reaction, but also by being swept into the cold space by the attending pressure increase. Such additional loss of reactant will appear as a higher effective order of reaction and as a higher inverse power in the t_1 vs $[N_2O]_0$ relation.

The approximate quantum yield of 10^{-5} for the ratio of quanta emitted per molecules of N_2O decomposed leads to an interesting comparison. Neuberger and Duncan[21] recently reported the lifetime of NO_2 excited by radiation of wavelengths 3900 to 4600 A to be 44 μsec. If every decomposing N_2O molecule gave rise to an excited NO_2^* which could be deactivated by collision or could radiate, the observed quantum yield would be equal to the ratio of collision to radiation half-life. That ratio, at the conditions of our experiments, and using Neuberger's value, does turn out to be about 10^{-5}. This would seem to indicate that the above assumption is approximately correct; that NO_2^* is a major intermediate; and that reaction (4) is really a succession of two steps, binary activation, (4'), and collisional deactivation. However, it is more likely that the identification of NO_2^* present in fluorescence and in the $NO+O$ continuum is not permissible. In that case, one might expect the recombination forming NO_2^* to have a normal half-life of 10^{-7} to 10^{-8} sec, and radiative recombinations would then account for only a small fraction (about 10^{-3}) of the normal termolecular reaction (4).

In agreement with their effect on the rate of formation of NO, added inert gases decrease the glow in the order $O_2>N_2>A>He$ with O_2 giving the greatest reduction. This can be thought to represent relative quenching efficiency for NO_2^*, similar to third body efficiency in (4) as discussed above for the decrease of $p_\infty NO$.

The experiments describing the slow onset of the glow at low N_2O pressures and its much faster rise with addition of some NO (Fig. 4) is also well explained by the above expressions. At low rates of decomposition, the first two terms in the denominator of (e) cannot be neglected and L will reach its maximum value slowly.

Using the calculated values for $k_{2\,to\,5}$ and the experimental values for $[NO]$ as function of time, we calculate a rise time of about 2 minutes under the experimental conditions, in good agreement with the observed value.

The strong inhibition of the glow by atomic halogen is in line with the decrease of NO formed. The fact that p_X is between 10 to 100 times smaller than the corresponding pressure of halogen which lowers the initial rate of formation of NO by one-half is also easily explained. p_X, the concentration of halogen which reduces the glow by one-half, determines the product $[NO][O]$, and since atomic halogen decreases the steady-state oxygen concentration and thereby also the rate of formation of NO, the product $[NO][O]$ is lowered more than $[NO]$ alone by a given amount of halogen. Thus, the glow is more sensitive to addition of inhibitor than is the rate of formation of NO.

[21] D. Neuberger and A. B. F. Duncan, J. Chem. Phys. 22, 1693 (1954).

Electronic and Vibrational States of Anthracene*†

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(Received August 18, 1955)

The polarized absorption and fluorescence spectra of anthracene have been measured in dilute solid solution in single crystals of naphthalene and phenanthrene at 20°K. The lowest singlet-singlet transition is proven to be polarized along the short molecular axis, and hence $^1B_{2u}{-}^1A_g$ ($^1L_a{-}^1A$), in agreement with theoretical predictions. Vibrational frequencies are compared in the ground state and in the first excited state. The polarization of the fluorescence of anthracene in phenanthrene has also been studied as a function of temperature. The fluorescence is partially polarized at 300°K, but is depolarized at 20°K.

I. INTRODUCTION

THE electronic spectrum of anthracene has recently received considerable study from both an experimental and theoretical viewpoint. The intense short

wavelength absorption has been photographed in the crystalline state by Craig and Hobbins.[1] The weaker long wavelength absorption spectrum of single crystals of anthracene has been photographed at 20°K by Obreimov and Prikhotjko,[2] and the fluorescence of crystalline anthracene has been photographed at 20°K

[1] D. P. Craig and P. C. Hobbins, J. Chem. Soc. 1955, 539.
[2] I. W. Obreimov and A. F. Prikhotjko, Physik. Z. Sowjetunion 9, 48 (1936).

by Obreimov and co-workers,[3,4] and more recently at 14°K by Pesteil and Barbaron.[5]

Theoretical treatments of the spectra of the polyacenes have been given by Klevens and Platt,[6] Moffitt,[7] and Pariser.[8] These workers agree that the lowest transition in anthracene should be polarized along the short molecular axis ($^1L_a-^1A$ in Klevens and Platt's notation, $^1B_{2u}-^1A_g$ in gronp theoretical notation[9]).

