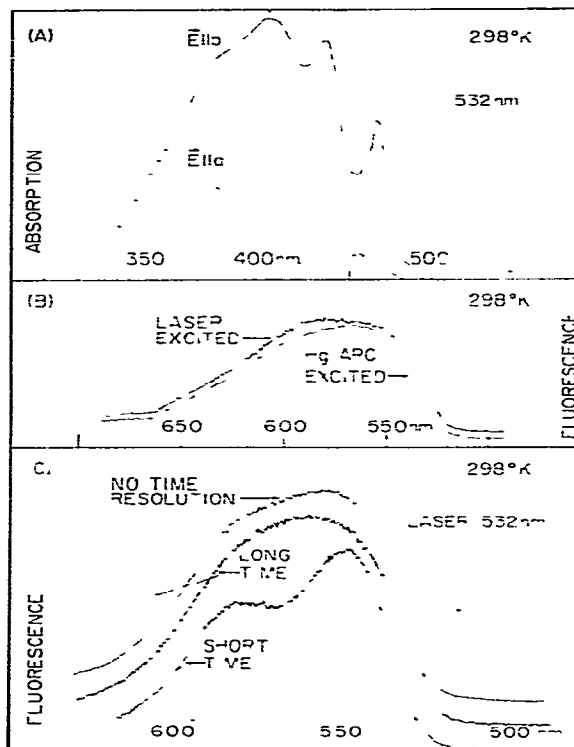


Fig. 1. Absorption and emission of perylene crystals at 298 K. (A) Absorption spectrum of the two allowed ungerade exciton states reproduced from ref. [13]. (B) Upper trace: fluorescence excited by picosecond pulses at 532 nm. Lower trace: arc lamp excitation at 350 nm. (C) Time resolved fluorescence following picosecond excitation at 532 nm.

the strong absorption (fig. 1A). The upper spectrum was obtained using the second harmonic of a mode-locked Nd:YAG laser at 532 nm for excitation. The two curves are virtually identical and characteristic of excimer emission. The important point is that laser excitation well to the red of the allowed absorption produces excimer emission. The absorption of the laser is *not* due to hot band absorption since it is undiminished at 1.7 K. Thus the laser is exciting a state distinct from the ungerade Davydov components.

In fig. 1C time-resolved fluorescence spectra are shown. These were taken with a gated boxcar integrator following excitation with an 80 ps, 532 nm pulse. The "short time" spectrum, which represents the state initially prepared by the laser, is substantially different from the long-lived ($\tau = 65$ ns) "long time" excimer

spectrum. The spectral change occurs in less than the several nanosecond time resolution of the boxcar. It demonstrates that the initially prepared state is distinct from the excimer state and that there is a rapid relaxation into the excimer.

The room temperature picosecond probe pulse results are shown in fig. 2A. For both excitation and probe, 532 nm, 80 ps pulses were used. Crystalline perylene is relatively weakly absorbing at 532 nm. The extinction coefficient is down 10^4 – 10^5 from the peak allowed absorption of the ungerade Davydov components. Thus the bulk of a thick crystal can be excited, avoiding the problems associated with thin crystals and surface effects. The probe pulse signal corresponds to a decrease in transmission upon excitation, i.e. the sample becomes more absorbing upon excitation. This

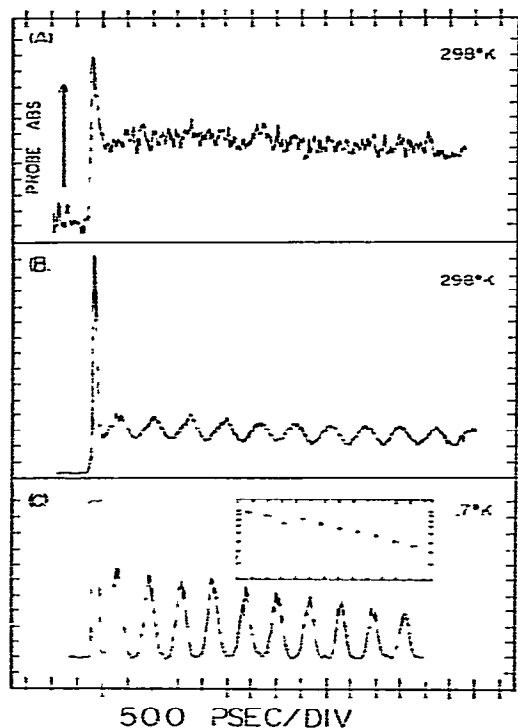


Fig. 2. (A) Time dependence of excited state–excited state absorption at 532 nm, 298 K, measured by picosecond probe pulse experiment. (B) Transient grating data at 298 K. Grating fringe spacing, 1.8 μm . (C) Transient grating data at 1.7 K, 1.8 μm fringe spacing. Excitation via two-photon absorption. Inset displays modulation peaks, yielding decay envelope.

is due to an allowed S_1 to S_4 excited state–excited state transition at 532 nm. The probe signal falls rapidly immediately after excitation and then within signal-to-noise appears flat for the remaining 8 ns. The rapid decrease is due to a decrease in excited state–excited state absorption*. It is reasonable to postulate that this change is associated with the time-dependent fluorescence spectral change and corresponds to the decay of the initially prepared state into the excimer state. The measurement is limited by the laser pulse duration. This places an upper bound of 30 ps on the relaxation of the initially prepared state into the excimer. The flat part of the probe signal is due to excimer absorption which is relatively constant on the time scale of this experiment.

