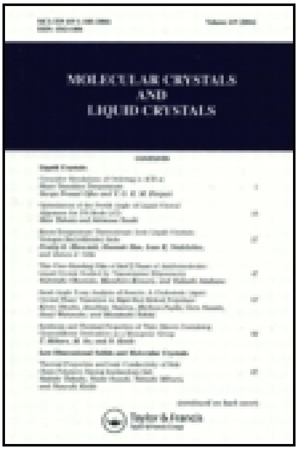

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Homogeneous and Inhomogeneous Triplet Exciton Absorption Lines in Molecular Crystals

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Triplet exciton absorption lines in pure anthracene and pyrene crystals are investigated at very high resolution using photoexcitation in the lower temperature (<90 K) regime. The profiles for the lower Davydov components (zero-phonon) are observed to be most sensitive to crystal quality. Linewidths as small as 0.02 cm^{-1} are observed for the lowest exciton of anthracene with the upper component about 50 times broader. The T-dependences of the linewidths for the Davydov components of anthracene are shown to be explicable in terms of combined linear and quadratic exciton-photon coupling. The T-dependence of the zero-phonon to phonon sideband intensity ratio for pyrene is well described by the linear exciton-photon interaction in which the exciton is taken to be localized.

1 INTRODUCTION

For the study of weakly absorbing triplet states in organic molecular crystals photoexcitation spectroscopy with a tunable dye laser has been shown to be appropriate optical method. Preliminary investigations on anthracene, naphthalene and pyrene[1,2,3,4] have characterized the vibronic structure in the triplet excitation spectra, the excitonic line shape behavior and its temperature dependence between 2 K and 300 K.

The purpose of this work was to obtain more precise data on the low temperature line broadening effects (below 90 K), and as a result an improved understanding of exciton-phonon coupling processes. The role of structural properties of the organic solid, with respect to both the molecular packing and the crystal quality, influencing the optical lineshapes is also of primary interest.

In this paper data for anthracene and pyrene crystals are compared. Both possess monoclinic unit cells, containing two and four molecules, respectively.[5,6] In addition both represent prototype crystals for monomeric and dimeric (sandwich type) molecular configurations, respectively.

2 EXPERIMENTAL

Highly purified ingots have been used to prepare crystal samples of both anthracene and pyrene by different crystal growth methods: Bridgman or sublimation under inert gas atmosphere. The narrowest triplet exciton linewidths (section 3) have been observed with sublimation flakes developed in the ab-plane, typically 0.05 ÷ 0.1 mm thick.

The samples were cooled in helium gas in a variable temperature cryostat. Special care has been taken to minimize strain effects during the cooling cycle. By extremely slow cooling of sublimed pyrene crystals through the crystal phase transition the usual cracking of the crystal[7] was avoided. Thin samples were loosely held between paper masks.

The photoexcitation method with tunable CW dye laser described previously[1] was improved and used in two modes of operation: very high resolution of better than 0.001 cm^{-1} and high resolution of about 0, 1 cm^{-1}, necessary typically for anthracene zerophonon line studies below and above 25 K, respectively (see section 3). The experimental spectra shown below give the relative triplet absorption intensities on a linear scale as measured indirectly via phosphorescence or delayed fluorescence.

The excitation spectra presented concentrate on the pure electronic 0. 0 transition of the lowest triplet excitonic state T_1, lying at about 14,749 cm^{-1} and 16,776 cm^{-1} for anthracene and pyrene, respectively (4.2 K).

3 EXPERIMENTAL RESULTS

3.1 Low temperature lineshapes

The 0. 0 region of a typical excitation spectrum at 4.2 K is given in Figure 1a and Figure 1b for anthracene and pyrene, respectively. In both cases two zerophonon Davydov components (hereafter referred to as the upper and lower components) are accompanied on their high energy side by structured phonon sidebands. The energy scales in the two spectra are different. In the pyrene spectrum the zerophonon lines are not fully resolved being only 1.9 cm^{-1} apart compared to 21.6 cm^{-1} for anthracene, and for the former the sideband maxima are concentrated at lower energies.