There are several indirect lines of experimental evidence which support this. Jones[10] has studied the effects of methyl substitution on the absorption spectrum of anthracene, and Pesteil[5] has studied the polarization of the fluorescence of anthracene in the crystalline state and in solid solutions in stilbene and in tolane. Both Jones and Pesteil have concluded that the lowest transition is polarized along the short molecular axis.

The most direct method for determining the polarization of an electronic transition is to study the absorption spectrum in solid solution in a single crystal of another aromatic hydrocarbon. Using this technique, McClure[11] has shown that the transition with the lowest excited singlet state of naphthalene is long axis polarized, whereas the transition with the second excited singlet state of naphthalene is short axis polarized, in agreement with theoretical predictions.[6-8] Since theory predicts that the lowest excited singlet states of naphthalene and anthracene have different polarizations, it appeared desirable to determine directly the
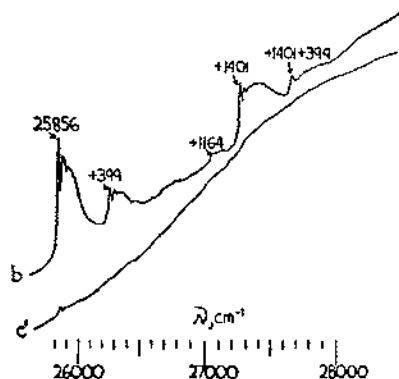

FIG. 1. Polarized absorption spectrum of anthracene in naphthalene, bc' plane, 20°K, tuugsten source. The slope is due only to a decrease in the intensity of the source at higher frequencies.

TABLE I. Crystal structures of naphthalene, anthracene, and phenanthrene.

Space group Unit cell	Naphtha-lene[a] $P2_1/a$	Anthra-cene[b] $P2_1/a$	Phenanthrene[c,d] $P2_1/a$	Phenanthrene[c,d] $P2_1$
a, A	8.29	8.56	8.66	8.57
b, A	5.95	6.04	6.11	6.11
c, A	8.68	11.16	19.24	9.47
β	122.1°	124.6°	98°	82°30'
Molecules per unit cell	2	2	4	2

[a] J. M. Robertson, Proc. Roy. Soc. (London) A141, 594 (1933); A142, 659 (1933).
[b] Sinclair, Robertson, and Mathieson, Acta Cryst. 3, 245 (1950).
[c] J. D. Bernal and D. Crowfoot, J. Chem. Soc. 1935, 93.
[d] B. Basak, Indian J. Phys. 24, 309 (1950).

polarization of the lowest transition in anthracene by the technique which has been successful for naphthalene[11] and for azulene.[13]

II. EXPERIMENTAL

Eastman Kodak anthracene of the blue-violet fluorescence grade was used without further purification. The naphthalene and phenanthrene exhibited no absorption in the region 26 000 to 28 000 cm^{-1} in crystals as thick as 1 mm.

Single crystals of naphthalene containing trace amounts of added anthracene were grown by a method which has been previously described.[11] Further attempts to increase the concentration of anthracene in naphthalene were unsuccessful, indicating that the naphthalene crystal was saturated with dissolved anthracene, corresponding to an anthracene concentration of 0.001%.[13] The bc' plane of naphthalene, which is perpendicular to the cleavage plane, was selected for observation,[12] and the small crystal was polished to 0.3 mm thickness. Observation of the crystal under the polarizing microscope indicated the presence of only one phase, and the extinction properties of the crystal between crossed Nicol prisms showed it to be a single crystal.

Single crystals of phenanthrene containing 0.2% added anthracene were also prepared. The absorption of a crystal of 0.3 mm thickness was too great, so that a thinner crystal was prepared by solidification from a melt between quartz disks, and a monocrystalline area of the thin crystal was used to photograph the spectra. Microscopic examination of the isogyre pattern of the thin crystal which solidified from the melt indicated that the plane under observation was the ab plane, which is the most prominent cleavage plane of the phenanthrene crystal. Diagrams showing the molecular arrangements in the crystals of naphthalene and anthracene can be readily found in references given in Table I.

