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Polarized Absorption and Fluorescence Spectra of Crystalline Anthracene at 4°K: Spectral Evidence for Trapped Excitons*

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The long-wavelength absorption and fluorescence spectra of anthracene crystal have been examined in the *ab* (cleavage) plane at 4°K. The spectra are compared with those reported previously, and are related to the spectra of the solid solution. The spectra of the crystal and the mechanism of the fluorescence process are interpreted in terms of Frenkel's theory of free and trapped excitons. The relative shift of the electronic transition in the vapor, mixed crystal, and pure crystal is related to the possibility of detecting trapped exciton states in molecular crystals.

I. INTRODUCTION

THE absorption and fluorescence spectra of crystalline anthracene have been extensively studied by many workers. Obreimov and Prikhotjko[1] have measured the absorption spectra of crystalline anthracene at 20°K, and Obreimov, Prikhotjko, and Shabaldas[2] have measured the fluorescence spectra of crystalline anthracene at 20°K. More recently, Pesteil and Barbaron[3] have measured the fluorescence of crystalline anthracene at 14°K. In a series of papers, Craig and co-workers[4–6] have discussed the absorption spectra of anthracene crystals.

In spite of the large number of investigations, the exact relation between the absorption and fluorescence spectra of crystalline anthracene has not been satisfactorily explained. Recently, Sidman[7] has studied the absorption and fluorescence spectra of anthracene in mixed crystals in naphthalene and phenanthrene at 20°K. In the present investigation, the spectra of the crystal are compared with the spectra of the mixed crystalline solid solution, and the electronic structure of the crystal is discussed in relation to the absorption and fluorescence spectra.

II. EXPERIMENTAL

The spectrograph was a 3-meter Hilger quartz prism instrument with a Littrow prism mounting. A Wollaston prism placed 18 cm behind the slit of the spectrograph gave two separate plane-polarized images of the slit in the focal plane. A Hartmann diaphragm and a movable curtain in front of the focal plane made it possible to record separate iron arc spectra for each polarization direction without moving the plate or Wollaston prism. This eliminated any possible shift of the calibration spectrum relative to the absorption or fluorescence spectrum of the crystal. Other details of the spectrograph have been described in a previous communication.[8]

In this work, a single glass Dewar vessel with plane windows was used to hold liquid helium. A 700-cc charge of liquid helium lasted approximately ten minutes, which was sufficient time to photograph several absorption and fluorescence spectra. The vessel was refilled when necessary, and the sample was always immersed in the refrigerant during the measurements.

In order to grow anthracene crystals which were thin enough to show structure in the absorption spectrum, a sample of Eastman Kodak anthracene of the blue-violet fluorescence grade was melted between optically flat fused quartz disks and was allowed to solidify under pressure. Oriented areas of the desired thickness could be obtained by this procedure. The best crystals for spectroscopic investigation showed a gray-black first-order interference color when examined with a quartz wedge in white light between crossed Nicol prisms in the polarizing microscope. Optical examination of the crystal in converging monochromatic light from a sodium vapor lamp enabled the *a* and *b* axes to be identified in the *ab* (cleavage) plane.[9] The *b* axis is the crystallographic axis of symmetry. An oriented area which did not show cracks was masked off and mounted for spectroscopic investigation. The crystal was cooled above liquid nitrogen and then immersed directly into liquid nitrogen. It was then magnified approximately three times in length and was rotated between crossed Polaroid disks until either the *a* or *b* axis of the crystal was parallel to the slit. The crystal acted as its own polarizer, and the Wollaston prism produced two spectra, corresponding to the *a* and *b* polarizations in the *ab* plane of the crystal. Rotation of the crystal by 90° led to a reversal of *a* and *b* polarizations on the plate but did not cause any detectable change in the observed polarization properties of the absorption or fluorescence spectra, proving that the spectrograph was not pro-

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[1] I. W. Obreimov and A. F. Prikhotjko, Physik Z. Sowjetunion **9**, 48 (1936) (in English).

