Molecular Crystals

The Absorption Spectrum of Phenanthrene Crystals Beyond 3000 Å

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The Absorption Spectrum of Phenanthrene Crystals Beyond 3000 Å

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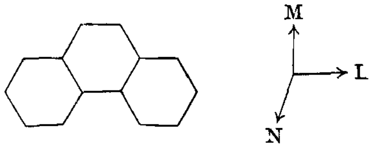
Abstract—The polarized absorption spectra of phenanthrene and phenanthrene-d_{10} crystals have been measured at 4°K, 77°K, and room temperature from 33,000 cm^{-1} to a cutoff at 37,500 cm^{-1}. The absorption, which rises steeply towards shorter wavelengths and is twice as intense in the *b*- as in the *a*-polarized spectrum, corresponds to the moderately weak 3000 Å system superimposed on the tail of the intense 2500 Å system. The former is assigned to a B_2—A_1, and the latter to an A_1—A_1 transition. No measurable Davydov splitting was observed in the 3000 Å system.

Introduction

The crystal spectra of naphthalene[1] and anthracene[2, 3] have been extensively studied, and the relation between free molecule and crystal absorption is fairly well understood.[9,10] The polarized ultraviolet absorption spectra of phenanthrene and phenanthrene-d_{10} crystals have now been studied to see whether a similar relation holds, and to determine the polarizations (A_1—A_1, *M*-axis polarized; or B_2—A_1, *L*-axis polarized) of the transitions involved.



The electronic absorption spectrum of an aromatic hydrocarbon typically contains a very weak, a moderately weak, and an intense band system. Other moderately intense transitions are found at higher energies. The very weak system ($f = 0.003$) occurs near

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3400 Å in phenanthrene and has been described elsewhere.[4] The present paper deals with crystal absorption beyond 3000 Å, corresponding to the moderately weak ($f = 0.2$) bands at 3000 Å and the intense ($f = 1$) *absorption at 2500 Å in solution.*

Phenanthrene forms monoclinic crystals of space group $P2_1$, with two molecules in the unit cell.[5,6] The factor group is C_2, and corresponding to every free molecule transition two transitions are allowed in the crystal, polarized respectively parallel and perpendicular to the unique *b* crystal axis. Thin sublimation flakes can be grown in which the *ab* face is well developed, and spectra were recorded with light polarized parallel to *a* and *b* respectively. Direction cosines, relating crystal and molecular axes, and oriented gas polarization ratios are listed in Table 1.

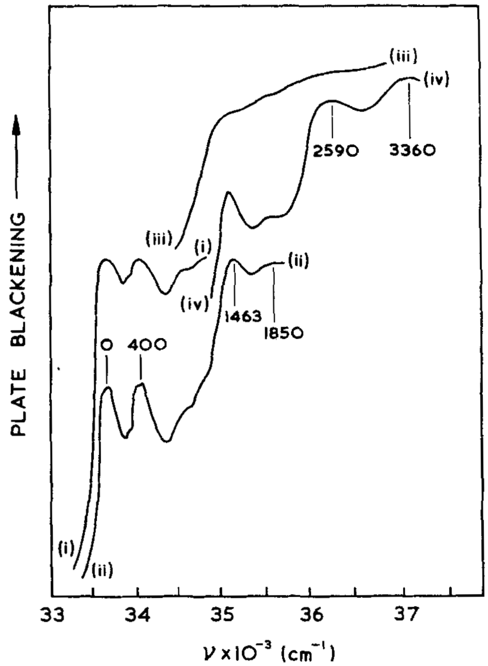

Figure 1. Low temperature crystal spectrum of phenanthrene. 0.9 μ crystal, 4°K: (i) *b*-polarized, (ii) *a*-polarized. 0.6 μ crystal, 77°K, 5 hour exposure with wide slit: (iii) *b*-polarized, (iv) *a*-polarized.

The experimental methods used have been described elsewhere.[4]

Observed Crystal Spectrum

The phenanthrene crystal spectrum at low temperatures is shown in Fig. 1. Crystal and solution spectra at room temperature are shown in Fig. 2. Absorption is stronger in the *b*- than in the *a*-polarized spectrum throughout, and increases rapidly towards higher energies. Broad, flat bands are observed at room tempera-

