Light Absorption by Pyrene Single Crystals Between 4 and 300 °K

A Search for the Ground-to-Excimer State Absorption

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(Z. Naturforsch. **28 a**, 973—979 [1973]; received 7 February 1973)

Pyrene single crystals have been grown from zone refined material by sublimation and from the melt. The absorption edge has been measured for thick and thin crystals at room temperature. Thin crystals have been successfully cooled below the phase transition temperature (123 °K) without cracking. The sharp absorption peak at 376 nm vanishes at this temperature while the fluorescence spectrum remains unchanged. Using polarized light below 50 °K, a band with a maximum at 410 nm appears whose intensity increases with decreasing temperature. It is concluded that this band is due to ground-to-excimer state absorption in the ground state equilibrium distance of the pyrene molecules. The consequences of this finding for excimer-exciton transport is discussed.

I. Introduction

The spectral properties of crystalline pyrene are due mainly to the sandwichlike arrangement of the molecules in the crystal lattice[1, 2]. Ferguson[3] interpreted the broad structureless fluorescence band as emission from excited dimers (excimers) which are stable only in the excited state[4]. Stevens[5] showed that excimer fluorescence is characteristic of many crystals of aromatic hydrocarbons in which the molecular planes have a large overlap. The decay time of pyrene fluorescence has been studied in detail by Birks[6] who also investigated the excimer interaction potential[7] which shows that the two molecules closely approach each other during excimer formation. After deactivation they return to the ground state equilibrium distance. Excimer emission has been found to be polarized in the long axis of the molecule[8].

More recently, investigations have been carried out on singlet energy transfer in crystalline pyrene[9–13]. The excimer-exciton diffusion was found to be a thermally activated process[10, 12, 13]. The apparent activation energy has been reported to be 112[12], 350[14], and 450[13] cm^{-1}.

In a previous paper of our group[13], we proposed three possible mechanisms for the excimer transfer from one pair of pyrene molecules to a neighboring one (Figure 1):

(a) Excimer state dissociation into excited (S_1) and ground state monomer (S_0) followed by S_1 transfer to a pyrene molecule of an adjacent pair and excimer formation of this pair.

(b) If the energy of the excimer at the ground state equilibrium distance (3.53 Å)[1] is still smaller than S_1, this position could be reached by thermal activation of the excimer without dissociation. The excimer state could then be transferred to a neighboring pair in its ground state position.

(c) If the ground state repulsion potential is rather flat, a pair adjacent to the excimer could be compressed by lattice vibrations to the excimer equilibrium distance and take up the excimer from the excited pair.

Mechanism (a) seems to be rather unlikely, since the excimer level should be very close (<500 cm^{-1}) to S_1 of the pyrene molecule and monomer fluorescence should be observed, which in fact has only been found in disordered crystals[15]. It should be possible to distinguish between mechanism (b) and (c) by the absorption spectra of carefully purified pyrene crystals in the region of the absorption edge: According to (b), a weak absorption band (solid arrow in Fig. 1 b) which is due to the direct ground-to-excimer state transition is to be expected at low temperature. According to (c), on the other hand, adsorption at longer wavelengths (roughly corresponding to excimer emission; Fig. 1 c) should be observed at elevated temperature. Absorption at low temperature is not to be expected in this case.

The absorption spectrum of a very thin pyrene crystal has been published by Tanaka[16] and spectra of thicker crystals by Ferguson[3]. Since these spectra only show the region of high absorption intensity, it is not possible to recognize any excimer absorption. Chu, Kawaoka, and Kearns[12] observed a broad shoulder in the fluorescence excitation spectrum at