[2] Obreimov, Prikhotjko, and Shabaldas, J. Exptl. Theoret. Phys. (U.S.S.R.) **6**, 1062 (1936) (in Russian).

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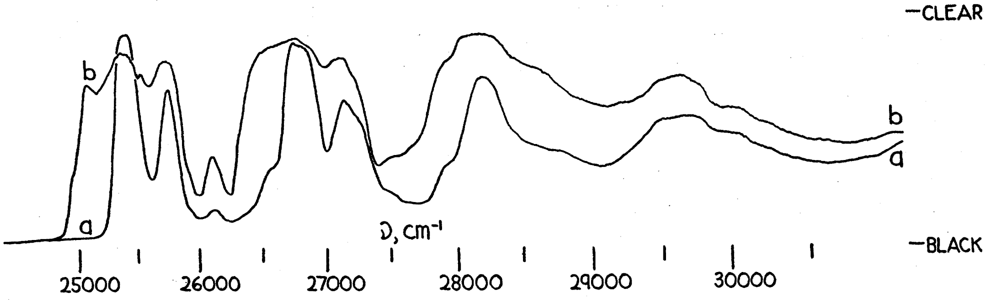

FIG. 1. Polarized absorption spectrum of anthracene crystal, *ab* plane, 4°K. Curve *a* is the spectrum for radiation polarized along the *a* axis, curve *b* for radiation polarized along the *b* axis.

ducing any polarization effects on the oppositely polarized beams.

A Hanovia high-pressure xenon arc and a tungsten strip filament lamp were used as light sources for studying the absorption spectra, and a General Electric Company AH–6 high-pressure mercury arc was used to excite the fluorescence. The filter combination used to remove the visible light from the source consisted of a Corning 9863 filter and a 2-cm path of a saturated aqueous solution of $NiSO_4 \cdot 6H_2O$. The glass of the Dewar absorbs source light of wavelengths less than 3200 A, so that the intense group of lines at 3650–3660 A was effective in exciting fluorescence. The crystal was not moved between measurements of absorption and fluorescence spectra. A 50-micron slit was used to photograph the spectra. Absorption spectra could be recorded in one-half to three minutes, and fluorescence spectra in one to five minutes.

The fluorescence spectra and the sharp structure in the absorption spectra were measured with a comparator, and wavelengths were calculated from a Hartmann dispersion formula which reproduced the wavelengths of the lines in the iron arc spectrum to 0.1 A. The centers of the lines were measured in all cases. The wavelengths of the broad maxima in the absorption spectra were measured from recording microdensitometer tracings of the plates.[10]

The accuracy of the measurements of the spectra is limited by the sharpness and background. Some of the lines are quite sharp, and are reproducible to 2 or 3 cm^{-1}. The accuracy of most of the fluorescence and absorption lines is less than this, and the broad absorption maxima are considered uncertain to ± 20 cm^{-1}. Many absorption and fluorescence lines are partially obscured by the broad and continuous absorption and fluorescence background which is seen on the plates and in the tracings.

III. RESULTS AND DISCUSSION

A. Absorption Spectra

1. The Strong Absorption

Several absorption spectra of crystals of different thickness were recorded. The absorption spectrum is quite complicated, and consists of at least two regions. In the *a*-axis polarization, the first detectable absorption begins with a strong, broad peak centered at $25\,400 \pm 20$ cm^{-1}. This peak coincides within limit of error with the first absorption maximum at 25 380 cm^{-1} reported by the Russian workers.[1] Craig and Hobbins[6] report the first peak at 25 350 cm^{-1}. The spectra from 25 400 to 30 000 cm^{-1} are very similar in both the *a* and *b* polarizations. The over-all absorption strength is somewhat greater in the *b* polarization. The energy of the absorption maxima is the same in both the *a* and *b* polarizations, within the limit of error of approximately 20 cm^{-1}. The dichroic splittings reported by Craig and Hobbins[6] are too small to be detected with certainty.

