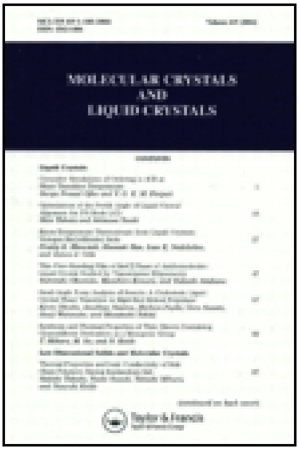

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PICOSECOND SPECTROSCOPIC STUDY OF EXCITON RELAXATION IN AROMATIC MOLECULAR CRYSTALS

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Abstract Transient luminescence which is attributed to optical transition from excitonic states to the ground states is studied, applying picosecond luminescence techniques to a pyrene crystal. The very fast decaytime (>4 ps) was observed at the shorter wavelengths than 0-0 luminescence band and the same decaytime component was included in the 400 nm-region of luminescence spectrum. A conclusion is drawn that rate of bypass process within free exciton band is larger at higher temperature than at lower temperatures. Transient luminescence emitted during excitons are sliding down on the adiabatic potential energy curve between self-trapping barrier and self-trapped state bottom was observed. Transient luminescence in an α-perylene is also briefly discussed.

1. INTRODUCTION

Self-trapping of excitons in solids has been the subject of great interest for many years. Excimers in organic solid was recognized experimentally as a sort of self-trapped excitons. Luminescence spectra and luminescence decay in pyrene crystals have been measured by many research groups for the study of electronic states and exciton relaxation processes. It was found that the free exciton luminescence decay of the order of 100 ns is equal to that of self-trapped exciton luminescence.[1] Based on this fact it was suggested that the free excitons and the self-trapped excitons are thermally equilibrium at room temperature. A few years later, a weak but faster decay of a few tens of picosecond time regime was found.[2] This faster component was caused by the radiative annihilation of free excitons which were thermallized at the bottom of the free exciton band immediately after introduced into a crystal. Excitons that reached the bottom of the free exciton band and thermallized there annihilate either radiatively or nonradiatively.