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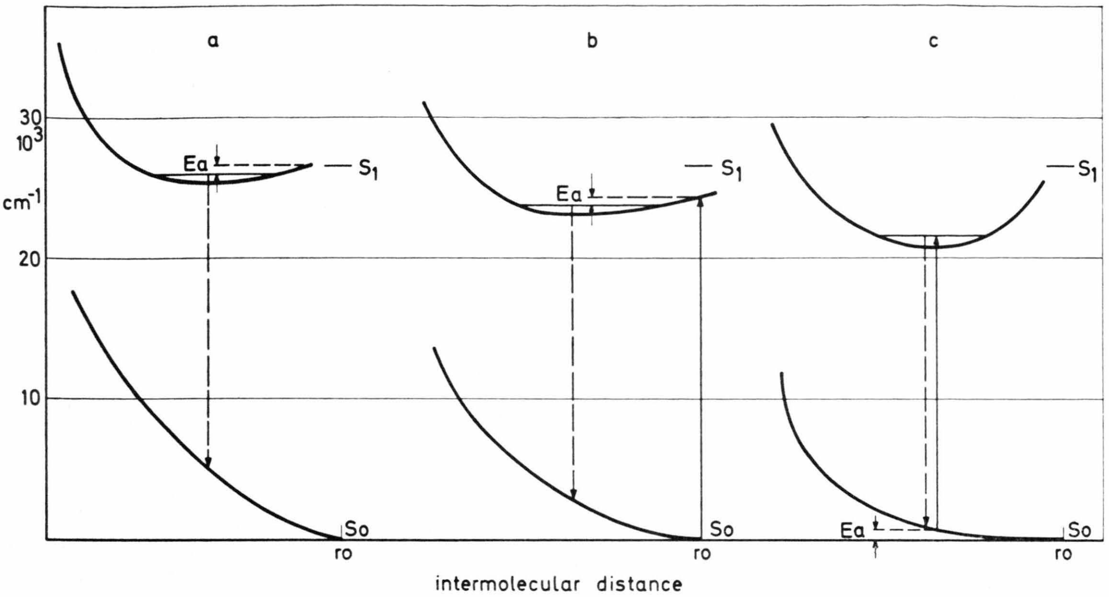

Fig. 1. Diagrammatic view of excimer and ground state potentials for different mechanisms of excimer-exciton transport (see text). E_a = activation energy for excimer-exciton hopping. Possible ground-to-excimer state absorption is indicated by solid arrows. Dashed arrows indicate excimer fluorescence; their length corresponds to the experimentally measured maximum.

4 °K and interpreted it as being due to ground-to-excimer state absorption.

The difficulty of measuring direct absorption spectra of pyrene crystals at low temperature has been due to the cracking of the crystals near the phase transition at 123 °K. We have succeeded in cooling thin single crystals (about 10 μm) below 123 °K without cracking by very slow reduction of the temperature, with cold nitrogen gas and using a special sample holder. We present in this paper the absorption spectra of thick and thin crystals at room temperature and the spectra of thin crystals down to the temperature of liquid helium. Furthermore, the excimer and delayed fluorescense lifetimes and the excitation spectra of prompt and delayed fluorescence have been measured for crystals of different purity and preparation.

II. Experimental

A) Purification and Crystal Growth

Starting with pyrene puriss. (Fluka), two sublimation steps in vacuum were carried out before the material was transferred to the evacuated zone melting tubes attached to the sublimation apparatus with the aid of brake seals. After sublimation, the material still had a slightly green color, and we needed 120 zone passes to obtain a colorless substance over about half of the ingot length. The purification process used is described in greater detail in [17, 18].

The zone melting tube has three brake seals at its bottom to which crystal growth tubes are sealed after purification. The material is transferred by melting to the evacuated crystal growth tubes. In this way, oxygen is kept away during the whole preparation process.

Two crystals were grown from the melt by use of the Bridgman method. For one of them, K 1, colorless pyrene was used from the front quarter of the zone-refined bar. The other crystal (K 2) was grown from a slightly green colored material which was taken from the second half of the bar. The crystals were grown at a rate of 0.5 mm/h and then annealed for about 150 hours at 130 °C (melting point 153 °C). Since pyrene crystals are very brittle compared, for example to anthracene, it is difficult to cleave them. The cleaved crystals always showed subgrain boundaries in the cleavage plane, although they were optically clear. Most crystal slices were prepared by sawing and polishing the surface.

Sublimation grown crystals were prepared from pieces of K 1. The simple apparatus we used is shown in Figure 2.