Absorption and fluorescence spectra of the single crystals were photographed as previously described.[11] The λ3130 A Hg lines from a high-pressure Hg arc[12]

[3] I. W. Obreimov and A. F. Prikhotjko, J. Exptl. Theoret. Phys. 6, 1062 (1936).
[4] I. W. Obreimov and C. G. Shabaldos, J. Pbys. U.S.S.R. 7, 168 (1943).
[5] P. Pesteil and M. Barbaron, J. phys. radium 15, 92 (1954).
[6] J. R. Platt, J. Chem. Phys. 17, 484 (1949).
[7] W. Moffitt, J. Chem. Phys. 22, 320 (1954).
[8] R. Pariser, Talk at the Symposium on Molecular Structure and Spectra at the Ohio State University, June, 1954; J. Chem. Phys. 24, 250 (1956).
[9] Herzberg, Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Company, Inc., New York, 1945).
[10] R. N. Jones, J. Am. Chem. Soc. 67, 2127 (1945).
[11] D. S. McClure, J. Chem. Phys. 22, 1668 (1954).

[12] J. W. Sidman and D. S. McClure, J. Chem. Phys. 24, 756 (1956).
[13] G. T. Wright, Proc. Phys. Soc. (London) A66, 777 (1953).

were used to excite the fluorescence of anthracene in the mixed crystals. The crystal was immersed in the liquid refrigerant during the low temperature measurements.

III. ANTHRACENE IN NAPHTHALENE AT 20°K

A. Polarization Measurements

The absorption spectrum of anthracene at 20°K in the bc' plane of naphthalene is quite sharp and is completely polarized along the b axis. A microphotometer tracing of this transition is shown in Fig. 1. The sharpness of the anthracene absorption spectrum in this medium indicates that the anthracene molecules all occupy equivalent lattice positions and orientations.

The crystal structure of anthracene is quite similar to the crystal structure of naphthalene, as is shown in Table I. It is therefore reasonable to assume that the anthracene molecules are oriented in the substitutional solid solution in the same manner as the naphthalene molecules, so that the short and long axes of the anthracene molecule correspond, respectively, to the b and c' axes in the bc' plane of the mixed crystal. The polarization of the absorption transition of the mixed crystal then indicates that the molecular transition is polarized along the short molecular axis, and is therefore $^1B_{2u} \leftarrow {}^1A_g ({}^1L_a \leftarrow {}^1A)$, in complete agreement with all previous evidence.

The corresponding fluorescence spectrum of anthracene in naphthalene at 20°K has also been photographed. Although the naphthalene fluorescence does appear, it is not intense enough to mask the anthracene fluorescence, which begins strongly at 25 856 cm^{-1}. The anthracene fluorescence spectrum was recorded with the same crystal used to photograph the absorption spectrum, and the crystal was not moved between exposures. A microphotometer tracing of the fluorescence of anthracene in naphthalene is shown in Fig. 2. Since the absorption transition is polarized along the b axis, it is surprising to find that the fluorescence spectrum is depolarized. Anomalies in the polarization of fluorescence have been noted in the fluorescence spectra of naphthalene in durene[11] and azulene in naphathalene,[12] as well as fluorescence spectra of other solid solutions studied in this laboratory.

B. Vibrational Analyses

The lowest frequency line of the absorption spectrum coincides within 2 cm^{-1} with the highest frequency line of the fluorescence spectrum. This line at 25 856 cm^{-1} is therefore assigned to the O—O line of the $^1B_{2u} - {}^1A_g$ electronic transition of anthracene in naphthalene. The vibrational analysis of the absorption spectrum is given in Table II, and the vibrational analysis of the fluorescence spectrum is given in Table III.
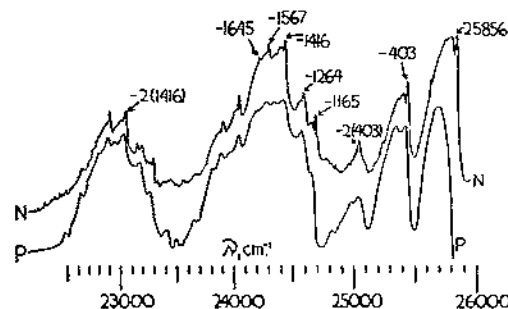

Fig. 2. Fluorescence spectrum of anthracene. N: in naphthalene, b axis of bc' plane, 20°K. The c' axis fluorescence is slightly less intense than the b axis fluorescence, but is otherwise identical. P: in phenanthrene, b axis of ab plane, 20°K. The a axis fluorescence is nearly identical (see Fig. 4). This spectrum has been shifted 224 cm^{-1} to lower energies in order to show the similarity in vibrational structure to the fluorescence spectrum of anthracene in naphthalene.