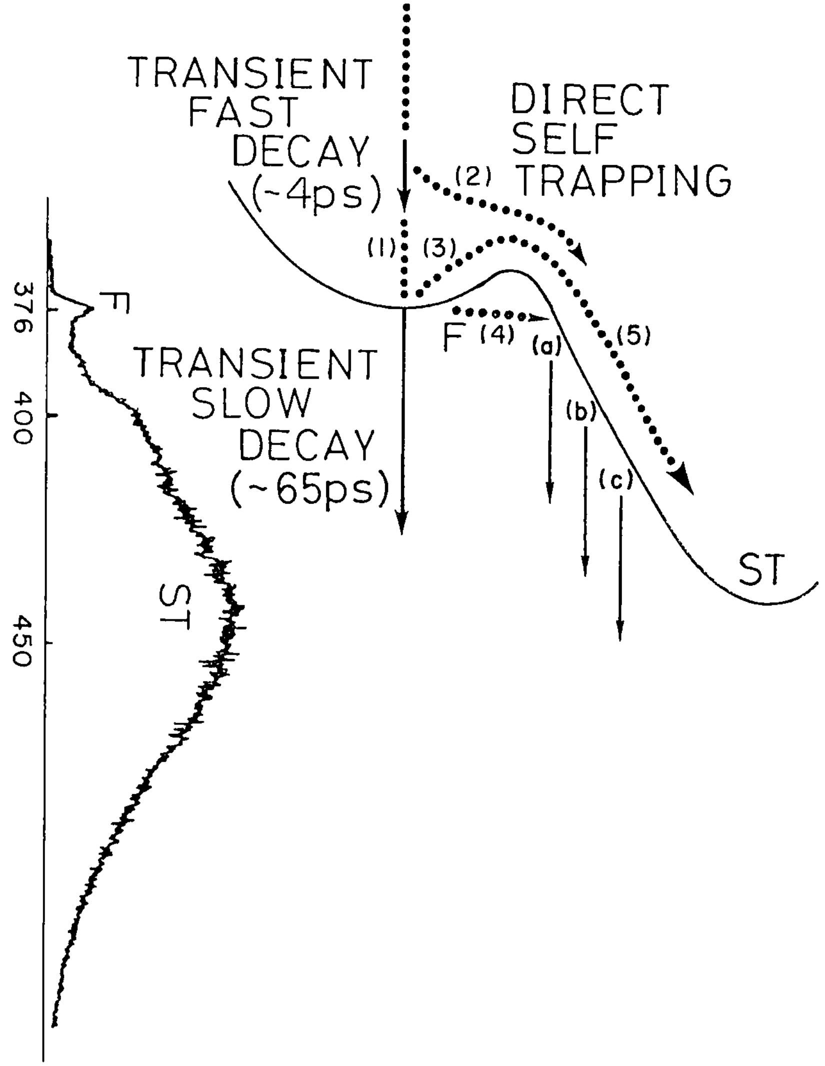

FIGURE 1. Exciton relaxation paths shown schematically on the adiabatic potential energy curve for pyrene at 140 K.

The luminescence spectrum at room temperature is shown as a reference. The letter F shows the free exciton band bottom and the letter ST shows the self-trapped state.

The adiabatic potential energy curve of the excited state is shown in FIGURE 1 to explain clearly about exciton relaxation paths. The integrated luminescence spectrum at room temperature is shown as reference. The letters F and ST on the spectrum denote free exciton and self-trapped exciton luminescence bands, respectively. Exciton relaxation paths are indicated by dotted lines. Excitons produced optically in the exciton band go down toward the exciton band bottom F.(process (1) in FIGURE 1) Excitons that reached the band bottom (F in FIGURE 1) annihilate radiatively or nonradiatively. Luminescence is shown by vertical solid lines with arrows. The free exciton luminescence intensity due to the exciton going through process (1) was, however, too weak compared to the expected intensity in a low temperature phase pyrene crystal.^{3} From this fact, it was suggested that most of the optically produced excitons relaxed directly to the self-trapped state without going through the free exciton band bottom.(process (2) in FIGURE 1) Some of the excitons, which are surmounted over (process(3)), or tunneled through (process (4)) the self-trapping barrier via the process (1), or directly relaxed in process(2), arrive at the place near the exit of the tunnel of the self-trapping barrier, and then slide down on the slope of the adiabatic potential energy curve toward the bottom of the self-trapped state.(process (5)) When excitons are sliding down on the slope, part of the excitons annihilate radiatively. Optical transitions denoted by solid vertical lines are those which we will discuss in this report.

In FIGURE 1, the branched-off process (process (2)) is shown as direct self trapping. Process (5) is shown as transient ST. In this report the exciton relaxation processes (1)-(5) will be discussed in a high temperature phase pyrene crystal and briefly in an α-perylene crystal.

2.EXPERIMENTAL

Commercial pyrene was highly purified by extensive zone refining. Single crystals with well developed ab faces were grown with a sublimation method, and were obtained with typical size of 3 mm(a-axis) x 1 mm(b-axis) x 3 μm(c-axis). Time correlated single photon counting techniques were applied to measure luminescence decay by using a measurement system similar to that reported by Yamazaki et al[4]. Our experimental time resolution is about 4 ps. Measurements at reduced temperatures were performed with a variable temperature, by a gas flow cryostat[5].

3.RESULTS AND DISCUSSION

3-A PYRENE CRYSTALS

3-A-1 Exciton Relaxation Paths within the Free Exciton Band

Luminescence decay was monitored at several wavelengths under excitation of constant light intensity at 140 K. Two decay components appeared in the transient luminescence.(the fast component<4ps, the slow component~65ps) We will refer the fast decay luminescence as transient fast luminescence (in FIGURE 1, a short solid line). The fast decay component (~4 ps) is found in the wavelength ranges shorter than 374.5 nm or longer than 376.5 nm, but it is not included for luminescence monitored in the wavelength range between 374.5 and 376.5 nm. At shorter wavelengths than 370.5 nm, only the fast decay component was found.