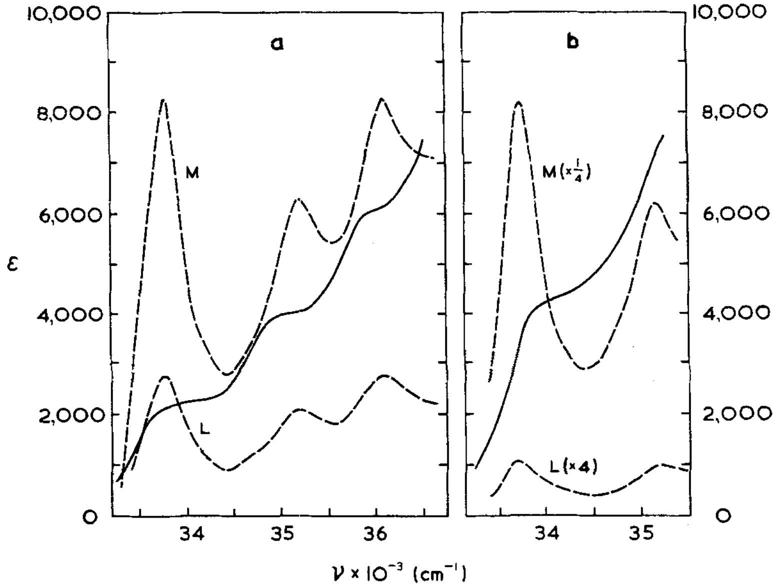

Figure 2. Room temperature crystal spectrum of phenanthrene. Solid curve: observed spectrum. ϵ is in (cm moles/l)$^{-1}$ and is accurate to ±(500–700). Broken curves: oriented gas predictions, *M* assuming *M*-polarization of the 3000 Å system, *L* assuming *L*-polarization. These curves were obtained by multiplying the extinction coefficients in solution (reference 7) by the appropriate geometric factors and shifting the spectrum to lower energies. The origin band is thus at 33,775 cm^{-1}, the observed position in the crystal spectrum at 4°K.

Table 1 Molecular Orientations in the Phenanthrene Crystal (Reference 5)

	Direction cosines of molecule 1			*Oriented gas polarization ratios*
	a	*b*	*c'*[a]	(ϵ_b/ϵ_a)
L	0.2546	−0.0856	0.9633	1/8.9
M	0.4411	−0.8761	−0.1945	3.9/1
N	−0.8606	−0.4744	0.1853	1/3.3

[a] The *c'* axis is normal to the *ab* plane.

ture. At 77°K peaks of half-width 150–300 cm^{-1} are resolved which are only slightly sharper at 4°K.

Measured frequencies for phenanthrene and phenanthrene-d_{10} crystals are listed in Table 2 where the vibrational structure is compared with that observed for the 3000 Å system in solution.[7, 8] This comparison leaves no doubt that the sharp features in the crystal spectrum correspond to the 3000 Å system in the free molecule.

In solution this system is superimposed on the tail of the intense 2500 Å absorption. This overlapping appears to be more extensive in the crystal, where the intensity rises much more rapidly towards shorter wavelengths. In solution the origin band is strong, the 1450 cm^{-1} is slightly weaker, and the 400 cm^{-1} band appears only as a shoulder. In the crystal the 400 cm^{-1} band is as strong as the origin, and the 1450 cm^{-1} band is much stronger. At room temperature several bands are resolved in solution, but in the crystal they appear only as shoulders on a sharply rising background. Finally, the crystal spectrum shifts to higher frequencies as the temperature is raised and the tail of the overlapping 2500 Å system becomes more intense. A shift to lower frequencies would otherwise be expected as hot transitions in the 3000 Å system became more important.

Vibrational Analysis and Davydov Splitting

Frequencies of approximately 400 and 1450 cm^{-1} correspond to the prominent 395 and 1376 cm^{1-} vibrations in the 3400 Å system.[4]

TABLE 2. The Low Temperature Absorption Spectra of Phenanthrene and Phenanthrene-d_{10} Crystals

Phenanthrene-h_{10}					Phenanthrene-d_{10}						
Intensity	4°K		77°K		Intensity	4°K		77°K		Solution[a]	Analysis
	ν	$\Delta\nu$	ν	$\Delta\nu$		ν	$\Delta\nu$	ν	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
S	33775	0	33840	0	S	33960	0	34035	0	0	0
sh	33875	100			sh	34018	58				
sh	34045	270			sh	34095	135				
sh	34140	365			sh	34260	300				
S, b	34175		34180[b]		S, b	34360		34395[c]			
S, a	34175		34235[b]		S, a	34360		34437[c]			
S, av	34175	400	34207	367	S, av	34360	400	34416	381	350	400
sh	34245	470			sh	34427	467				
sh	34285	510			sh	34475	515				
sh	34395	620									
sh	34665	890									
sh	34750	975	34800	960	S	34775	815	34824	789	1060*	1000(h) 815 (d)
sh	34860	1085									
					sh	35160	1200				
VS	35240	1465	35260	1420	VS	35410	1450	35437	1402	1400	1450
VS, br			35690	1850	VS, br	35790	1830	35870	1835		400 + 1450 = 1850
										2290	2300
VVS, br			36430	2590						2640	400 + 2300 = 2700
VVS, br			37200	3360						3340*	1000(h) + 2300 = 3300
										3690	1400 + 2300 = 3700

Notes: S, strong; VS, very strong; VVS, very very strong; sh, shoulder; br, broad; a, *a*-polarized spectrum; b, *b*-polarized spectrum; av, average of a and b. All values are in cm^{-1} and are accurate to ± 25 cm^{-1} except for shoulders where the accuracy is much less.