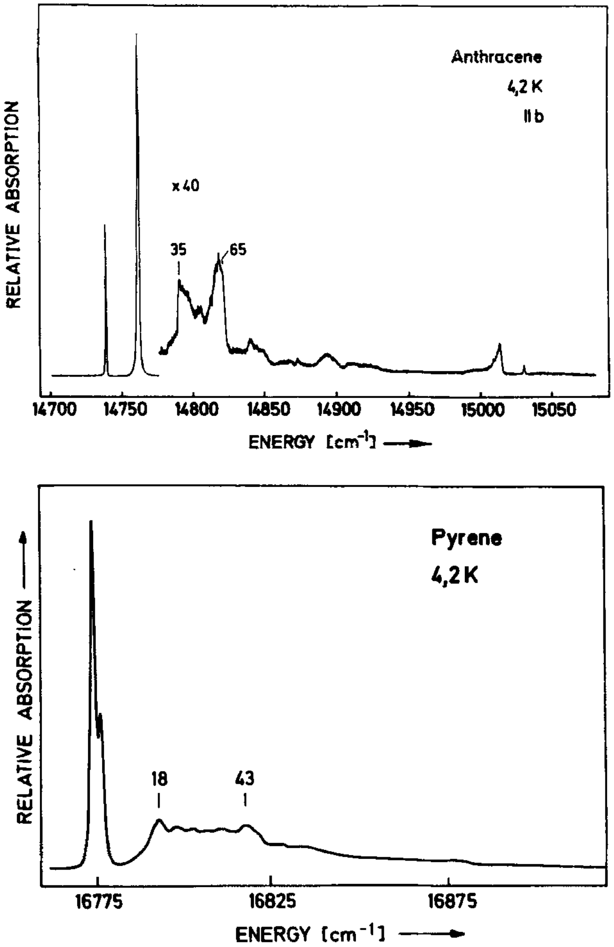

FIGURE 1 Excitation spectrum at 4.2 K, 0.0 region; (a) anthracene (above) and (b) pyrene (below). The anthracene spectrum is measured in light polarized parallel to the crystal b-axis and with increased sensitivity (× 40) for the sideband contribution.

Whereas the sideband intensity in pyrene is comparable to the zerophonon lines, the sidebands in anthracene are observed only with increased photoelectric sensitivity. In the example for anthracene, Figure 1a, only the spectrum after excitation polarized parallel to the crystal b-axis is given. As reported previously,[3] both the relative intensities of the two zerophonon components and the sideband structure are changed in the a-polarized spectrum. For pyrene no such pronounced polarization effect was observed.

In the previous experiments[2,3] uncorrelated variations of the optical linewidth from crystal to crystal had been observed. In this work crystal samples grown from different starting material and by different methods were compared systematically. These samples did not show any correlation between the absorption linewidth and residual impurity concentration. In general Bridgman crystals gave broader zerophonon lines than the sublimation crystals, but only the width of the low energy zerophonon component is very markedly affected. For anthracene, a typical value for the linewidth of the lower component for a Bridgman crystal is 0.4 cm^{-1}, but for sublimation crystals can be as narrow as 0.02 cm^{-1}. In the latter case the lower zerophonon component is almost two orders of magnitude narrower than the upper component (Figure 2a). The lineshape of the lower component is Gaussian and symmetric for the Bridgman samples but slightly asymmetric for sublimation samples, Figure 2a; the shape of the upper component is closer to a Lorentzian and always symmetric.

In the pyrene case the two zerophonon lines can be completely resolved for sublimation crystals only (Figure 2b). The low energy component is narrower than the high energy one, which exhibits a substructure similar to that observed for the upper Davydov component of naphthalene.[4] The narrowest linewidths achieved for the lower component are larger than in anthracene and still on the order of 0.1 cm^{-1}.

The linewidth turned out to be more sensitive to the cooling rate through the phase transition than the spectrum itself.[2] In contrast to previous findings with Bridgman samples,[2] the sublimation flakes could be cooled without cracking, but the lowest temperature linewidth still strongly varied with minor changes in the cooling rate. The linewidth also increases after repeated cooling cycles. On the other hand in a typical good sample as in Figure 2b, a 20% change[8] in the ratio of zerophonon line intensities, which could not be observed in previous experiments with Bridgman crystals,[2] was found for excitation polarized parallel to the a and b crystal axes, respectively.

