Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Temperature Dependence of Width and Position of the Lowest Singlet-Singlet Transition in Crystalline Tetracene

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Version of record first published: 21 Mar 2007.

To cite this article: G. Vaubel & H. Baessler (1970): Temperature Dependence of Width and Position of the Lowest Singlet-Singlet Transition in Crystalline Tetracene, Molecular Crystals and Liquid Crystals, 12:1, 39-45

To link to this article: http://dx.doi.org/10.1080/15421407008082758

Molecular Crystals and Liquid Crystals. 1970. Vol. 12, pp. 39–45

Printed in Great Britain

Temperature Dependence of Width and Position of the Lowest Singlet-Singlet Transition in Crystalline Tetracene

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Received July 29, 1970; *in revised form October* 27, 1970

Abstract—Linewidth and position of the lowest singlet-singlet transition in crystalline tetracene are investigated in the temperature range 130 °K to room-temperature. It is found that below 200 °K the linewidth is temperature independent. The values for both Davydov components are 450 ± 50 cm^{-1} ($\|$**b**) and 300 ± 50 cm^{-1} ($\perp$**b**), i.e., at least twice as much as for crystalline anthracene. Upon slow cooling the redshift of the absorption peaks, which is reported to occur below 70° K, is found to occur almost continuously in the temperature range 300 to 180 °K. This raises doubts whether it results from a first order phase transition of the crystal lattice.

Crystalline tetracene is reported to undergo a phase transition near 70 °K.(1,2) This was inferred from optical absorption measurements: the zero vibronic component of the $^1A_g \rightarrow {}^1B_{2u}$ transition displays a redshift from 19200 ± 20(3) to about 18860 cm^{-1} (1,4) upon cooling below 70 °K and illuminating with light polarized parallel to the crystallographic **b** direction. For $\perp$ **b** polarized light the shift is less pronounced: The absorption peak moves from 19900 ± 20 cm^{-1} to about 19800 cm^{-1}. This leads to an increase in the energy gap between the peaks of the two Davydov components from 700 cm^{-1} to 940 cm^{-1}. The effect has been explained in terms of a change in the crystal structure below 70 °K leading to an increase in the resonance interaction between neighboring molecules.

This paper reports on an indirect determination of width and peak

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position of both Davydov components of the lowest singlet–singlet transition in crystalline tetracene as a function of temperature in the range 130 to 300 °K. Experimentally the method of recording the excitation spectrum of crystal fluorescence in the presence of trapping sites for singlet excitons at the crystal surface was employed. It turned out, that the oxidized surface layer, which develops on the *ab*-plane during storage of the crystals in an air atmosphere and which in analogy to anthracene most likely is composed of tetraquinone, is capable of effectively trapping singlet excitons striking the surface.

According to diffusion theory(5) the relative number $\Delta n/n$ of trapped excitons is given by

$$\Delta n/n = g\frac{l_d}{l_d + 1/\alpha} \tag{1}$$

adopting the boundary condition that the density of free excitons at the illuminated surface, which is identical with the trapping surface, is zero. In Eq. (1) l_d is the diffusion length for singlet excitons perpendicular to the *ab*-plane, α is the crystal absorption coefficient in cm^{-1}, i.e. $1/\alpha$ the penetration depth of the light, and g is the probability that an exciton hitting the surface gets lost for ordinary crystal fluorescence. In the following paper experimental evidence will be presented that g equals unity under the present conditions. Setting $\Delta n/n = \Delta I_f/I_{f,0}$ and $\Delta I_f = I_{f,0} - I_f$, where $I_{f,0}$ is the fluorescence intensity normalized to the incident photon flux at large penetration depths and I_f is the fluorescence intensity at an arbitrary wavelength, Eq. (1) yields

$$\Delta I_f/I_f = l_d\,\alpha \tag{2}$$

Thus the quantity $\Delta I_f(\tilde{\nu})/I_f(\tilde{\nu})$, which can be determined experimentally from the excitation spectrum of crystal fluorescence (see the following paper)(5) is a simple measure for the *relative* absorption coefficient as a function of excitation wavenumber $\tilde{\nu}$. The diffusion length l_d plays the role of a parameter, the exact value of which need not to be known. It must only fulfill the condition that it does not depend on α, which is a straightforward assumption.

The experimental procedure is described elsewhere.(6) Only a few points shall be emphasized here: (1) The crystals were sublimation grown and had a thickness of 50 to 100 μ. Relatively large crystals were selected and mounted as free as possible by means of an adhesive tape attached to one crystal corner. Thus the main (and illuminated) portion of the crystal area ($>95\%$) was not in contact with any kind of substrate. (2) Cooling occurred by a stream of N_2-gas. Cooling and heating rates were slow, about 30 degrees per hour or less. (3) The bandwidth of the exciting light was 2 nm. (4) The incident photon flux was below 10^{13} photons cm^{-2} s^{-1}. Hence triplet–triplet interaction leading to delayed fluorescence could be neglected.(7)

Figure 1 shows the relative absorption spectrum of crystalline tetracene in the excitation range 18000–20000 cm^{-1} for $\parallel$ **b** and $\perp$ **b**

