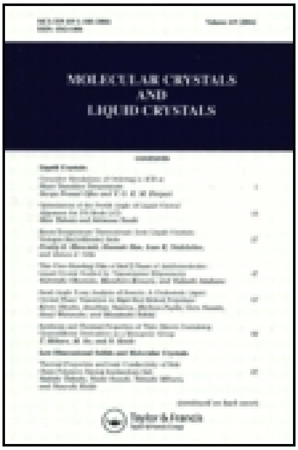

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Photophysical Study of Frenkel Exciton States Using a Novel Microcrystallization Technique

A. H. Matsui [a]

[a] Department of Physics, Konan University, Okamoto, Kobe 658, JAPAN

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Photophysical Study of Frenkel Exciton States Using a Novel Microcrystallization Technique

A.H. Matsui

Department of Physics, Konan University, Okamoto, Kobe 658, JAPAN

A method determining the exciton bandwidth in aromatic microcrystallites is presented, and the behavior of Frenkel excitons in these substances is reviewed. The spectral bandwidth of excitation spectra of luminescence from microcrystallites is found to increase linearly with the microcrystallite size in anthracene and superlinearly in pyrene. A strong exciton scattering component at microcrystallite surfaces is found in anthracene microcrystallites. The k selection rule that is lost in small microcrystallites is recovered for large microcrystallites at a size of 134 Å in anthracene and 50 Å in pyrene. With these values, the surface scattering layer thickness is estimated to be 32 Å in anthracene, but nearly zero in pyrene microcrystallites. We suggest that the concept of the exciton migration in microcrystallites can be applied to biological systems where only 5 ~ 10 molecules are arranged.

Keywords: exciton; bandwidth; aromatic crystal

INTRODUCTION

The exciton bandwidth is one of the very important parameters in studying Frenkel excitons in aromatic materials. In such solids, the excitonic processes basically depend on four parameters, exciton bandwidth, molecular vibration energies, lattice phonon energies, and thermal energy. Among these parameters, the exciton bandwidth has been less studied involved in its measurements, because of experimental difficulties involved in its measurements, though several experiments have been done [1,2], and theoretical attempts have also made [3-6]. However, no measurements of the exciton bandwidth have been made at low temperatures. Only recently a technique to determine the exciton bandwidth at low temperatures has been developed [7,8].

Due to the exciton confinement in small microcrystallites, the wavevector selection rule (Δ k=0 selection rule) does not hold and the optical transition occurs from the ground state to all the energy levels which lie within the exciton band range corresponding to the k=0 component. Therefore, in microcrystallites one obtains the optical absorption spectrum which expands over the entire exciton band. The exciton bandwidth is, therefore, obtained as the optical absorption bandwidth of the microcrystallite. The bulk exciton bandwidth can be obtained, as the upper bound of the spectral bandwidth in microcrystallites.

EXCITONIC STATES AND OPTICAL TRANSITIONS

Figure 1 illustrates excitonic states in microcrystallites together with that of a bulk crystal. The diagrams are assumed to be applicable for pyrene crystallites which are the direct material, but basically they are applicable for any aromatic crystallites. Thus the exciton band bottom is located at k=0. At the right of the diagram (Fig. 1) is shown the excitonic state in bulk crystals (crystallite of an infinite size). The optical transition from the ground state occurs only to the band bottom which is located at k=0 because of the k selection rule. The optical transition is indicated as an upward solid arrow. The absorption spectrum, therefore, appears as a sharp line as indicated on the left hand side, and does not give a direct information of the whole exciton band (2B) for bulk crystal. Even in a crystallite whose size is as