We will discuss the origins of the fast and slow decay components. In a pyrene crystal the exciton annihilation probability within the free exciton band is described as a sum of the vibrational relaxation probability toward the free exciton band bottom and the nonradiative annihilation probability to the self-trapped exciton states. The vibrational relaxation time in solids is generally fast, say 10^{-12} s. The fast decay we observed was less than a few picoseconds. Therefore it is evident that the fast decay corresponds to the life time of excitons that are relaxing within the free exciton band.(process(1))

The slow component of about 65 ps is too slow to attribute it to the exciton relaxation time within the free exciton band. This decay was close to the rise of the self-trapped exciton luminescence of about 73 ps at 140 K. We suggest that the decay time of about 65 ps is attributed to the exciton surmounting time over the self-trapping barrier (process (3)) and to tunneling time through the self-trapping barrier (process(4)). In order to investigate the bypass process within the free exciton band, the decaytime was measured by monitoring the luminescence at 400 nm. The 400-nm luminescence is expected to be attributed to the transition from the place near the exit of the tunnel in the self-trapping barrier ((a) in FIGURE 1) to the ground state on the adiabatic potential energy curve. The fast component (<4ps) of the decaytime was observed over the temperature range from 140 to 250 K by monitoring the 400 nm-luminescence. The 400 nm-luminescence may include the side band of the free-exciton luminescence. However the side band does not have the fast component, because the resonance free exciton luminescence (376 nm) did not include the fast component as mentioned above. The fact, that the 400 nm-luminescence has the fast decay component, means that the photo-induced excitons within free exciton band directly relax to the self-trapped state without passing through the bottom of the free exciton band (process (2)). Thus in a high temperature phase pyrene crystal, there are two paths for exciton relaxation within the free exciton band at above 140 K.

3-A-2 Direct Exciton Relaxation Rate within the Free Exciton Band

In order to estimate direct exciton relaxation rate, luminescence intensity for the each decay component of 400 nm-luminescence is investigated at several temperatures. Below 200 K the 400 nm-luminescence has two decay components. One can estimate separately individual luminescence intensity by calculating a product of the corresponding amplitude and decaytime. At 200 K, the direct relaxation rate is about 37 % of all amount of 400 nm-transient luminescence intensity. The rate decreased with decreasing temperature (13 % at 140 K).

Presence of this direct relaxation process in a high temperature phase pyrene crystal is consistent with the report[3] in the low temperature phase of a pyrene crystal that branching of exciton relaxation paths occurred within the free exciton band.

Our result is in good agreement with the theoretical work of Ioselevich and Rashba which demonstrated the presence of the direct exciton self-trapping and the rate decreases with decreasing temperature.[6] Also, Abe[7] suggested that a direct relaxation process occurs. Since his theory is applicable to 0-K crystal and our