The polarized absorption spectrum of the anthracene crystal at 4°K is shown in a microphotometer tracing in Fig. 1. The energies and vibrational analysis of this absorption transition are given in Table I. The general agreement between these measurements and the measurements of the Russian workers[1] is fairly satisfactory. Although the Russian workers report some sharp lines in the *b*-polarized absorption above 25 300 cm^{-1}, these did not appear in the present work or in the work of Craig and Hobbins. The vibrational analysis indicates the prominence of vibrations of 350 and 1400 cm^{-1}. These are probably analogous to the prominent vibrations of 399 and 1401 cm^{-1} which appear in the absorption spectra of the anthracene in naphthalene or

TABLE I. Strong absorption spectrum of anthracene crystal, 4°K. The frequencies are uncertain by 20 cm^{-1}, and are the same in both *a* and *b* polarizations.

Intensity	ν, cm^{-1}	$\nu - 25\,400$	Assignment	Mixed crystal with naphthalene
vvs	25 400	0	0−0, free exciton band	$0-0=25\,856$, ${}^1B_{2u} \leftarrow {}^1A_g$
s	25 535	135		
vs	25 760	360	350, a_g	399, a_g
w, shoulder	25 930	430		
m	26 100	700	2(350)	
s	26 580	1180	1170, a_g	1164, a_g
vvs	26 790	1390	1400, a_g	1401, a_g
vs	27 140	1740	1400+350	
m, shoulder	27 500	2100	1400+2(350)	
ms	27 930	2530	1400+1170	
vs	28 200	2800	2(1400)	
s, very broad	28 650	3250	2(1400)+350	
m, broad	29 650	4250	3(1400)	
w, broad	30 000	4600	3(1400)+350	

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[10] The author is grateful to Professor John Phillips of the Astronomy Department for allowing him to use the recording microdensitometer in this and other investigations.

phenanthrene.[7] The difference between 350 cm^{-1} in the pure crystal and 399 cm^{-1} in the mixed crystal may be partly due to the breadth of the absorption maxima in the pure crystal, but some of the difference may also be due to differences in the environment. A vibration of 1170 cm^{-1} appears as a shoulder in the absorption spectrum of the crystal, corresponding to the 1164-cm^{-1} vibration in the mixed crystal.[7]

The strong band at 25 400 cm^{-1} is the origin of vibrational progressions in the broad absorption which appears in both the *a* and *b* polarizations. Above 25 400 cm^{-1}, the spectra are identical except for the greater intensity in the *b* polarization. Since there is no absorption in the *a* polarization which does not also appear in the *b* polarization, the dichroic splitting is therefore 0±20 cm^{-1}.

It is now necessary to consider the nature of the excited molecular state which gives rise to the free exciton band in the molecular crystal. The studies of the spectra of mixed crystals of anthracene in naphthalene and in phenanthrene have shown that the λ 3800 A transition is ${}^1B_{2u} \leftarrow {}^1A_g({}^1L_a \leftarrow {}^1A)$, polarized along the short molecular axis.[7] The transition is pure in the sense that the upper state is not perturbed by vibrational-electronic interaction in the mixed crystal, and all vibrations appearing in absorption and fluorescence are best assigned as a_g vibrations.

The small dichroic splitting of this transition in the crystal has been discussed by Craig,[4-6] who has shown it to be compatible with a short-axis molecular transition. Craig has shown that the red shift of this transition from the vapor[11] (27 540±20 cm^{-1}) to the crystal (25 400±30 cm^{-1}) is also compatible with a short-axis molecular transition. The ratio of absorption strength of the *b* to the *a* polarizations is much less less than the value calculated for the oriented gas model or the rigid lattice exciton model. Craig has interpreted this an an effect of crystal-induced mixing of a ${}^1B_{3u} \leftarrow {}^1A_g$ transition with the ${}^1B_{2u} \leftarrow {}^1A_g$ transition in the crystal.[5] Crystal-induced mixing of molecular states in naphthalene has been discussed by McClure and Schnepp.[12] It is significant that electronic mixing does not occur in the mixed crystal of anthracene in naphthalene,[7] even though the site symmetry (C_i) is low enough to permit such mixing. Crystal-induced mixing of molecular states may cause considerable difficulty if one attempts to deduce the symmetry of the upper electronic state from the polarization properties of the absorption spectrum of the crystal.[12]