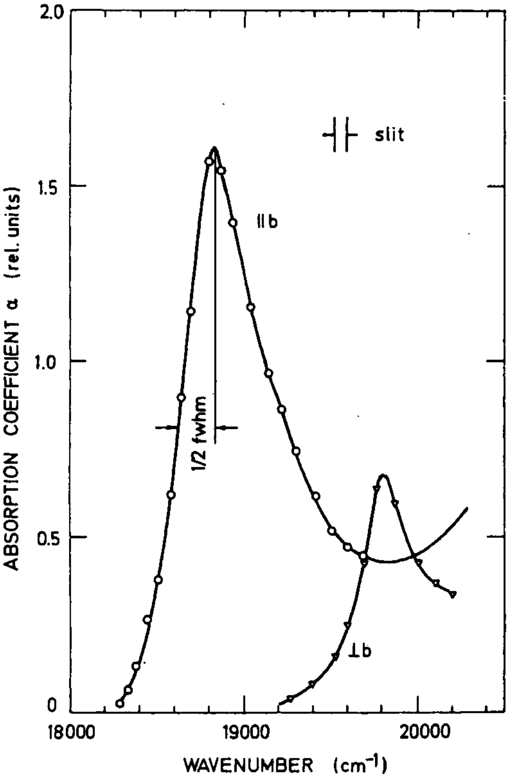

Figure 1. Relative absorption coefficient for both Davydov components of the zero-vibronic ${}^1A_g \rightarrow {}^1B_{2u}$ transition as a function of wavenumber. Temperature: 163 °K.

polarized light at 163 °K. The lineshape of the lowest band is asymmetric. This, however, could be an artifact due to contribution of absorption into a vibronically excited S_1 state involving a 400 cm^{-1} molecular vibration. The " full width at half maximum " (fwhm) of the purely electronic S_0–S_1 transition is therefore calculated from the low energy portion of the absorption line which accordingly gives a lower limit (see Fig. 1). In Fig. 2 the fwhm values are plotted

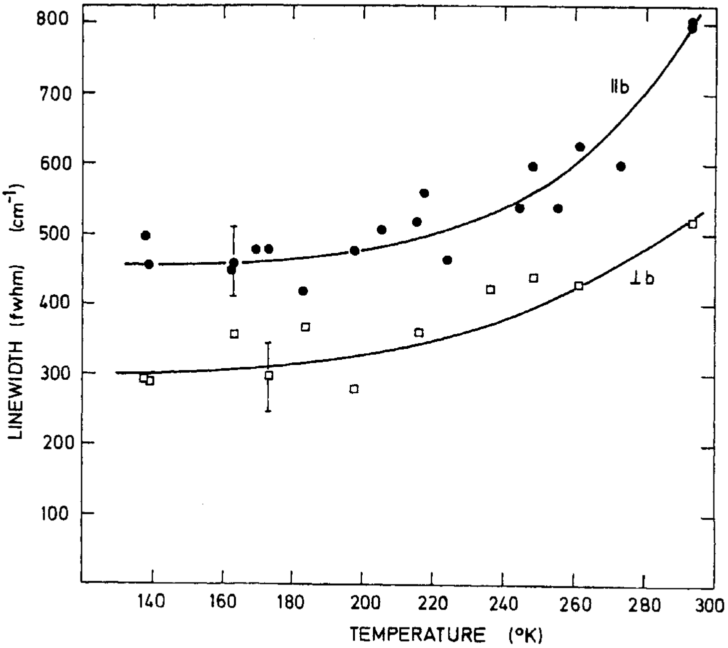

Figure 2. Dependence of the linewidth (full width at half maximum) of the $^1A_g \rightarrow {}^1B_{2u}$ transition as a function of temperature.

versus temperature. Despite the scatter of the data it is obvious that the fwhm values decrease upon lowering the temperature and become constant below 200 °K:

$$\text{fwhm}_{\parallel b,\text{min}} = 450 \pm 50 \text{ cm}^{-1}$$

for the lower Davydov component ($\parallel b$) and

$$\text{fwhm}_{\perp b,\text{min}} = 300 \pm 50 \text{ cm}^{-1}$$

for the upper Davydov component. Zanker and Preuss$^{(8)}$ have observed similar fwhm values at 112 °K. This demonstrates (1) that absorption processes starting from thermally excited S_0-levels do not play a significant role below 200 °K, and (2) that like in crystalline anthracene the line width for the ${}^1A_g \rightarrow {}^1B_{2u}$ transition does not reach its limiting value of a few cm^{-1} at low temperatures as might be expected from the selection rule $\mathbf{k} = \mathbf{Q}$ for transitions from the ground state into an exciton band. In particular, the linewidth for tetracene is by a factor of 2 to 2.5 higher than for anthracene. This is parallelled by an increase in the Davydov splitting from 170 cm^{-1} (9) to about 700 cm^{-1} indicating also an increase in the exciton bandwidth. Such a correlation is to be expected if line broadening arises because of breakdown of the **k**-selection rule for optical transitions into the exciton band taking place within a—most likely—disturbed surface region(10) of the crystal as has been suggested by Rice, Morris and Greer.(11) Note that the oscillator strengths for the lowest single transitions in anthracene and tetracene are almost the same. An explanation of the effect on the basis of exciton phonon coupling can be ruled out, because this should lead to comparable linewidths for anthracene and tetracene.