IV. ANTHRACENE IN PHENANTHRENE AT 20°K

A. Polarization Measurements

The absorption and fluorescence spectra of anthracene have also been studies in the ab (cleavage) plane of phenanthrene. Microphotometer tracings of the absorption and fluorescence spectra of anthracene in the ab plane of phenanthrene at 20°K are shown in Figs. 2 and 3.

Anthracene and phenanthrene are known to form solid solutions over the entire concentration range,[14] and considerable care is necessary to completely remove the anthracene from phenanthrene. Thus, the polarized absorption spectrum of phenanthrene crystal in the ab plane has been photographed at 20°K by Obreimov and Prikhotjko,[15] who report the appearance of a "forespectrum" consisting of bands at energies lower than the main phenanthrene spectrum. The "forespectrum" is more intense in the b component ("broad" spectrum) than in the a component ("narrow" spectrum), and is sharper and much weaker than the "main" spectrum at 20°K. The absorption spectrum of anthracene-free

TABLE II. Vibrational analysis of the absorption spectrum of anthracene in naphthalene, 20°K.

Int.[a]	ν, cm^{-1}	$\nu - 25\,855$	Assignment
vvs	25 855	0	$^1B_{2u} \leftarrow {}^1A_g$
s, l	25 881	26	26, lattice
s	26 254	399	399, a_g
m, l	26 280	425	399+26
m	27 019	1164	1164, a_g
vs	27 256	1401	1401, a_g
m, l	27 283	1428	1401+26
m, l	27 306	1451	1401+2(26)
m, l	27 331	1476	1401+3(26)
w, l	27 357	1502	1401+4(26)
w	27 649	1794	1401+399
w	28 662	2807	2(1401)

[a] v =very. s =strong. m =medium. w =weak. l =lattice.

[14] Bradley and Marsh, J. Chem. Soc. 1933, 650.

[15] I. W. Obreimov and A. F. Prikhotjko, Physik. Z. Sowjetunion 9, 34 (1936).

TABLE III. Vibrational analysis of the fluorescence spectrum of anthracene in naphthalene, 20°K.

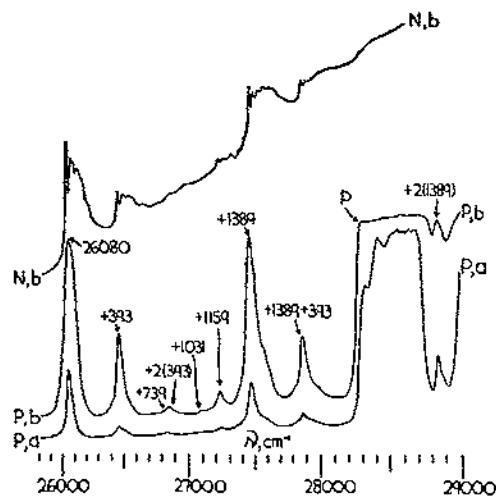| Int.	ν, cm^{-1}	25 857 $-\nu$	Assignment
vs	25 857	0	$^1B_{2u}\rightarrow{}^1A_g$
s, l	25 827	30	30, lattice
s, l	25 807	50	50, lattice
m, l	25 776	81	50+30
s, l	25 755	102	2(50)
w	25 535	322	
w	25 459	398	
vs	25 454	403	403, a_g
w, l	25 428	429	403+30
w, l	25 408	449	403+50
w, l	25 369	488	403+50+30
w, l	25 356	501	403+2(50)
w	25 235	622	622, a_g
w	25 105	752	752, a_g
m, broad	25 057	800	2(403)
vw	24 854	1003	1003, a_g
s	24 692	1165	1165, a_g
w	24 673	1184	
s	24 593	1264	1264, a_g
vvs	24 441	1416	1416, a_g
vs, l	24 413	1444	1416+30
vs, l	24 397	1460	1416+50
vs	24 290	1567	1567, a_g; 1165+403
s, l	24 263	1594	1567+30
s, l	24 244	1613	1567+50
s	24 212	1645	1645, a_g
s	24 042	1815	1416+403
m	23 894	1963	1567+403
w	23 812	2045	1645+403
m	23 276	2581	1165+1416
m	23 173	2684	1264+1416
w	23 120	2737	
s	23 027	2830	2(1416)
ms	22 875	2982	1165+1416+403
w	22 802	3055	1645+1416 ?
w	22 721	3136	
vw	22 616	3241	2(1416)+403
vw	22 586	3271	
vw	22 477	3380	1165+1416+2(403)