To summarize, the strong, broad absorption bands which appear from 25 400 to 30 000 cm^{-1} in both *a* and *b* polarizations in crystalline anthracene at 4°K are interpreted as electronic-vibrational transitions to the two translationally allowed levels of the free-exciton band derived principally from the ${}^1L_a$, ${}^1B_{2u}$ state of anthracene. The two translationally allowed levels of the free-exciton band are accidentally degenerate, or nearly so, since the dichroic splitting[13] is undetectably small.

2. *The Weak, b-Polarized Absorption*

In addition to the strong, broad bands which appear in both *a* and *b* polarizations, there are many bands and "lines" which appear in this work in the *b* polarization but which are entirely absent from the *a* polarization. Even in crystals which are so thick that there is complete absorption in the *b* polarization above 25 400 cm^{-1}, absorption in the *a* polarization is undetectable at energies lower than the beginning of the 25 400 cm^{-1} absorption band. The structure of the *b* polarized absorption below 25 400 cm^{-1} is quite complex, due to the presence of both sharp "lines" (~20 cm^{-1} wide) and continuous absorption in the same region. From 25 060 to 25 400 cm^{-1}, a region of fairly strong absorption is seen in the *b* polarization in Fig. 1. A region of medium absorption intensity begins abruptly at 24 926 cm^{-1} in the *b* polarization and extends to the beginning of the strong *b* absorption at 25 060. Below 24 926 cm^{-1}, the absorption is very weak. A weak, sharp line appears at 24 809 cm^{-1}, followed by both continuous and discrete absorption in the same region. Weak absorption lines can be detected at 24 989 and 24 836 cm^{-1}, although the latter is so weak that it must be considered uncertain.

The *b*-polarized absorption of crystalline anthracene at 4°K is listed in Table II, and is seen in Fig. 1. Obreimov and Prikhotjko[1] report *b*-polarized absorption below the main absorption, but they report a weak, broad band at 24 760 cm^{-1} which has not been found in this work. They report a narrow band at 24 961 cm^{-1}, which may correspond to the line at 24 926 cm^{-1} found in this work, although the difference appears too great for the experimental error inherent in the measurements. The narrow band reported by them at 25 046 cm^{-1} is in fair agreement with the absorption at 25 060 cm^{-1} in this work. The Russian workers do not report the narrow bands between 24 809 and 24 926 cm^{-1} which have been found in this work. Craig and Hobbins[6] report the band at 25 060 cm^{-1} in both the *a* and *b* polarizations, and also report in both *a* and *b* polariza-

TABLE II. Weak absorption spectrum of anthracene crystal, 4°K. The absorption appears in the *b* polarization only.

Intensity	ν, cm^{-1}
vw, sharp	24 809±5
vvw, obscured	24 836 (?)
vw	24 989±10
m, sharp	24 926±5
m, continuous	<25 060
s, broad	25 060±20
w, continuous	<25 400

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[11] P. K. Seshan, Proc. Indian Acad. Sci. **3A**, 148 (1936).

[12] D. S. McClure and O. Schnepp, J. Chem. Phys. **23**, 1575 (1955).

[13] A. S. Davydov, J. Exptl. Theoret. Phys. (U.S.S.R.) **18**, 210 (1948) (in Russian).

tions other bands which have not been found in this work or in the work of Obreimov and Prikhotjko.[1] Although all workers agree that there is weak absorption to the red of the main absorption, the agreement about energies and polarization properties must be considered poor. These discrepancies will be discussed in the next section in reference to the fluorescence spectrum.