The residual low temperature linewidth is a function not only of the cooling cycle but related to the crystal quality of the high temperature phase as well. A correlation between long triplet lifetimes τ_T at room temperature (on the order of 20 msec) and achievable narrow absorption linewidths

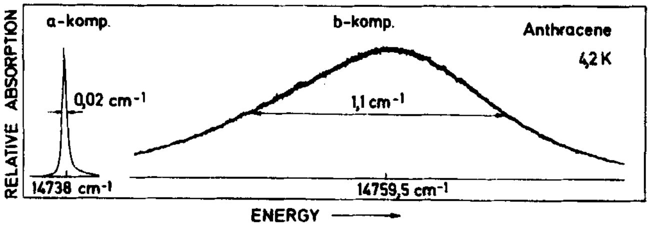

FIGURE 2a Zerophonon Davydov components of an anthracene sublimation crystal at 4.2 K. The energy scale is the same for both lines, which are normalized in their maximum intensity.

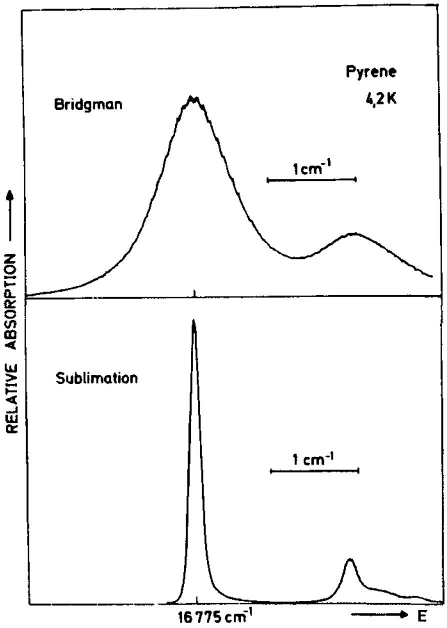

FIGURE 2b Zerophonon lines of pyrene at 4.2 K for a typical Bridgman and sublimation crystal, respectively. The energy scale is the same in both traces.

(typically 0, 5 cm^{-1}) was found for Bridgman crystals. The linewidth corresponding to a τ_T of ≈ 2 msec is typically 1.5 cm^{-1} at 4, 2 K.

3.2 Temperature dependence

The sharpness of anthracene's two Davydov components and their relatively large splitting has permitted an analysis of the T-dependences of their linewidths and shifts up to $T \approx 90$ K. At higher temperatures the components overlap the broader phonon sidebands, Figure 3a. A similar analysis for the two components of pyrene is not possible due to the small Davydov splitting. Nevertheless, the T-dependence of their intensity relative to that of the phonon structure can be determined. This also provides information on the exciton-phonon interaction.

Figure 4a presents the T-dependence of the halfwidth, Γ, for the two components of a sublimed anthracene crystal. For comparison, data for a Bridgman crystal are also given and it can be seen that such crystals give an incomplete picture for the broadening of the lower Davydov component at the lower temperatures. Above 30 K the relative increase of Γ is essentially identical for both components and approaches a T^2 dependence, Figure 4a.

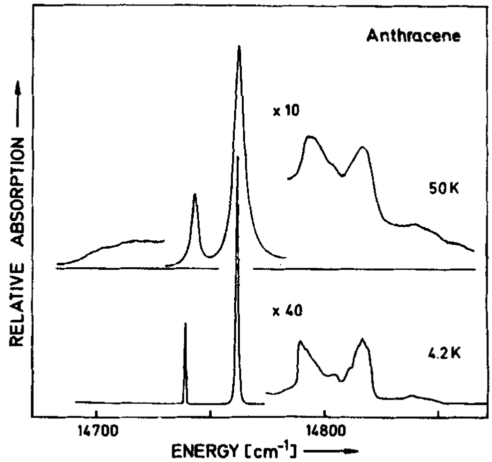

FIGURE 3a The 0.0 region of anthracene at 4.2 K and 50 K. The sideband contributions are recorded at higher sensitivity, ×40 and ×10, respectively.