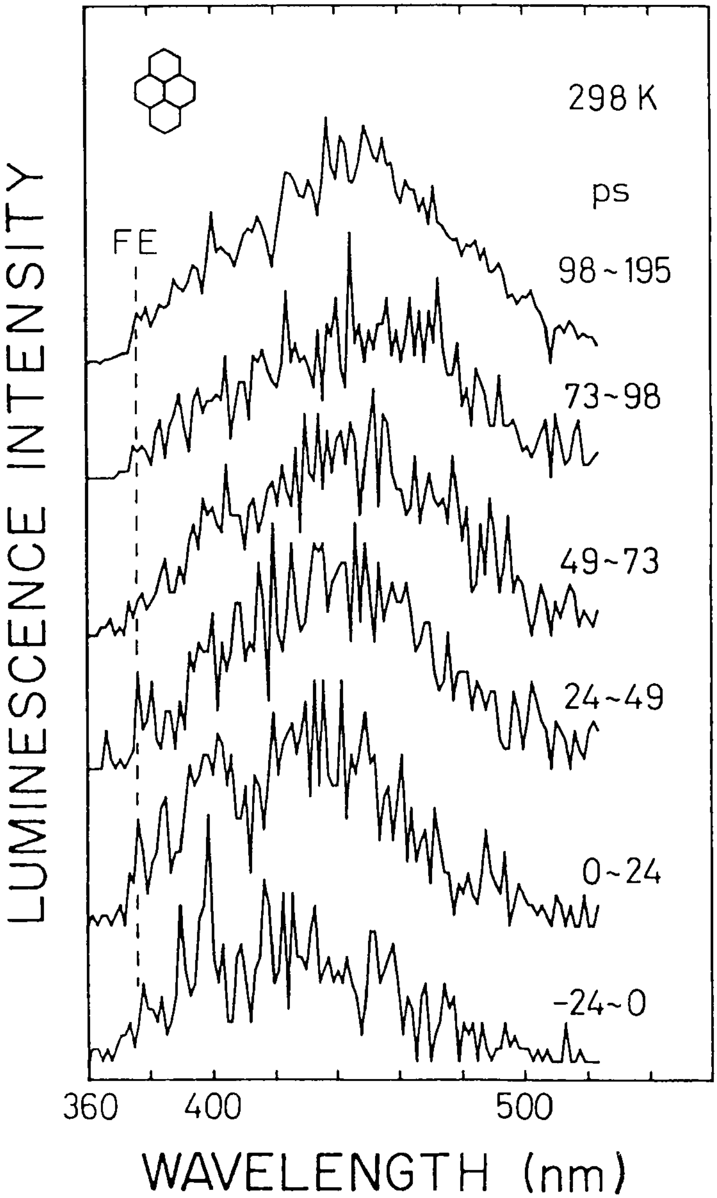

FIGURE 2. Time resolved luminescence spectra of a pyrene crystal at room temperature. The letter FE shows 0-0 peak position of free exciton absorption band.

experiments were performed at 140 K, direct comparison is not appropriate but our result is compatible with his theoretical result.

3-A-3 Luminescence due to the Excitons Sliding Down on the Adiabatic Potential Energy Curve

Excitons, sliding down on the adiabatic potential energy curve from the place near the exit of the tunnel of the self-trapping barrier to the bottom of the self-trapped state, can emit radiation of about 400-450 nm. In such a case the center of luminescence band should shift with time. FIGURE 2 shows time resolved luminescence spectra in a pyrene crystal at 298 K. *In this figure the time is taken to be zero* at the time when the intensity of the excitation light pulse becomes maximum. The peak position of luminescence spectrum are gradually shifting to red with time. These spectra shows the process that the excitons are sliding down on the adiabatic potential energy curve (process (5) in FIGURE 1).

3-B α-PERYLENE CRYSTALS

Picosecond spectroscopy was applied also to an α-perylene crystal in order to check the physics which appeared in a pyrene crystals, because an α-perylene crystal has similar physical properties to a pyrene crystal, an α-perylene crystal has dimeric structure in which one lattice site is occupied by two molecules, and belongs to the strong exciton-phonon coupling system. Therefore both crystals are described by a similar adiabatic potential energy curves. Wavelength dependence on decaytime of the luminescence was measured at 140 K. The decaytime of the transient free-exciton luminescence is composed of only a fast component (>4 ps). The fast decay component of the free-exciton luminescence are independent with crystal temperature. The luminescence spectrum for fast decay component peaks at 480 nm which corresponds to the 0-0 peak in the free-exciton absorption spectrum. These two facts means that the excitons which are photo-induced within free-exciton band go through the band bottom and then quickly relax to the self-trapped exciton state because the self-trapping barrier is very low in height or very thin in width. The self-trapping barrier height in an α-perylene crystal is quite different from that in a pyrene crystal. Transient ST luminescence was also observed in the time resolved luminescence spectra of an α-perylene crystal as same as in a pyrene crystal. Thus process (5) occurs independently on the height or on the width of the self-trapping barrier.

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