B. The Fluorescence Spectrum

The fluorescence spectrum is perhaps even more complex than the absorption spectrum. At 4°K, the fluorescence spectrum consists of broad bands with superimposed sharp structure. In agreement with the work of Pesteil and Barbaron[3] at 14°K and Obreimov, Prikhotjko, and Shabaldas[2] at 20°K, the fluorescence spectrum is polarized predominantly along the *b* axis. Craig[14] has concluded that the fluorescence and absorption spectra correspond to the same electronic transition, since both the absorption and fluorescence spectra are 1.5 to 2 times as intense in the *b* polarization as in the *a* polarization. His conclusions are based on observations of the spectra at room temperature. However, at 4°K, the spectra are much better resolved than at room temperature, and it is seen that the origin of the strong absorption at 25 400 cm^{-1} does not coincide with the origin of the fluorescence, which beings principally below 24 975 cm^{-1}. The fluorescence spectrum has several origins. Very weak continuous fluorescence which appears to be polarized completely along the *b* axis appears at 25 110±30 cm^{-1}. Prominent fluorescence appears at 24 975±20 cm^{-1} in both the *a* and *b* polarizations, and a broad, stronger origin appears at 24 946±10 cm^{-1} in both polarizations. The most prominent origins of the fluorescence are two narrow bands, one at 24 929±5 cm^{-1} and a very sharp band at 24 908±3 cm^{-1}. The fluorescence origins and the entire fluorescence spectra are more intense in the *b* polarization than in the *a* polarization, but the fluorescence is not completely polarized, except possibly for the very weak fluorescence at 25 110 cm^{-1}. As has been discussed in Sec. III A, the absorption spectrum shows completely polarized absorption along the *b* axis in the region of the origins of the fluorescence. Consequently, the fluorescence spectrum of the anthracene crystal at 4°K must be considered to be partially depolarized. The depolarization of the fluorescence relative to the corresponding absorption has been noted in the spectra of mixed crystals at low temperatures.[7] In the mixed crystal spectra, the fluorescence always originates from the 0−0 line of the absorption. The mixed crystal absorption spectra are polarized at all temperatures, but the polarization of the fluorescence of the mixed crystal depends on temperature. The polarization of the fluorescence of anthracene crystal at room temperature has been studied by Ganguly and Chaudhuri,[15] who find that the intensity is 1.54 times greater along the *b* axis than along the *a* axis. Although quantitative measurements were not carried out in this investigation at 4°K, visual observation of the tracings indicates that the ratio at 4°K is at least as great, and possibly greater. The fluorescence of crystalline anthracene at 4°K is partially polarized, whereas the fluorescence of anthracene in mixed crystals (solid solutions) with phenanthrene and naphthalene is depolarized at 20°K.

The vibrational analysis of the crystal fluorescence was carried out with the aid of the results of the solid solution fluorescence.[7] The analysis proves that the fluorescence is due to anthracene, and not to an impurity. Both the French[3] and Russian[2] workers agree that the prominent line at 24 908 cm^{-1} is the origin of the fluorescence analysis. This line was observed on one plate, but another plate showed strong fluorescence arising from a broader line at 24 929 cm^{-1}, corresponding to a prominent absorption line in the *b* polarization. However, the prominent origin at 24 929 cm^{-1} and other weaker fluorescence bands to the violet of 24 908 cm^{-1} have not been reported before. Fluorescence spectra of other molecular crystals which have been recorded by the author (i.e., biacetyl) occasionally showed slight but detectable differences. These observations suggest that the observed spectral variations may be due to dislocations in the different crystals, rather than to impurities.