The nature of the state initially prepared by the 532 nm excitation can be investigated by examining the temperature dependence of the fluorescent emission under relatively low intensity excitation conditions. (With high power excitation two-photon absorption populates the high-lying ungerade states. This is discussed below.) As the temperature is lowered (see fig. 3A) the spectrum develops more structure but otherwise remains unchanged. The spectrum at 1.7 K can be accurately assigned using the known perylene vibrational emission spectrum [15]. The principal progressions and combination bands can be identified. Thus the emission must arise from an excited state of perylene.

At 1.7 K excitation of the high-lying ungerade states using an arc lamp, a tripled Nd:YAG laser, a nitrogen laser [7], or a doubled ruby laser [16], results in the emission displayed in fig. 3B. It is significantly blue-shifted from the room temperature excimer emission also shown in fig. 3B. The state giving rise to this “blue” emission has been called a “partially relaxed excimer” [9,12]. At low temperature changes in crystal structure and loss of thermal activation energy prevent the formation of the excimer state [9,12]. At low temperature the state prepared with 532 nm laser excitation does not exhibit the room temperature time-dependent spectral change. It does not decay into the excimer since the partially relaxed excimer now lies high-

* The initial spike in the probe pulse data is *not* a coherence artifact which would appear as an increase in probe transmission [14]. This is clear because the probe pulse signal at all times corresponds to a *decrease* in transmission.

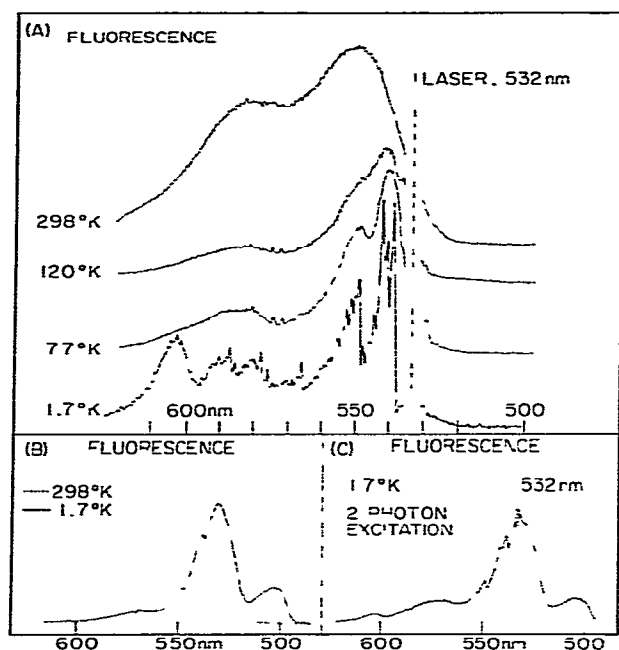


Fig. 3. (A) Temperature dependence of emission from one of the low-lying gerade exciton levels. (B) Fluorescence produced by arc lamp excitation at 350 nm. (C) Fluorescence following two-photon excitation at 532 nm. Excitation conditions are the same as for transient grating experiment (fig. 2C).

er in energy. Therefore it is reasonable to assign the state produced by the 532 nm excitation as a gerade Davydov component. For reasons discussed below it is the higher in energy of the two gerade states, i.e. the A_g state (see energy level diagram, fig. 4). Although this state is formally optically forbidden to the ground state, vibronic coupling can produce some oscillator strength. At room temperature, the crystalline perylene extinction coefficient at 532 nm is down four to five orders of magnitude from the peak ungerade absorption.