FIG. 3. Polarized absorption spectrum of anthracene in phenanthrene and in naphthalene. N,b: in naphthalene, b axis of bc' plane, 20°K, tungsten source. This spectrum has been shifted 224 cm^{-1} to higher energies in order to show the similarity in vibrational structure to the absorption spectrum of anthracene in phenanthrene. P,b: in phenanthrene, b axis of ab plane, 20°K, Xe source. P,a: in phenanthrene, a axis of ab plane, 20°K, Xe source (same crystal as for P,b).

phenanthrene does not show any of the "forespectrum" found by the Russian workers.[16] Most of the bands of the "forespectrum" of phenanthrene agree within limits of error with the absorption bands of anthracene in phenanthrene, as is seen in Table IV.[17]

B. Vibrational Analysis

The vibrational analysis of the absorption spectrum of anthracene in phenanthrene is given in Table IV. The vibrations agree with the values deduced from the absorption of anthracene in naphthalene. The O−O band of the $^1B_{2u}$−^1A_g transition lies at 26 080 cm^{-1}, which is a shift of 224 cm^{-1} to the violet from the O−O band of anthracene in naphthalene. The similarity of the vibrational structure of the spectra in the two different mixed crystals is readily seen in Figs. 2 and 3.

V. COMPARISON OF VIBRATIONAL FREQUENCIES

A. Comparison between the $^1B_{2u}$ and ^1A_g States

The vibrational frequencies of anthracene in the $^1B_{2u}$ and ^1A_g states are given in Table V. Several of the weak lines in the fluorescence spectrum have not been assigned, and these may correspond to other vibrational fundamentals or combinations. The most prominent vibrational frequency is 1416 cm^{-1} in fluorescence (1401 cm^{-1} in absorption). A corresponding vibrational frequency appears in the electronic transitions of other condensed aromatic hydrocarbons which have been studied in this laboratory.[11,12] This frequency generally lies between 1350 and 1430 cm^{-1} in these molecules, and is very prominent in all of the absorption and fluorescence spectra. The corresponding frequency in the ^1A_g state of naphthalene is 1380 cm^{-1}, and has been

TABLE IV. Vibrational analysis of the absorption spectrum of anthracene in phenanthrene, 20°K.

Int.	ν, cm^{-1}	ν−26 080	Assignment	Obreimov and Prikhotjko[a]
vs	26 080	0	$^1B_{2u}\leftarrow{}^1A_g$, O−O	26 073
s	26 473	393	393, a_g	26 467
w	26 819	739	739, a_g	
w	26 860	780	2(393)	
w	27 111	1031	1031, a_g	
w	27 239	1159	1159, a_g	
w	27 419	1339		
vs	27 469	1389	1389, a_g	27 468
w	27 512	1432	1031+393	
w	27 588	1508		
w	27 640	1560	1159+393; 1560 ?	
w	27 809	1729		
m	27 860	1780	1389+393	27 842
w	27 973	1893		
vvs	28 283	. . .	phenanthrene absorption	
m	28 841	2761	2(1389)	28 839

[a] See reference 15.

[16] D. S. McClure (unpublished results).
[17] The author is grateful to Professor D. S. McClure for suggesting this explanation of the "forespectrum" of phenanthrene.

TABLE V. Vibrational frequencies of anthracene.

Fluorescence of anthracene in naphthalene, 20°K	Fluorescence of crystal, 14°K [a]	In the ¹A_g electronic state			Absorption of anthracene in naphthalene and phenanthrene, 20°K	In the ¹B_{2u} electronic state		
		Phosphorescence of rigid solution 77°K [b]	Fluorescence of vapor [e]	Raman Spectrum of solution [d]		Absorption of crystal, 20°K [e]	Absorption of vapor, 470°K [c]	Absorpt ion of rigid solution, 90°K [f]
30, lattice					26, lattice			
50, lattice	42, lattice							
	114, lattice ?							
	319, w							
	367, s							
403, vs (398, w)	398, m	409	250	388 (1)	399, s	350 (400), s	360	400
	419, s							
	445, m							
	500, vs			521 (0)				
	559, s							
752, w	752, w			751 (½)				
1003, vw				1007 (½)	1031, w			
1165, s	1167, s			{1161 (½) / 1178 (½)}	1164, m			
1264, s	1266, vs	1268		1262 (1)				
1416, vvs	1411, vvs	1410	1350	{1400 (8) / 1478 (½)}	1401, vs	1400, vs	1430	1450
1567(1165+403), vs	1559, s	1556		1558 (3½)				
1645, s	1638, s			1631 (3)				

a See reference 5.
b Padhye, McGlynn, and Kasha, J. Chem. Phys. 24, 588 (1956).
c G. Kortüm and B. Finckh, Z. physik. Chem. B52, 263 (1942).
d G. Manzoni-Ansidei, Ricerca Sci. Ser. II, Anno VII, I, n. 7-8, 314-315 (1936).
e See reference 2.
f See reference 19.

assigned by Lippincott and O'Reilly[18] to the stretching of the central C—C bond (ν_4), called the gamma carbon stretching. This vibrational frequency therefore appears to be relatively constant in the various electronic states of the aromatic hydrocarbons.