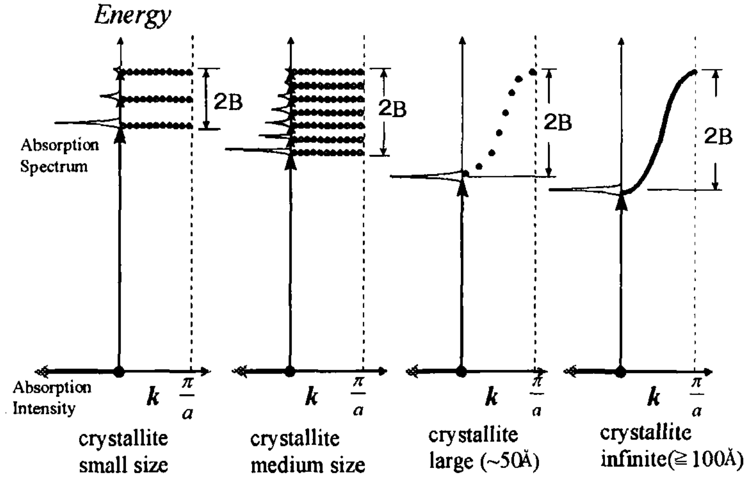


Fig. 1 The excitonic states in small and large crystallites. The wave vector k is taken to be 0 to π/a, where a is the lattice constant. On the left of each diagram the absorption spectrum is shown schematically. The energy separation between the ground state and the bottom of the exciton band decreases with increasing microcrystallite size. This decrease is caused due to the increase in the site shift energy and loosening in the confinement effect.

small as 50Å in diameter, the wavevector k can still be regarded as a good quantum number and the optical transition occurs to the exciton band bottom only. However, in such crystallites, k does not take continuous values but only discrete values, because only a few (6~8) molecules are constituents along each crystallographic direction.

In much smaller crystallites (medium size) the wavevector k is not a good quantum number and excitons are confined as standing waves. The excitonic states are shown in the second diagram from the left end. The optical transition from the ground state occurs to all the states in the exciton band, and the absorption spectrum appears as discrete lines. For such crystallites the term "exciton band" has got no more practical meaning, because only discrete levels exist. However, the term "exciton band" is used only for convenience even for very small crystallites. Since the energy levels are discrete, one does not observe a broad absorption band. The exciton bandwidth (2B) is obtained as the top-to-bottom energy separation. In practical spectra, however, one finds a broad band as the envelope of sharp lines except in the case where the spectra were measured at a high resolution.

PARTICLE SIZE AND THE 0-0 ABSORPTION ENERGY

Anthracene (or pyrene) and poly-methylmethacrylate (PMMA) were dissolved separately in toluene, and then these two solutions were mixed. The mixed solution was dried on a Petero dish in air under dark. The particle size was determined using an electron microscope image technique. The size of microcrystallites is found to follow a Gaussian function and so is the distribution of their 0-0 absorption bands. As both distributions are Gaussian, the energy of the 0-0 absorption peak for a specific particle size can be determined from one-to-one correspondence between the two curves. Fig. 2 shows the size distribution of anthracene crystallites and the 0-0 absorption bands of crystallite specimens. A similar diagram is obtained for pyrene microcrystallites. In Fig. 3, the absorption spectrum of an anthracene crystallite specimen is drawn as it can be compared easily with the size distribution curve.

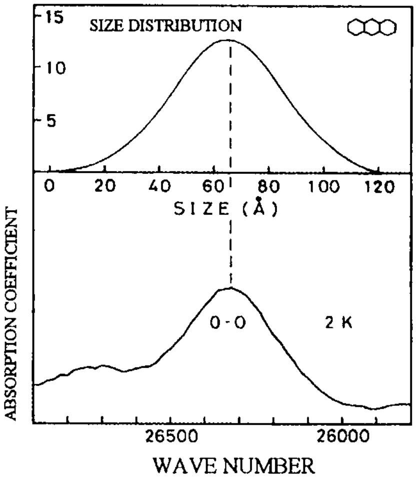


Fig. 2 The size distribution of anthracene microcrystallites (top diagram), which is compared with the 0-0 absorption band of the anthracene specimen dispersed in PMMA.

RESULTS AND DISCUSSION

Excitation Spectra

Fig. 3 shows the excitation spectra of crystallites with various sizes. In order to find the exciton bandwidth, we have measured excitation spectra of microcrystallites instead of measuring absorption spectra, because latter inevitably involves absorption spectra of various size crystallites. The excitation spectrum is size selective. As the luminescence originates from the exciton band bottom of respective crystallite, the luminescence photon energy differs in different crystallite sizes. The lowest energy edge of the exciton band shifts towards red with increasing size due to the site shift effect and loosening exciton confinement effect. The observed excitation spectrum consists of a sharp line at the band bottom energy and a tail on the high energy side of it as shown in Fig. 3.