After evacuation, the pot is filled with argon at 1 Torr. Powdered pyrene is deposited on the bottom and the pot is heated to about 80 °C by a hot

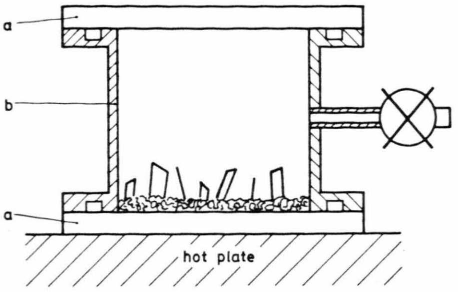

Fig. 2. Sublimation vessel for crystal growth.
(a) Glass plates, (b) Stainless steel flange.

plate. A variety of crystals of different thickness grow out from the powder after one or two days. (Only small quantities of the material sublime to the upper glass plate.) The thickness ranges from about 1 μm to 1 mm. It seems that the crystal flakes always develop preferentially along the a – b plane. This method of crystal growth proved to be very convenient.

B) Spectra and Lifetime Measurements at Room Temperature

a) Absorption Spectra

The measurements were made with a Beckman DK 2 A spectrophotometer using crystalline samples up to 15 mm in thickness.

b) Emission Spectra

Fluorescence, delayed fluorescence and the corresponding excitation spectra have been recorded by means of a Hitachi Perkin-Elmer fluorescence spectrophotometer MPF-2A, equipped with an R 136 photomultiplier tube. Delayed fluorescence decay curves have been obtained with an oscilloscope, connected to the fluorometer, by photographing the traces.

c) Fluorescence Decay

Singlet excimer lifetimes were measured upon exposure of the pyrene samples to a Fischer Nanolite lamp supplying flashes of 9 nsec halfwidth through a reflection filter with a narrow passband centered at 280 nm. The excimer fluorescence light which passed through a Zeiss monochromator M 4 A III at 450 nm, was detected by a RCA 1 P 28 photomultiplier tube. The decay curves were displayed on a Tektronix type 545 oscilloscope and then analyzed on a multiple exposed photograph yielding decay times with an accuracy of 10 percent.

C) Low Temperature Spectra

Many attempts to cool crystals down to the temperature of liquid nitrogen failed. Thicker crystals always become turbid at this temperature owing to the phase transition at 123 °K. Thin sublimed crystals crack into several clear pieces during slow cooling. Nevertheless, we succeeded in cooling sublimed crystals down to liquid helium temperature by using a special crystal holder which was attached to a cryostat described by Wurzbacher and Gebhard[19]. The holder and its connection to the inner helium tank are shown in Figure 3.

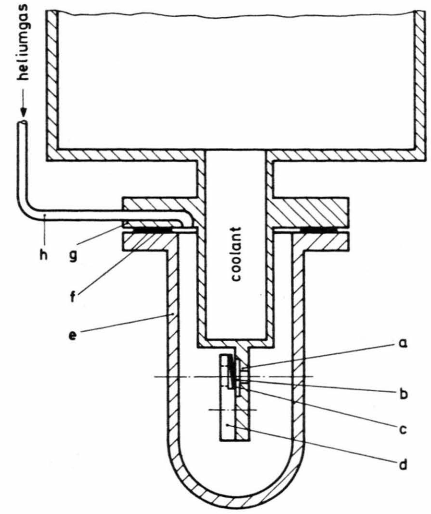

Fig. 3. Crystal holder.

(a) Copper bar (b) Quartz window
(c) Crystal (d) PTFE platelet
(e) Glass vessel (f) Indium gasket
(g) Copper flange (h) Stainless steel tube

The holder consists of a copper bar and carries a quartz window (b). The crystal (c) is inclined to the PTFE platelet (d), in order to have only poor thermal contact to the copper bar. It is isolated from the outer vacuum by a glass vessel (e) which is connected to the copper flange (g) and sealed with an indium gasket (f). After being evacuated through the tube (h), this inner space is filled with helium gas of 5 Torr which provides a uniform thermal contact over the whole crystal surface. Temperature is measured with a thermistor and a carbon resistor which are mounted on the copper flang (g). During the first stage of cooling, the helium tank is very slowly cooled down with cold nitrogen gas. Special precautions were taken near the transition temperature at 123 °K. The cooling rate was so low that we needed about 3 hrs to attain this temperature. Once the crystal survived this transition (as indicated by the spectrum), further cooling was effected very fast down to liquid helium temperature.

Absorption measurements were performed with a single beam method, using the emission monochromator of the MPF 2 A. A halide lamp (tungsten-iodine lamp) which has a smooth intensity distribution in the region between 360 and 450 nm (Fig. 7), served as light source.