From the present experimental results, however, the Davydov–Sheka model(12) cannot be disregarded as a possibility to explain the anomalous linewidth in absorption. It assumes that the exciton band structure is such as to yield a very high value for $dE(\mathbf{k})/d\mathbf{k}$ at $\mathbf{k} = 0$. This means that a transition caused by a light beam having a small spread in **k**-space can cover a rather large range in energy thus yielding a broad absorption line. It is likely that $dE(\mathbf{k})/d\mathbf{k}$ is proportional to the overall exciton bandwidth thus leading to an increase in linewidth when passing from anthracene to tetracene.

As a second result of the determination of the lineshape of the lowest singlet–singlet transition in tetracene crystals the dependence of the position of the absorption peaks on temperature is obtained. The data are plotted in Fig. 3. Obviously there is a large redshift of the absorption peak for **b**-polarized light with decreasing temperature. With the $\perp$ **b**-component the effect is small. With different crystals the data for the peak position at room temperature and below 180 °K were reproducible within the experimental uncertainty of ± 50 cm^{-1}. The temperature at which the "low temperature" value was reached varied between 170 and 200 °K among five crystals.

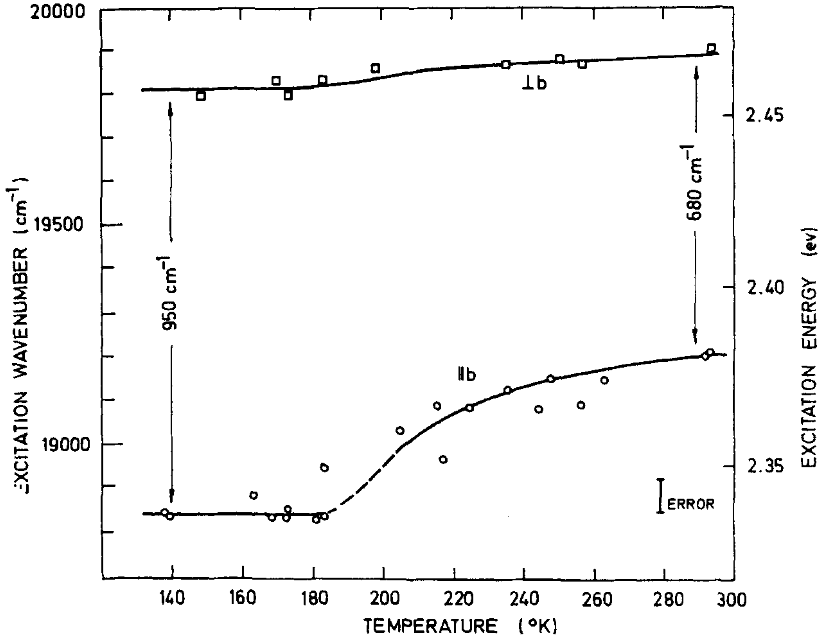

Figure 3. Temperature dependence of the position of the absorption peaks for the zero-vibronic ${}^1A_g \rightarrow {}^1B_{2u}$ transition in both polarization directions.

The limiting values of the transition energies at room temperature and below 180 °K coincide with literature data for the " high " and " low " temperature modification of crystalline tetracene. Consequently also the splitting between both Davydov components has the right values (700 cm^{-1} respectively 940 cm^{-1} (1) for the different phases). Because of the above mentioned difficulties regarding interpretation of the absorption lines, particularly identification of the exciton band edge ($E(\mathbf{k} \sim 0)$), it seems to be premature, however, to speak in terms of " Davydov splitting " in the original meaning.

The increase in the splitting between both components is indicative of some molecular rearrangement within the unit cell as has already been pointed out.(1) This rearrangement, however, seems to critically depend on the cooling rate. In the present experiments employing slow cooling rates and freely mounted crystals the effect is completed at T = 190 °K in contrast to what other workers have found.(1,2,13) Secondly at least the major portion of this molecular rearrangement extends over a temperature range of more than 50 degrees. This disregards the concept of a first order phase transition. A final " sudden " change leading to 30% of the total temperature-induced increase in the peak splitting cannot be excluded from the present measurements. In this context it would be interesting to conduct a differential thermal analysis-study of crystalline tetracene at low temperatures.

These observations illustrate the instability of the tetracene crystal lattice at temperatures near and not too far below room-temperature. It is further documented by the mechanical instability of the crystals and by the sensitivity of the " Davydov "-splitting on pressure.(12) The dependence of the position of the lowest singlet state on temperature and history, e.g. cooling rate, can also explain differences in the value found for the energy gap between singlet state and triplet-pair state deduced from experiments on singlet exciton fission.(15)

Acknowledgement

We wish to thank Professor N. Riehl for his interest in this work. Financial support by the " Deutsche Forschungsgemeinschaft " is gratefully acknowledged.

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