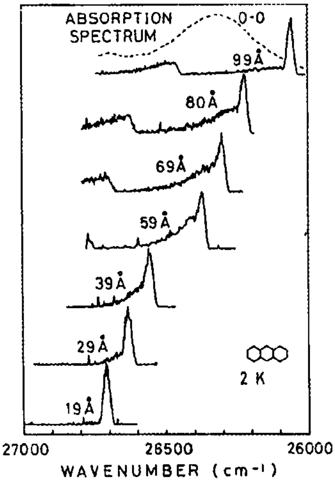
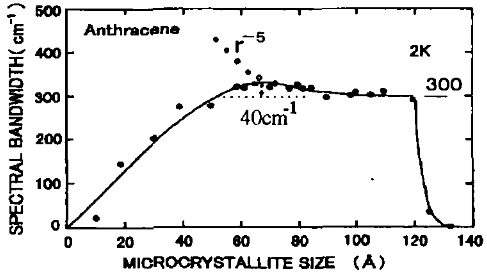


Fig. 3 Excitation spectra of crystallites with various sizes.

Exciton Surface Scattering

In order to obtain the exciton bandwidth, we have measured the excitation spectral width as a function of the particle size. Fig. 4 shows the spectral bandwidths (2B) thus obtained in anthracene and pyrene. Both diagrams are similar but differ in several important points. Let us discuss the exciton bandwidth of anthracene first. The bandwidth increases up to



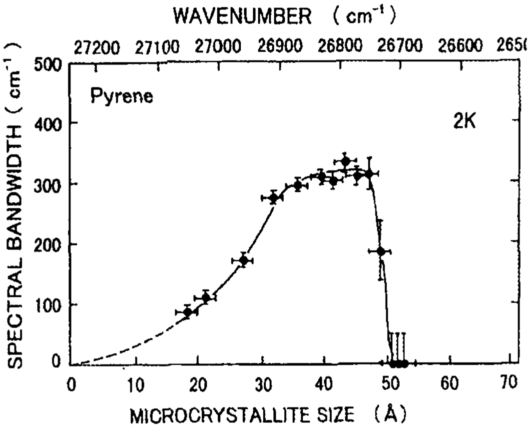


Fig.4 Observed spectral bandwidth 2B plotted as a function of the crystallite size. Top diagram is for anthracene crystallites and the bottom one for pyrene crystallites.

the maximum value 340cm^{-1} and then it decreases asymptotically toward 300cm^{-1}. The bulk exciton bandwidth is thus found to be about 300cm^{-1}. The excess bandwidth of 40 cm^{-1} has been interpreted to be due to the exciton surface scattering [7]. In the region where r is smaller than about 80 Å, the bandwidth 2B is proportional to r^{-5}, where r is the crystallite size. If the excess bandwidth is caused by merely the surface effect, then a change as large as r^{-5} would not occur, and it would only be proportional to r^{-1}, as the ratio of the surface area to the volume. The cause however, has not be clarified. In pyrene crystallites, the surface exciton scattering is expected to be very small. Any excess increase in the bandwidth, as found in anthracene microcrystallites, was not observed in pyrene microcrystallites.

Scattering Layer Thickness in Pyrene and Anthracene

We will discuss the layer thickness of the exciton surface scattering. In order to find such thickness, we discuss the critical size over which excitons show practically bulk crystal behavior. In Fig. 4, the observed bandwidth for pyrene crystallites appears to be zero for the crystallite size over 50 Å. This means that the wave vector k is a good quantum number and excitons propagate as if they are in a bulk crystal. This criterion for wave-like exciton behavior is substantiated by the dipole sum calculation. The dipole sum calculated for pyrene crystal approaches asymptotically to a constant value at the crystallite size of about 50Å [9]. This minimal size giving bulk crystal behavior agrees quite well numerically with the critical size (50Å) that we have shown in Fig. 3.

However, in anthracene crystallites the situation is different. The critical size in the k=0 selection rule was 134 Å as shown in Fig. 4, while the minimal size found in the dipole sum is 70 Å [10]. This discrepancy is explained reasonably well by the presence of the exciton surface scattering layer of thickness (134-70) Å /2 = 32Å.