A skeletal bending vibration is also prominent in both fluorescence (403 cm⁻¹) and absorption (399 cm⁻¹). A vibration of 1165 cm⁻¹ in fluorescence (1164 cm⁻¹ in absorption) may correspond to a C-H bending or skeletal stretching motion. A 1645 cm⁻¹ skeletal stretching motion appears in fluorescence. Its analog has not been located with certainty in absorption.

Lattice modes appear as fine structure in the electronic-vibrational transitions in the substitutional solid solution. Lattice modes of 31 and 51 cm⁻¹ are seen in the fluorescence of anthracene in naphthalene, whereas long progressions of a 26 cm⁻¹ lattice mode are seen in absorption of anthracene in naphthalene. The spectra of anthracene in phenanthrene are too broad to resolve lattice structure.

B. Comparison between Spectra in Different Media

In Table V, the vibrational frequeucies of anthracene in the ¹A_g and ¹B_{2u} states are compared, using the results of this and other work. The general agreement between different measurements is satisfactory, considering the lower resolution and broader spectra in references b, c, e, and f of Table V. Some of the differences are probably real, and are attributed to differences in the environment. Vibrational assignments are given in Table VI.

VI. VARIATION OF O—O BAND WITH ENVIRONMENT

The energy of the O—O band of the lowest singlet-singlet transition of anthracene is dependent on the

TABLE VI. Vibrational assignments for anthracene.

ν, cm⁻¹ in ¹A_g (electronic state)	ν, cm⁻¹ in ¹B_{2u} (electronic state)	Assignment	Related motion in naphthalene [a]
403	399	Skeletal bend, a_g	ν_9
752	739 ?	Skeletal bend, a_g	ν_8
1003	1031 ?	Skeletal breathing, a_g	ν_6
1165	1164	Skeletal breathing and CH bending, a_g	ν_6 ?
1264		CH bending, a_g	ν_5
1416	1401	Gamma C stretching, a_g	ν_4
1567		CC stretching, a_g	ν_1
1645		CC stretching, a_g	ν_3

a See reference 18.

18 E. R. Lippincott and E. J. O'Reilly, Jr., J. Chem. Phys. 23, 238 (1955).

TABLE VII. The O—O band of the lowest transition of anthracene, $^1B_{2u}-^1A_g$.

Medium	Absorption	Fluorescence	Average, cm⁻¹
Vapor, 470°K[a]	27 560	27 380	27 470
In methanol-ethanol solvent, 291°K[b]	26 695		26 695
In dioxane, 300°K[a]	26 500	26 220	26 360
In methanol-ethanol rigid glass, 90°K[b]	26 410		26 410
In phenanthrene crystal, 20°K	26 080	26 075	26 078
In naphthalene crystal, 20°K	25 857	25 855	25 856
In crystalline anthracene, 20°K[c] and 14°K[d]	25 370	24 899	(Crystal effects)[e]

[a] See reference c of Table V.
[b] See reference 19.
[c] See reference 2.
[d] See reference 5.
[e] The gap between absorption and fluorescence in crystalline anthracene is due to trapped excitons. See J. W. Sidman, Phys. Rev. 102, 96 (1956).

environment, as is seen in Table VII. The apparent difference between the O—O bands of absorption and fluorescence in the vapor of solution spectra is due both to partial reabsorption of the origin of the fluorescence and to lack of resolution of the lowest vibrational intervals. Both of these effects increase the gap between the first absorption and first fluorescence maximum. The effect of unresolved vibrational structure on the position of the first absorption maximum is seen in a comparison of the absorption spectrum of anthracene in methanol-ethanol at 291°K and at 90°K,[19] At 291°K, in the liquid solution, the 1450 cm⁻¹ progressions are resolved, but the 400 cm⁻¹ progressions are not, and the first broad absorption peak is at 26 695 cm⁻¹. At 90°K in the rigid glassy solution, the 400 cm⁻¹ progressions are resolved, and the first broad peak is resolved into three peaks, corresponding to the O—O band at 26 410 cm⁻¹ and vibrational additions of 400 and 2 (400) cm⁻¹.