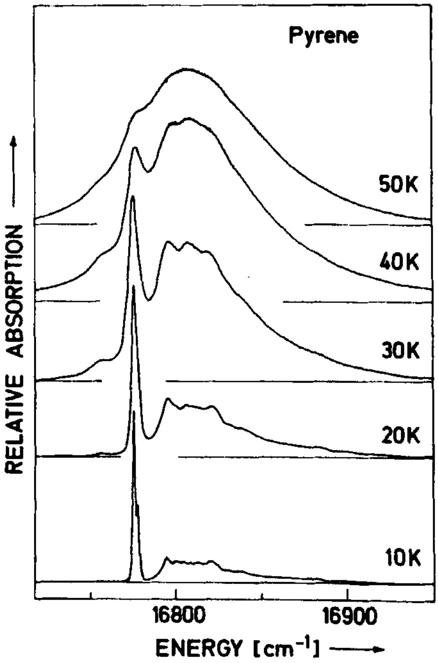

FIGURE 3b The 0.0 region of pyrene at different temperatures.

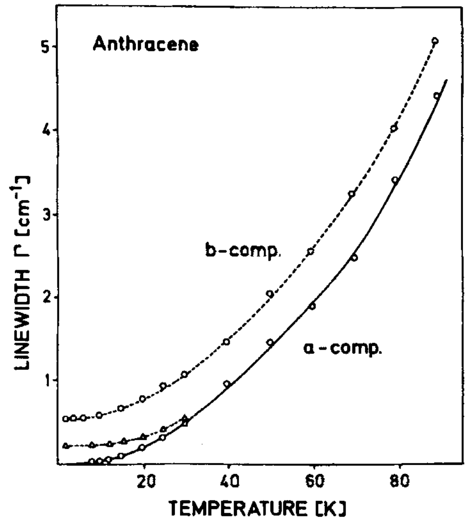

FIGURE 4a Zerophonon linewidth Γ for anthracene as a function of temperature; experimental points ○○○ for a sublimation crystal, △ △ △ for a typical Bridgman sample; the dotted lines merely connect the points, for the theoretical full line (a-component) see text.

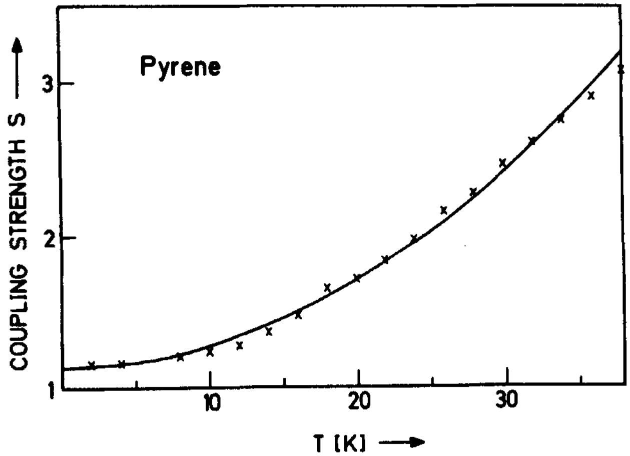

FIGURE 4b Temperature dependence of the parameter S (equ. 1) for pyrene, experimental points and theoretical fit according to equ. 2.

The small exciton spatial dispersion for pyrene has prompted us, *vide infra*, to determine the Debye–Waller factor, R, for the triplet exciton, Figure 4b. R is defined as the ratio I_o/I_{tot} where I_o is the sum of the zero-phonon intensities for both components (since they cannot be distinguished with respect to the sidebands) and I_{tot} is the total intensity (zero-phonon plus phonon sidebands). In Figure 4b the experimental values of S:

$$S = -\ln(I_o/I_{tot}), \tag{1}$$

are given as a function of T. S is a measure of the linear exciton-phonon coupling strength and in the Debye approximation (for $T \ll T_D$; T_D—Debye temperature of the crystal) is defined by the relationship:

$$S(T) = S(o)\left[1 + \frac{2\pi^2}{3}\frac{T^2}{T_D^2}\right] \tag{2}$$

The curve fitting with eq. (2) leads to excellent agreement with the experimental temperature dependence in Figure 4b (fitting parameter $T_D = 72$ K).