The presence of the surface layer is illustrated schematically in Fig. 5. The suggestion that there is a surface scattering layer in anthracene crystallites is consistent with the presence of the bandwidth increase of 40 cm^{-1}. We can conclusively say that the presence of the exciton surface scattering layer of 30Å is the cause, of the additional bandwidth of about 40 cm^{-1}. When electric dipoles are located at a crystallite surface, the electric field due to the charges may penetrate into the crystallite by 30 Å.

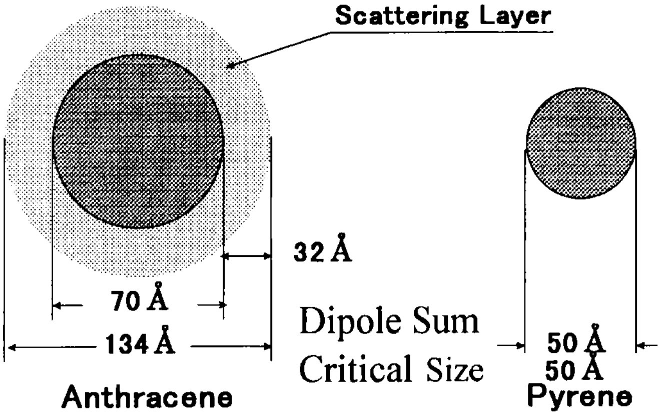


Fig. 5 Schematic diagrams in anthracene, showing the presence of a surface exciton scattering layer, which does not exist in pyrene crystallites.

In pyrene, the surface layer thickness is negligible since the critical size is exactly equal to the theoretical minimal size as discussed above. The absence of the surface exciton scattering layer in pyrene microcrystallites is consistent with the fact that we did not find any excess increase in the spectral bandwidth which could be attributed to surface exciton scattering.

4. 1D Model Calculation

The presence of a sharp line followed by a tail in the excitation spectrum which are demonstrated in Fig. 3 has been reproduced using one dimensional (1D) model [11]. An example of the calculated results is shown in Fig. 6. A sharp line followed by an approximately exponential tail which should be compared with diagrams in Fig. 3, is clearly seen. The excitation spectra of pyrene microcrystallites are also composed of the sharp line and an exponential tail, and reproduced by the 1D model calculation.

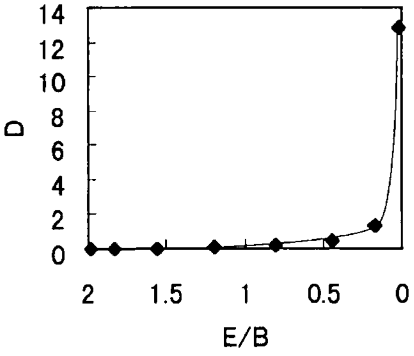


Fig. 6. Calculated optical transition rate D for 1D crystallites with 16 molecules. The abscissa is normalized with 2.

The fact that 1D model explains observed excitation spectrum (absorption spectrum) well suggests that exciton behavior is of high anisotropy in aromatic materials [12]. However, it fails to explain the Davydov splitting, which is not negligible. In fact sometimes it is quite large, for instance, in bulk anthracene it is as large as the exciton bandwidth. Nevertheless, the excitation spectra of anthracene microcrystallites are well reproduced by 1D model calculation. This implies that the optical transition rate to one specific polarized component is large in anthracene. In fact, the optical transition rate to the ac-polarized

Davydov component in anthracene is extremely small compared to the b-polarized component. In contrast to the case in anthracene, the Davydov splitting of the lowest exciton band in pyrene bulk crystal is very small. Therefore, in discussing the applicability of the 1D model to pyrene we can forget about the Davydov splitting. Since the 1D model explain the excitation spectral shape of pyrene microcrystallites satisfactorily, as we mentioned above, the 1D model is possibly applicable to both pyrene microcrystallites and bulk pyrene crystal. The present results suggest that the exciton in pyrene provides a good example to which the 1D model is applicable.

Remarks

The wavevector k is a good quantum number at the critical size of 50 Å in pyrene and 75 Å in anthracene. This means that the exciton propagates as a wave in the crystallites whose size is only 6 lattices in length in pyrene and only 12 lattices in anthracene, if the dominant exciton propagation direction is assumed to be the shortest crystal lattice. The concept of the exciton migration is, therefore, applicable to the crystallites of that size. Since in biological systems such small molecular arrangements do exist, most of the energy transfer problems in biological systems may need to be analyzed using the concept of excitons.

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