The vibrational analyses of two fluorescence plates are given in Table III. The vibrational structure of the fluorescence of the crystal differs from that of the mixed crystal in several details. The crystal fluorescence shows prominent vibrational frequencies of 371 and 497 cm^{-1} which do not appear in the mixed crystal fluorescence, whereas the mixed crystal fluorescence shows a vibrational frequency of 1645 cm^{-1} which is not prominent in the crystal fluorescence. These differences are attributed to differences in the environment. Most of the vibrations which appear in the mixed crystal fluorescence also appear in the crystal fluorescence, as can be seen in Table III. Differences in the vibrational structure of the fluorescence in naphthalene crystal and in mixed crystals of naphthalene durene have been noted and discussed by McClure and Schnepp.[12]

A microphotometer tracing of the fluorescence of the crystal is shown in Fig. 2. The sharp structure is more prominent on the plate than on the tracing, and measurements were made from the plate. The spectra show no trace of tetracene impurity fluorescence.[16]

IV. INTERPRETATIONS—EVIDENCE FOR TRAPPED EXCITONS

It is possible to account for the gap between fluorescence and strong absorption, the appearance of several origins of fluorescence, and the appearance of the weak absorption on the basis of the trapped exciton theory

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[14] D. P. Craig, Rev. Pure Appl. Chem. (Australia) **3**, 207 (1953).

[15] S. C. Ganguly and N. K. Chaudhuri, J. Chem. Phys. **19**, 617 (1951).

[16] J. W. Sidman, J. Chem. Phys. (to be published).

TABLE III. Fluorescence spectrum of anthracene crystal, 4°K. The frequencies are uncertain by approximately 5 cm^{-1}, and are the same in both a and b polarizations.

(Plate A)

Intensity	ν, cm^{-1}	24 929 $-\nu$	Assignment	Mixed crystal with naphthalene
vs	24 929	0	0–0, trapped exciton level	0–0 = 25 856, $^1B_{2u}\rightarrow{}^1A_g$
vs, broad	24 892	37	37, lattice	30, 50, lattice
vs, broad	24 816	113	114, lattice	absent
vs, broad	24 783	146	114+37	
s	24 604	325		
vs	24 563	366	371	absent
s	24 516	413	415, a_g	403, a_g
s	24 489	440		
vs	24 435	494	497	absent
w	24 228	701		
w	24 172	757	757, a_g	752, a_g
m	23 909	1020		
s	23 766	1163	1163, a_g	1165, a_g
s	23 747	1182		
vs	23 665	1264	1264, a_g	1264, a_g
s	23 630	1299	1264+37	
m	23 545	1384		
vs	23 522	1407	1407, a_g	1416, a_g
s	23 494	1435	1407+37	
m	23 398	1531	1163+371	
vs	23 370	1559	1559, a_g	1567, a_g
s	23 153	1776	1407+371	
m	23 085	1844		
m, broad	22 367	2562	1407+1163	
s, broad	22 264	2665	1407+1264	
s, broad	22 113	2816	2(1407)	
s, broad	21 975	2954	1407+1559	

(Plate B)

Intensity	ν, cm^{-1}	24 908 $-\nu$	Assignment	Mixed crystal with naphthalene
vw; violet edge	25 110±20		Trapped exciton level	
m; violet edge	24 975±15		Trapped exciton level	
s; violet edge	24 946±10		Trapped exciton level	
vs, sharp	24 908	0	0–0, trapped exciton level	0–0 = 25 856, $^1B_{2u}\rightarrow{}^1A_g$
vvs, broad	24 872	36	37, lattice	30, 50, lattice
vvs, broad	24 793	115	114, lattice	absent
vs, broad	24 532	376	371	absent
vs, broad	24 490	418	415, a_g	403, a_g
vs, broad	24 407	501	497	absent
s, broad	24 288	620		
w	24 173	735	2(371)	
w	23 905	1003	1003, a_g; 2(497)	1003, a_g
w	23 795	1113		
w	23 768	1140		
m	23 744	1164	1163, a_g	1165, a_g
m	23 670	1238		
s	23 644	1264	1264, a_g	1264, a_g
s	23 531	1377		
vs	23 500	1408	1407, a_g	1416, a_g
s	23 470	1438	1407+37	
vs	23 383	1525	1163+371	
vs	23 350	1558	1559, a_g	1567, a_g
w?	22 371	2537	1407+1163?	
m, broad	22 256	2652	1407+1264	
s, broad	22 106	2802	2(1407)	
s, broad	21 958	2950	1407+1559	