The spectra have to be corrected for the lamp intensity which increases with the wavelength.

The light source for the fluorescence measurements was a 200 W xenon lamp with a UV transmittant filter UG 11 and a $CuSO_4$ solution.

III. Results

A) *Lifetimes*

a) Singlet Excimer Lifetimes

Singlet lifetimes of pyrene powder and of sublimation grown crystals have been published by several authors [6, 12, 13]. The highest values range between 110 and 120 nsec. Our sublimation grown crystals also showed singlet lifetimes in this range. In our melt-grown crystals, however, we measured lifetimes between 160 and 190 ns. There was no remarkable difference between the purer crystal K 1 and the greenish crystal K 2. This indicates that the mean impurity distance in K 2 is greater than the mean free path of the excimers.

b) Triplet Lifetimes

The difference in triplet lifetimes between sublimation and melt-grown crystals is even more pronounced than in singlet lifetimes. Using the relation $\tau_T = 2\,\tau_{DF}$, we measured lifetimes for sublimation-grown crystals (K 1 material) of 6 msec and for the melt-grown crystals of 24 msec (K 1) and 8 msec (K 2). A triplet lifetime of about 0.3 ms at 10 °C has been reported for sublimed crystals [20].

B) *The Absorption Edge at Room Temperature*

Figure 4 shows the adsorption edge of the pyrene crystal. Curve 1 is based on spectra of the purest crystals (K 1) of different thicknesses; curve 2 has been derived from the spectra of the less pure materials (K 2). In this spectrum, an impurity with maxima at 455 and 428 nm can easily be recognized. If the molar extinction coefficient of the impurity is of the order of 10^3 to 10^4, its concentration is in the range of 1 to 10 ppm. For K 1, the concentration of this impurity then is <1 ppm, since no absorption can be detected even in very thick crystals. The unidentified impurity [21] seems to sensitize the host triplet production since the absorption maxima plus

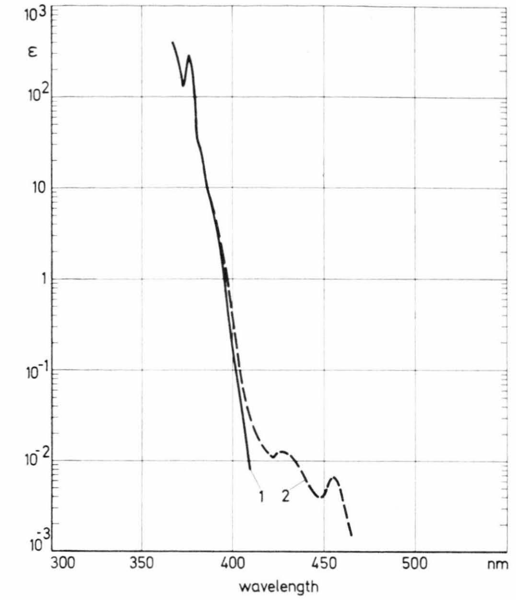

Fig. 4. Absorption edge of pyrene single crystals at room temperature. Curve 1 is based on spectra of high-purity crystals (K 1), thickness 6.9 μm, 91 μm, and 5 mm; curve 2 has been obtained from spectra of the less pure pyrene (K 2), thickness 0.3 mm and 15 mm; ε is the molar decadic absorption coefficient.