4 DISCUSSION

To our knowledge a triplet exciton linewidth as narrow as 0.02 cm^{-1} has not previously been observed and for anthracene's lowest Davydov component we have shown that such a narrow width is only attainable with strain-free mounted sublimed crystals. It is premature at this point to speculate as to whether the 0.02 cm^{-1} width is homogeneous. Nevertheless we have undertaken a theoretical analysis of the T-dependence of the reduced half-width ($\Gamma(T)$–Γ(residual)).[9] The theoretical analysis is based on the following rationale: because the exciton bandwidth of ca. 25 cm^{-1} is less than the maximum phonon frequency one should treat the phonons (interacting with the excitons) whose frequencies are less than or greater than $\approx$25 cm^{-1} on a different footing. For the former, full consideration of the exciton and phonon spatial dispersions for energy and pseudomomentum conservation in the exciton-phonon scattering should be given. Fortunately, *intrabranch* scattering can be excluded due to the small spatial dispersion of the excitons relative to that for the acoustic phonons. For the latter (frequency $>$25 cm^{-1}) lattice relaxation renders k an ineffective quantum number so that one can consider the scattering between a localized exciton and delocalized phonons. The curve through the data points for the thermal broadening of the lower component, Figure 4a, is the calculated curve based on the above theory[10] and the fit is obviously very good. The fit for the upper component is also satisfactory. It should be emphasized that an important clue for the theoretical understanding of the thermal broadening is the observation that the broadening approaches a T^2 dependence in the high *T* limit. It is worth noting that our data is not consistent with the exchange coupling theory recently proposed by Harris.[11] The observation that the upper Davydov component for anthracene is about 2 orders of magnitude broader than the lower component in the low *T* limit is understandable in terms of interbranch phonon emission available to the higher energy component even at 0 K.[3] The residual lineshape for this component, unlike that for the lower, is not sensitive to crystal quality. This is consistent with other data which indicate that our observed lineshape is homogeneous.

The larger residual linewidth for pyrene's lowest triplet Davydov component (relative to that for anthracene) may well be a result of the strain introduced while cooling through the phase transition. It has been emphasized that the residual widths do increase with increasing cooling rate particularly through the phase transition. It does appear, however, that the observed lineshape for the upper component (sublimed crystals) is homogeneous despite its substructure. This substructure is similar to that observed for the upper triplet exciton component of naphthalene[4] but is not, as yet, understood. In view of the above discussion on anthracene it seems appropriate, given the significantly smaller exciton spatial dispersion for pyrene, to examine the *T*-dependence of the zero-phonon to phonon sideband intensity ratio in terms of a theory appropriate for the interaction between a localized exciton and delocalized phonons. Additional support for this approach stems from the fact that several of the phonon peaks accompanying the Davydov components do not correspond to phonon bands observed in the low *T* Raman spectrum.[12] The linear electron-phonon coupling theory[13] appropriate for this situation was successfully applied in the preceeding section. We should note that the requirement that the total intensity (zero-phonon plus phonon sidebands) be independent of *T* is met for pyrene.

Finally we remark, that the excitonic transport properties of pyrene are determined, in part, by the exchange interaction between translationally inequivalent molecules in the unit cell (yielding the 1.9 cm^{-1} Davydov splitting), although this interaction according to theoretical calculations[14] is two orders of magnitude smaller than the internal exchange interaction within the dimer (pair). The excitation is rapidly exchanged within the pair, but quite localized with respect to the transfer to next nearest neighbors. The present results show that the coupling of the excitation to the Debye phonon spectrum is dominant. No coupling to an intra-pair vibrational mode of 90 cm^{-1} [15] which seems important for the singlet excited state is observed. From comparison with the monomeric absorption in isotopically mixed crystals no measurable stabilization energy for the triplet state in the pyrene crystal was deduced. These experimental findings further support the idea of an effective triplet excitonic pair state (of the pair-supermolecule) in pyrene, introduced in Reference 2.

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