The gerade exciton emission spectra at 77 K and 1.7 K are strikingly similar, yet there is a major difference in the behavior of the system at the two temperatures. At 77 K the lifetime is > 50 ns. At 1.7 K the lifetime is subnanosecond. This suggests that there is a "dark" state immediately below the state initially excited. This may be the B_g Davydov component. The symmetry difference between this state and the A_g state can result in large differences in the vibronic coupling necessary to give oscillator strength to the transi-

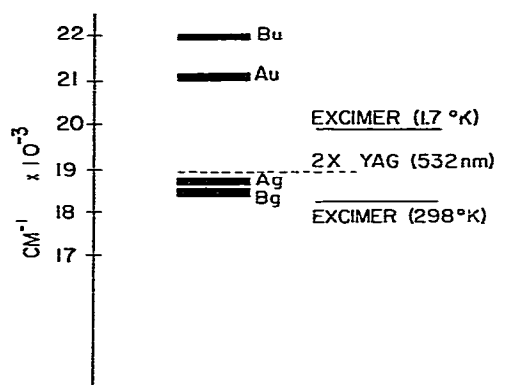


Fig. 4. Perylene energy level diagram. The wide bands indicate the energies of the four exciton Davydov components; the thin lines indicate the excimer energy at high and low temperatures.

tion. At 77 K the thermal distribution keeps both levels populated and decay of the fluorescence occurs with something like the average lifetime of the two levels. But at 1.7 K, the thermal distribution shifts the population into the lower dark level, and the fluorescence decays rapidly with the relaxation rate from A_g to B_g . If this model is correct it allows a very rough estimate of the A_g - B_g splitting to be put at a few tens of wavenumbers. This results in the states having populations on the same order at 77 K (≈ 50 cm^{-1}) but not at 1.7 K (≈ 1 cm^{-1}). The placement of the gerade Davydov components is shown in fig. 4.

The low temperature emission characteristics of perylene are unusual in that there are two distinct states which fluoresce. The "blue" emission arises from self-trapping of the ungerade Davydov states. Apparently this localized ungerade excitation is only weakly coupled to the lower lying gerade band states and decay to the ground state competes with relaxation into the gerade band states.

The transient grating experiment is sensitive to changes in the nature and population of the excited states as well as spatial transport of the excitations. The experiment involves two excitation beams crossed in the sample. Initially a spatially varying sinusoidal distribution of excited states is formed. The probe pulse is Bragg diffracted from this sinusoidal distribution of excitations. Excitation transport destroys the initial spatial distribution, reducing the intensity of the diffracted signal. Details of the transient grating

experiment and its application to excitation transport in molecular crystals are given elsewhere [10]. In the absence of transport, the transient grating signal will decay with twice the decay rate constant associated with the excited state lifetime. Transport increases the grating signal decay rate in a well-defined way.

As in the probe experiment, the room temperature transient grating data (fig. 2B) exhibits an initial rapid change corresponding to the relaxation of the initial state into the excimer. The oscillatory nature of the signal is due to the thermal production of acoustic waves probably arising from the phonons created upon relaxation into the excimer state. This phenomenon is well understood [10,11,17] and does not prevent analysis of the grating data. The signal-to-noise in the grating experiment is far superior to that of the probe experiment and thus permits the decay time to be measured. The decay of the grating signal appears to be slightly faster than the excimer excited state lifetime although this must be considered an estimate since the experiment covers only 16 ns of the 65 ns lifetime. Since excited state transport will increase the signal decay rate it is possible to place an upper bound on the room temperature excited state diffusion coefficient, i.e. $D < 3 \times 10^{-3} \text{ cm}^2/\text{s}$.

In fig. 2C the 1.7 K transient grating data is displayed. These experiments were performed using high power pulses producing two-photon excitation of the ungerade Davydov components. An emission spectrum taken using this high power excitation is shown in fig. 3C. Note that it is identical to that obtained with an arc lamp filtered to directly excite the ungerade levels (fig. 3B) although there is also some structured emission from the A_g state superimposed. This emission spectrum and comparison with low power grating data demonstrates that the fig. 2C data arises from the partially relaxed excimer except for the initial fast transient. Unlike the room temperature data (fig. 2B), after the initial fast change the low temperature data shows significant decay. Although the experiment covers only 8 ns, over this time span the decay of the data is exponential with an 8 ns lifetime. This is too fast to arise solely from the 35 ns lifetime of the partially relaxed excimer. The probe signal at this temperature is very weak but appears constant with time. The results are complicated by the acoustic modulation, but if the rapid decay of the transient grating signal is caused by transport then the partially relaxed excimer is mobile

at 1.7 K with a diffusion coefficient $D = 0.07 \text{ cm}^2/\text{s}$. It is important to recognize that the room temperature and low temperature diffusion coefficients arise from different self-trapped states of the crystal (excimer versus "partially relaxed excimer") and are therefore not directly comparable.

We are currently pursuing a number of experiments to enhance our understanding of excimer formation and the perylene system. These include tunable laser excitation experiments to more accurately locate the absorption origin of the gerade Davydov components, Kerr gate picosecond resolved fluorescence lifetime measurements to confirm the time scale of the evolution of the room temperature initially prepared state into the excimer state, and picosecond transient grating experiments using tunable wavelength excitation and probe to produce stronger signals and minimize the acoustic wave modulation, thus permitting a more detailed examination of excited state mobility.

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