of Frenkel[17] and Davydov.[18] According to Frenkel's original theory of the free exciton,[19] absorption of light by a molecular crystal can lead to an excited electronic state in which the excitation may move through the crystal in a manner which is formally equivalent to the motion of a particle (exciton). Frenkel's exciton theory was applied by Davydov to the ultraviolet spectra of molecular crystals,[13] and Davydov was able to account for the dichroic splittings observed in the spectra of many crystals on the basis of the free exciton theory. Frenkel has also considered the case in which the crystal lattice may become distorted in the vicinity of the exciton.[17] In such a case, the local distortion produced by the exciton can lead to its trapping at the site of the lattice distortion if the energy of the trapped exciton is less than the energy of the free exciton. Frenkel has discussed the necessary conditions for observing trapped excitons, and has predicted that they should be capable of existence in most molecular crystals. No experimental verification of Frenkel's predictions has been previously proposed.

The strong absorption band observed in both a and b polarizations at 25 400 cm^{-1} has been assigned to a transition from the ground electronic state to the two translationally-allowed levels of the free-exciton band of the molecular crystal. The weak absorption bands observed in the b polarization from 24 809 to 25 400 cm^{-1} are now assigned to transitions to trapped exciton levels of the molecular crystal. These transitions are weak in absorption because they correspond to non-vertical Franck-Condon transitions of the lattice, since the orientation of the molecule in the lattice is different in the upper and lower electronic states. Fluorescence from the free exciton level at 25 400 cm^{-1} is totally absent, indicating that radiationless conversion to the trapped exciton levels is very rapid. In this sense, the trapped exciton levels of the crystal are similar to levels of an added impurity, such as tetracene,[16] since they quench the fluorescence from the free exciton level by trapping the excitation. The trapped exciton levels at 24 929 and 24 908 cm^{-1} are particularly effective in trapping the excitation and emitting it as fluorescence. The probabilities of both radiative transitions from and nonradiative transitions to these trapped exciton states should be markedly affected by other crystal imperfections, such as dislocations. This could conceivably account for the differences in the weak absorption spectra and the fluorescence spectra reported by different workers. However, the significant fact that the origin of fluorescence is several hundred cm^{-1} below the origin of the strong absorption has been verified by all workers, and it is felt that this gap is not due to any spurious effects. In this connection, it should be noted that a similar gap between the origins of the absorption and the several origins of the fluorescence occurs in crystalline naphthalene[12] and in crystalline phenanthrene.[20] The trapped exciton theory of Frenkel is capable of

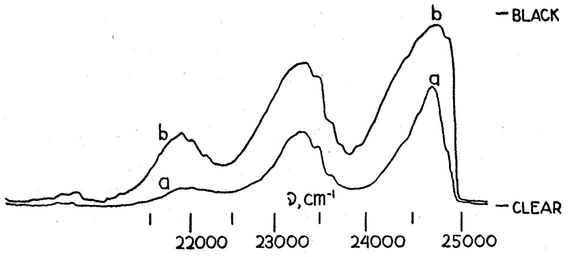

FIG. 2. Polarized fluorescence spectrum of anthracene crystal, ab plane, 4°K. Curve a is the spectrum for radiation polarized along the a axis, curve b for radiation polarized along the b axis.

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[17] J. Frenkel, Physik Z. Sowjetunion **9**, 158 (1936) (in English).

[18] A. S. Davydov, Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. **12**, 608 (1948) (in Russian).

[19] J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931).

[20] D. S. McClure (to be published).

accounting for this important phenomenon which is observed in the spectra of many molecular crystals.