VII. DISCUSSION OF THE POSSIBILITY OF A HIDDEN LONG-AXIS TRANSITION

The correlation scheme of Klevens and Platt[6] predicts a weaker long axis transition, $^1B_{3u}\leftarrow^1A_g$ ($^1L_b\leftarrow^1A$), to be hidden under the $^1B_{2u}\leftarrow^1A_g$ ($^1L_a\leftarrow^1A$) transition of anthracene. This hidden transition has also been predicted by Pariser's calculations.[8] The absorption spectrum of the rigid solution of anthracene in menthanol-ethanol has been recorded by Clar,[19] who finds evidence for a hidden transition in the spectrum. A vibrational analysis of the absorption spectrum of anthracene in the rigid glassy solution at 90°K is given in Table VIII. All of the maxima can be assigned to combinations and progressions of the 400 and 1450 cm⁻¹ vibrations in the absorption spectrum of the mixed crystal. The analysis of the rigid solution spectrum therefore does not provide evidence for a hidden transition.

The hidden $^1B_{3u}\leftarrow^1A_g$ transition in the mixed crystal of anthracene in naphthalene should appear in the c' polarization in the bc' plane. This transition is expected to be only one-tenth as intense as the $^1B_{2u}\leftarrow^1A_g$ transition, so that a single crystal of several centimeters in thickness would be necessary in order to detect the hidden long-axis transition in the mixed crystal. It has not been possible to grow a mixed crystal which was both thick enough and optically perfect to detect the possible hidden transition. Consequently, it is not possible at the present time to say anything more definite about the hidden long-axis transition of anthracene.

Thus, the long wavelength absorption is best interpreted as a single electronic transition which is polarized along the short molecular axis, and the vibrational intervals which combine with the O—O line are therefore interpreted as a_g vibrations of anthracene in the $^1B_{2u}$ electronic state.[20] The blue-violet fluorescence of anthracene corresponds to the reverse of the lowest absorption, and the vibrations appearing in the fluorescence spectrum correspond to a_g vibrations in the ^1A_g ground electronic state.

VIII. TEMPERATURE DEPENDENCE OF THE ANOMALOUS DEPOLARIZATION OF THE FLUORESCENCE OF ANTHRACENE IN PHENANTHRENE

The anomalous depolarization of the fluorescence spectra of many mixed crystalline solid solutions at 20°K has been mentioned. Several workers[21] have reported polarized fluorescence spectra of anthracene

TABLE VIII. Vibrational analysis of the absorption spectrum of anthracene in a methanol-ethanol solvent.[a]

(a) $T=290°K$ (liquid solution)				
Int.	λ, A	ν, cm⁻¹	ν—26 690	Assignment
vs	3745	26 690	0	Apparent O—O band
s	3545	28 200	1510	1450, a_g
m	3380	29 580	2890	2(1450)
w	3230	30 950	4260	3(1450)
vw	3080	32 460	5770	4(1450)

(b) $T=90°K$ (rigid glassy solution)				
Int.	λ, A	ν, cm⁻¹	ν—26 410	Assignment
vs	3785	26 410	0	$^1B_{2u}\leftarrow^1A_g$, O—O band
s	3730	26 800	390	400, a_g
m	3675	27 200	790	2(400)
vs	3590	27 850	1440	1450, a_g
s	3543	28 200	1790	1450+400
m	3485	28 690	2280	1450+2(400)
s	3410	29 320	2910	2(1450)
m	3355	29 800	3390	2(1450)+400
m	3250	30 760	4350	3(1450)
w	3105	32 200	5790	4(1450)
vw	2975	33 600	7190	5(1450)

[a] See reference 19.

[19] Clar, Spectrochim. Acta 4, 116 (1950).