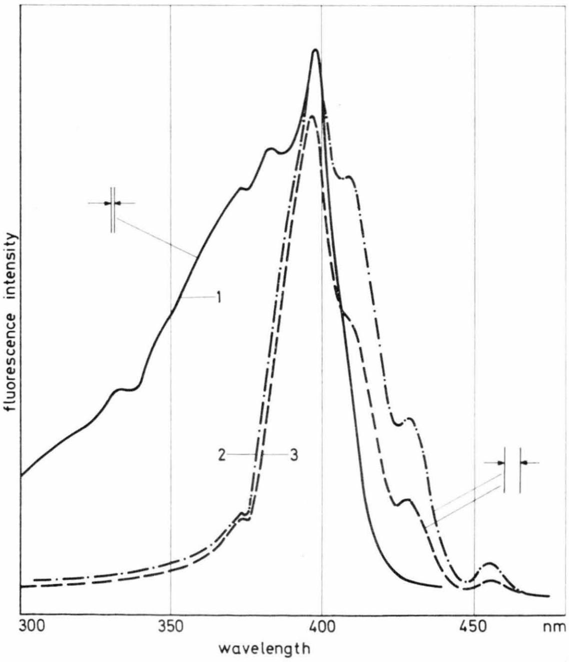

Fig. 5. Excitation spectra of prompt (1) and delayed (2, 3) fluorescence of pyrene single crystals. Curves 1 and 2 have been obtained with high-purity material (K 1), curve 3 with less pure pyrene (K 2). Excitation slit width is indicated.

a third one at 409 nm are detected in the delayed fluorescence excitation spectrum (Fig. 5). The maxima are also observed in the excitation spectrum of the purest crystal, however less intense (Fig. 5, curve 3). They are not detected in the prompt fluorescence excitation spectrum, since the electronic impurity level is below the excimer level [7, 13]. The minor differences in the shorter wavelength region of the absorption spectrum (Fig. 4, curve 1 and 2) may be due to different orientations of the crystals and partial polarization of the light beam leaving the monochromator of the spectrometer.

The shoulder at about 382 nm is not a hot band as might be assumed when comparing it with the absorption spectrum of pyrene solution [22] because it is also observed at low temperature. The first distinct maximum is at 376 nm, as has already been reported by Ferguson [3] and Tanaka [16]. The 376 nm maximum appears as minimum in the excitation spectrum (Figure 5).

C) *The Effect of Cooling and Phase Transition*

Cooling of single crystals leads to sharper resolution of the absorption spectrum (Figure 6). Peaks appear at 367.5 and 365 nm which seem to correspond to the non-resolved solution peak at 362 nm [22] with a shoulder on the long-wave length side. The sharp peak at 376 nm would then correspond to the 0 – 0 peak in solution at 372 nm [22, 23].

If this interpretation is correct, the crystal spectrum is red-shifted by 300 cm^{-1} compared to the light petroleum solution spectrum [22]. This seems reasonable in view of the small oscillator strength of the ^1L_b transition ($f = 0.0016$) [16]. The interpretation, however, does not explain the shoulder at 382 nm (Figs. 4 and 8) which is too strong to be likely an impurity absorption. If the 382 nm shoulder is due to a weak 0 – 0 transition, the red shift, compared to solution, is about 1000 cm^{-1}. It should be noted here that the absorption spectrum at 141 °K (Fig. 6) is very similar to Ferguson's [3] "77 °K" spectrum, but our spectra show drastic changes at the transition temperature.

The phase transition can be identified as follows:

- The TDA diagram shows an endothermic peak at 123 °K [13],
- The $Cp(T)$ curve by Jacobs and Parks [24] shows a "hump" from 108 to 124 °K, corresponding to a transition enthalpy of 24 cal/mole.
- Changes in host and guest fluorescence intensities in the range between 122 and 129 °K have been observed by Hochstrasser and Malliaris [25].

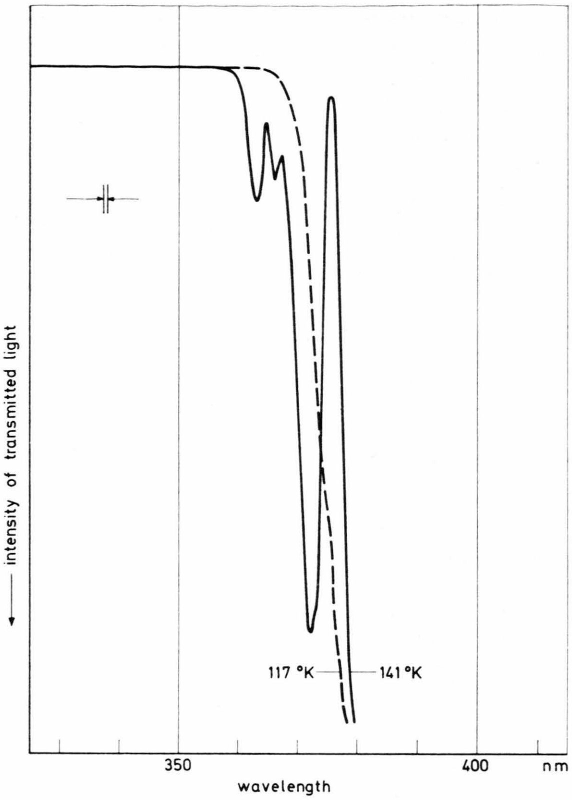

Fig. 6. Absorption edge of pyrene single crystal above and below the transition point (123 °K); below 360 nm no light is transmitted by the crystal.