V. FURTHER INTERPRETATIONS—A SEMIQUANTITATIVE VERIFICATION OF FRENKEL'S PREDICTIONS

The calculations by Craig give some quantitative support to Frenkel's trapped exciton theory. Craig has calculated the excitation exchange integrals for the $k=0$ levels of the anthracene crystal in the approximation which neglects electron exchange between different molecules and which also neglects all terms higher than dipole-dipole interaction terms in the expansion of the intermolecular potential of the crystal.[4] In another paper,[5] Craig has calculated the second-order effects due to crystal-induced mixing of the crystal states derived from different molecular states.

It is instructive to apply the calculations of Craig to Frenkel's predictions. The transition to the $k=0$ levels of the free exciton band is 2140 cm^{-1} lower than the $0-0$ band of the ${}^1B_{2u} \leftarrow {}^1A_g$ transition in the vapor.[7] The -2140 cm^{-1} shift is composed of two terms. One term, called D in Frenkel's and Craig's notation, is an exciton "Coulomb" energy term. This term is a measure of the change of the potential energy of interaction between a molecule and the surrounding molecules if this molecule is raised to an excited electronic state. Terms analogous to D are important even if the surrounding molecules are not identical with the molecule under consideration, as is the case in a solution or in a mixed crystal. The other term which contributes to the shift of the transition energy is an exciton "exchange" energy term, which determines the probability of exciton migration and the width of the free exciton band. This term is called J in Frenkel's notation and $(\sum_p I_{lp} \pm \sum_m I_{lm})$ in Craig's notation. Frenkel states that a necessary condition for trapping the exciton is that $|D_{mk}| \gg |J_{mk}|$. Since Craig has calculated the J_{mk} term, it is possible to evaluate D_{mk} from the difference between the vapor spectrum and crystal spectrum. Using Table III of reference 4, and setting $M=0.61$ A $(f=0.1)$, the value of $\sum_p I_{lp}$ is -450 cm^{-1}, whereas $\sum_m I_{lm}$ is negligible for the ${}^1B_{2u} \leftarrow {}^1A_g$ transition. The experimental spectral shift is -2140 cm^{-1} from vapor to crystal, and D is therefore calculated to be -1690 cm^{-1}. If second-order effects are considered (reference 5, Table III), the value of $\sum_p I_{lp}$ is approximately -650 cm^{-1}, which changes D to -1490 cm^{-1}. In either case, $|D|$ is seen to be considerably greater than $|J|$, in agreement with Frenkel's condition for trapping the exciton.

The above calculation has considered only the $k=0$ levels of the free exciton band, since these are the only levels which can be observed in the spectrum. The results should not be drastically different for the other levels in the band.

The value of D calculated from the crystal spectrum should be similar to the shift of the spectrum from vapor to mixed crystal, since the environment due to the neighboring molecules in the mixed crystal is not greatly different from the environment in the pure crystal. The principal difference is the inability to exchange excitation with the surrounding molecules in the mixed crystals, so that the only exciton state of the impurity molecule in the mixed crystal is necessarily a trapped exciton state. The spectral shift from vapor to mixed crystal is -1460 cm^{-1} in the mixed crystal of anthracene in phenanthrene and -1680 cm^{-1} in the mixed crystal of anthracene in naphthalene. These values agree well with the D values of -1490 to -1690 cm^{-1} calculated from the spectrum of anthracene crystal. Although this approximate calculation has neglected many terms which may be important in a more refined treatment, the results appear to indicate that Frenkel's condition for trapping an exciton is fulfilled in the anthracene crystal.

In a future paper, it will be shown that the spectra of other molecular crystals lend considerable support to Frenkel's theory of the trapped exciton.[21]

VI. CONCLUSIONS

The theory of free and trapped excitons appears to give a qualitative and semiquantitative interpretation of the observed gap between the origins of the absorption and fluorescence spectra of crystalline anthracene. Further experimental and theoretical work will be necessary before the electronic structure of molecular crystals and mixed crystals can be understood in all details.

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[21] D. S. McClure and J. Sidman (to be published).