[20] H. Sponer and E. Teller, Revs. Modern Phys. 13, 75 (1941).
[21] (a) S. C. Ganguly and N. K. Choudhury, J. Chem. Phys. 21, 554 (1953). The fluorescence ascribed by these workers to crystalline phenanthrene is due to anthracene impurity. I am grateful to Professor D. S. McClure for this observation. (b) K. S. Krishnan and P. K. Seshan, Acta Phys. Polon. 5, 289 (1936).

in phenanthrene or tetracene in anthracene at room temperature. As is expected in a crystalline medium, the polarization of the fluorescent light is independent of the polarization of the exciting light.[21b] Since the fluorescence spectra of anthracene in naphthalene or in phenanthrene are depolarized at 20°K, it was decided to study the spectra at different temperatures. The fluorescence spectra of anthracene in the ab plane of phenanthrene are shown in Fig. 4 at 300°K, 77°K, and 20°K. In agreement with other workers,[21a] the fluorescence at 300°K is polarized, and is more intense along the b-axis than along the a-axis. This is expected from the observed polarization of the absorption spectra at 300°K. However, the fluorescence at 77°K is almost depolarized. At 20°K, the fluorescence is completely depolarized near the O—O band. In contrast, the absorption spectrum is polarized at all temperatures. The results are easily reproducible, and a similar effect has been observed in the spectra of tetracene in anthracene.[22]

These experiments show that the polarization of the absorption spectrum of this mixed crystal does not depend on temperature, whereas the polarization of the fluorescence spectrum does depend on temperature. The fluorescence spectra become depolarized as the temperature decreases.

It is difficult to account for these results. At higher temperature, the spectra are broader, and the absorption and fluorescence spectra overlap at the origin. This leads to partial reabsorption of the fluorescence bands of highest energy, and this is apparent in the spectra shown in Fig. 4. In randomly oriented rigid glassy solutions, reabsorption of polarized fluorescent light causes depolarization of the observed fluorescence.[23] Reabsorption is not expected to have any effect on the polarization of the fluorescence of a mixed crystalline solid solution in which the molecules are oriented. In any event, the low temperature spectra in which there is no overlap of absorption and fluorescence (except for the O—O band) and in which reabsorption is minimized are the spectra which show depolarization of the fluorescence.

Pesteil and Barbaron[5] have observed that the fluorescence of crystalline anthracene is polarized predominantly along the b axis in the ab plane at 300°K,

[22] J. Sidman, J. Chem. Phys. 25, 122 (1956), following paper.
[23] T. Förster, *Fluoreszenz und Phosphoreszenz Organischer Verbindungen* (Springer-Verlag, Berlin, 1952).
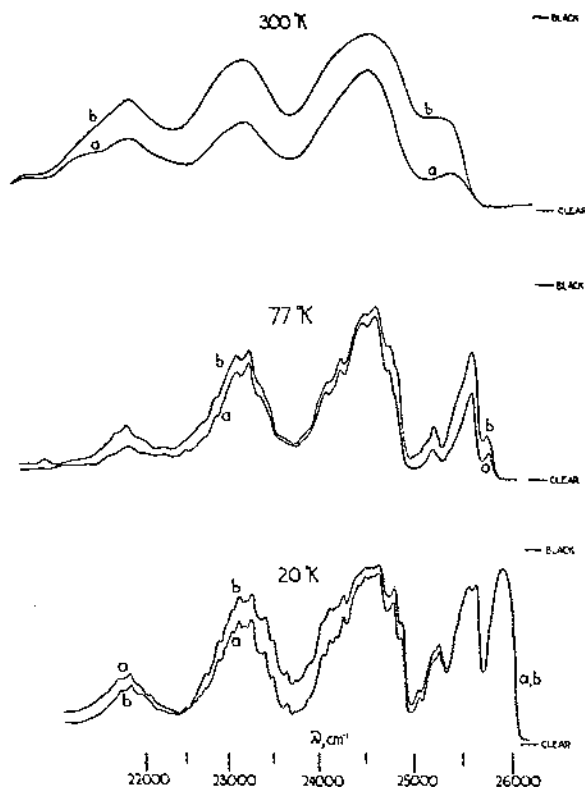
FIG. 4. Polarized fluorescence spectrum of anthracene in phenanthrene, ab plane, at 300°K, 77°K, and 20°K. The high-energy region of the fluorescence is reabsorbed at high temperatures, owing to overlap of absorption and fluorescence.

77°K, and 14°K. These results have been verified in this laboratory, indicating that the apparatus did not cause any anomalous depolarization and that the results of other workers could be reproduced.

Prolonged illumination of the mixed crystals did not change the polarization of the absorption or fluorescence spectra, indicating that no permanent reorientation of the molecules has occurred due to excitation. The anomalous polarization of the fluorescence of these mixed crystals as well as the observed temperature dependence are thought to be due to environmental effects. Further experiments on this subject are in progress.

IX. ACKNOWLEDGMENTS