It is not known what structural change occurs. The basic arrangement of the pyrene molecules with large overlap is surely not altered, since in single crystals only excimer fluorescence is observed below 123 °K (Figure 9).

A profound reversible change is observed in the absorption spectrum (Fig. 6) between 125 and 120 °K. The sharp peak at 376 nm disappears and is replaced by an unstructured absorption edge, whereas the 382 shoulder remains unchanged.

D) *Absorption Spectrum at Liquid Helium Temperature*

Lowering the temperature below 50 °K gives rise to a broad absorption band around 400 nm whose intensity increases with decreasing temperature. It is observed only when the light is polarized as indicated in Figure 7; the direction of the light beam is parallel to c′ (vertical to the ab plane of the high temperature modification) [1].

The true absorption spectrum (Fig. 8) has been obtained by subtracting the apparent spectrum from the spectrum of the lamp without crystal in a semi-logarithmic plot (Figure 7). The true absorption spectrum shows a distinct maximum of 410 nm ($\varepsilon \approx 20$). The peak at 382 nm ($\varepsilon_{\perp} \approx 100$) is polarized vertically to the 410 nm band.

The 4 °K fluorescence spectrum has been recorded and is compared with the room temperature

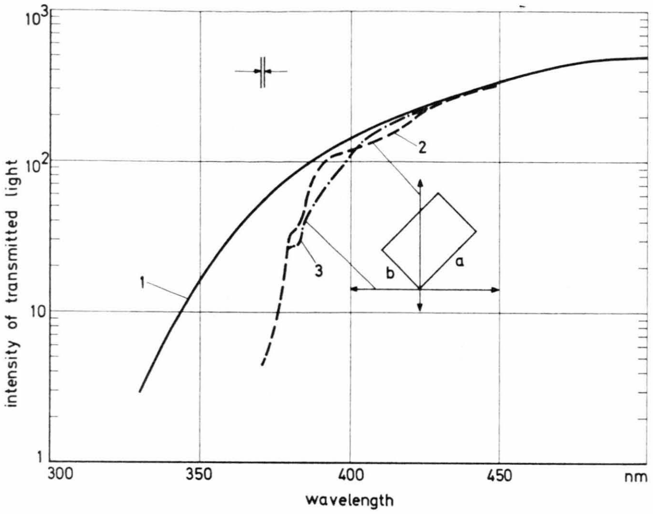

Fig. 7. Light transmitted by a pyrene single crystal cooled with liquid helium (curves 2 and 3) and apparent intensity distribution of light without crystal (1); direction of polarization is indicated, the light beam is vertical to the ab plane (c′) [1].

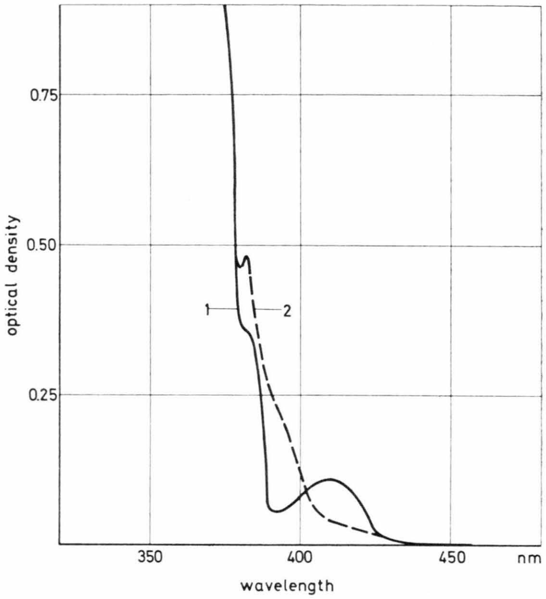

Fig. 8. Absorption edge of a pyrene single crystal cooled with liquid helium; curve 1 is obtained from curve 2 in Fig. 7, curve 2 from curve 3 in Fig. 7 by subtraction from curve 1 (optical density $= \log I_0 - \log I$); thickness of the crystal about 8 μm.

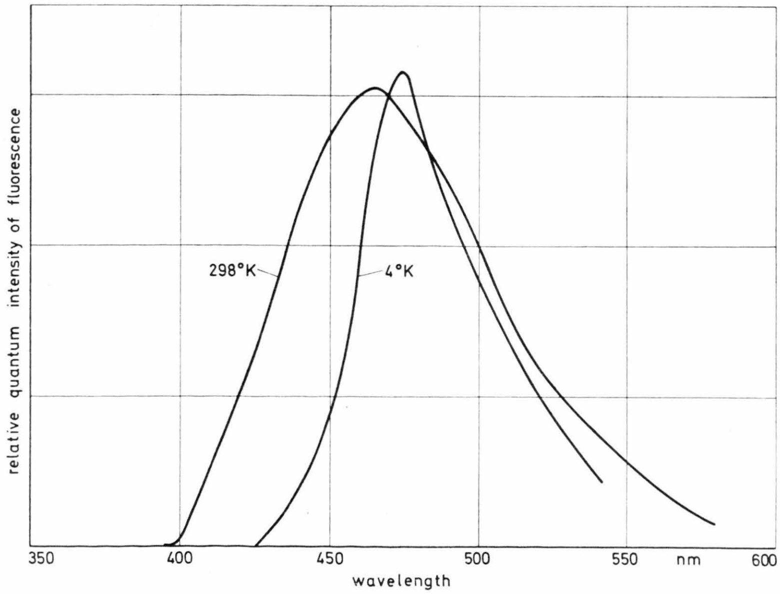

Fig. 9. Fluorescence of pyrene single crystal; the two curves are based on a different scale of the ordinate.

spectrum in Figure 9. It is very similar to that published by Birks[7] and shows no monomer emission pointing to disordered regions in the crystal[15]. The onset of excimer fluorescence is at 430 nm which corresponds to that of the 410 nm absorption band.

IV. Discussion

The study of the long wavelength absorption of pyrene single crystals down to 4 °K furnished two interesting results:

– the drastic reversible change of the absorption at the transition temperature and
– the appearance of a new band at 410 nm which can only be observed at very low temperatures.

It is difficult to discuss the change at 120 to 125 °K not knowing the structural change occurring during transition. Most probably the very strong ^1L_a transition which starts at about 360 nm at room temperature[16] is broadened or red-shifted in the low temperature modification. A study on very thin crystals would be worthwile in order to elucidate this point.

The most interesting question is whether the 410 nm band is due to direct ground-to-excimer state absorption, according to Figure 1 (b).

The absorption vanishing with increasing temperature favors this explanation, since vibrations of the pyrene molecules shortening or enlarging their mutual distance would broaden the weak band and prevent its detection. A further point in favor of this interpretation is the onset of 4 °K absorption and excimer fluorescence at about 430 nm. The maximum of the absorption band is consistent with the excimer level reported by Birks[7] (23,860 cm^{-1}) plus the activation energy of exciton hopping (450 cm^{-1})[13]. It is, however, not sure that these values are exactly the same in the high and low temperature modification of pyrene.

The polarization effect observed in the 4 °K spectrum cannot be explained on the basis of the high temperature structure and long axis polarization[8] of the excimer transition. The 4 °K excimer excitation spectrum[12] is similar to our 4 °K absorption spectrum polarized vertically to the direction favorable for observation of the 410 nm band (Figure 6, curve 2). The room temperature absorption spectrum (Fig. 4) clearly shows that the absorption edge is not a straight line in the semilog. plot Perhaps this deviation in the 390 – 400 nm range is due to ground-to-excimer absorption.

From our results, mechanism (b) (see introduction and Fig. 1) of excimer-exciton diffusion appears to be the most probable one. Mechanism (c) can be excluded because of the absence of absorption in thick crystals of pure pyrene at wavelengths of about 450 nm (Figure 2).

Acknowledgement

This work has been carried out a part of the Battelle Institute research in physical sciences. The authors wish to thank Professor W. Liptay for interesting discussion and Mr. K.-H. Rastofer for performing the fluorescence decay measurements.

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