[a] Intervals are for phenanthrene-h_{10} is iso-octane solution at room temperature (reference 7). Similar intervals are obtained for phenanthrene-h_{10} and -d_{10} in cyclohexane. Intervals marked * were measured at -100°C for phenanthrene-h_{10} only (reference 8).

[b] Apparent Davydov splitting of 55 cm^{-1} at 77°K.

[c] Apparent Davydov splitting of 42 cm^{-1} at 77°K.

The 2300 cm^{-1} interval is very large for a skeletal vibration, but is not changed (in the solution spectrum) by deuteration. Perhaps it is not a fundamental.

No well resolved feature is found in the phenanthrene-h_{10} spectrum corresponding to the band at 815 cm^{-1} in deuterated phenanthrene. The latter probably corresponds to one of the shoulders at 890, 975, or 1085 cm^{-1} in the phenanthrene-h_{10} spectrum. If a frequency of about 1000 cm^{-1} is chosen, the ν_h/ν_d ratio is close to that found for two similar frequencies in the 3400 Å system.[4] (1005 and 1025 cm^{-1}, h_{10}; 839 and 886 cm^{-1}, d_{10}. In both systems these vibrations are more intense in phenanthrene-d_{10}.)

No definite Davydov splitting is observed in this system at 4°K, although there appears to be a small splitting in the 400 cm^{-1} band at 77°K. A splitting of as much as 100 cm^{-1} may have escaped detection. The apparent splitting can be markedly reduced if the two polarized beams are not quite perfectly separated, especially when as here the bands are broad and intense.[9, 11]

Calculation of the Expected Crystal Spectrum

A complete description of the electronic states of a molecular crystal must consider interactions between dipole and higher multipole molecular transition moments, overlap between the orbitals of neighbouring molecules, and mixing between both neutral and ion-pair exciton states of the crystal.[9, 10] For strong transitions, however, the dipole–dipole interaction is dominant,[9] and the effects of overlap and mixing with ion-pair states are small.[10] It may then be possible to predict the crystal spectrum from a knowledge of the free molecule spectrum and the crystal structure only.

In particular, the crystal spectra of the intense ($f > 1$) transition in naphthalene[1] and anthracene,[2] and the intensities of the moderately weak ($f \approx 0.1$) transition in the same crystals[1, 2, 11] were satisfactorily predicted by considering dipole–dipole interactions only. For the intense system mixing was neglected, while for the moderately weak system mixing was considered only with the intense transition.

The same approximations have been used in predicting the phenanthrene crystal spectrum, and the results are given in Tables 4, 5, and 6. The author thanks Dr. M. Philpott for calculating the necessary dipole–dipole sums which are listed in Table 3.

TABLE 3 Dipole–Dipole Sums for Phenanthrene (cm^{-1}/Å^{2})

	1–1	1–2
LL	873.5	-2436.1
LM or *ML*	-207.1	835.6
MM	-969.1	333.3

These sums were calculated by Dr. M. Philpott and are defined in reference 9.

TABLE 4 Predicted Crystal Spectrum for the Intense 2500 Å System

	Assumed polarization	
	L	*M*
ν_a	49960 cm^{-1}	38440 cm^{-1}
ν_b	36790 cm^{-1}	40110 cm^{-1}
ϵ_a^{a}	12650	37800
ϵ_b^{a}	1430	150000

[a] $\epsilon_{\max}$ in (cm moles/l)$^{-1}$

TABLE 5 Predicted Extinction Coefficients for the Origin Band of the 3000 Å System (cm moles/l)$^{-1}$

	Assumed polarization of the 3000 Å system			
	L		*M*	
	ϵ_a	ϵ_b	ϵ_a	ϵ_b
Oriented gas	2730	307	8150	32300
Mixing assumed with *L*-polarized 2500 Å system	208	785	12380	30800
Mixing assumed with *M*-polarized 2500 Å system	7350	674	18310	50000
Observed	$\epsilon_a = 2200 \pm 500$		$\epsilon_b = 4500 \pm 700$	

TABLE 6 Calculated Davydov Splittings in the 3000 Å System of Phenanthrene ($\nu_b - \nu_a$, cm^{-1})

	L-polarized	M-polarized
System as a whole	-2265	$+309$
Origin band only	-521	$+72$

Calculated to first order in the dipole–dipole approximation.

The dipole–dipole approximation proved inadequate to predict the Davydov splitting in the moderately weak system of anthracene.[10, 11] Thus it is not surprising that the calculated splittings for phenanthrene listed in Table 6 do not agree at all with the observed zero or very small splitting.

Absorption Intensity and Polarization of the Transitions

The Intense 2500 *Å System*

Table 4 shows that if this system is M-polarized, both Davydov components are expected to be intense and to occur near 39,000 cm^{-1}. If, on the other hand, it is L-polarized, no strong absorption is expected in this region. The b-polarized component would be very weak, and the a-polarized component shifted to much higher energies. A weakly absorbing region would be expected between the 3000 Å system and the onset of higher energy absorption systems near 45,000 cm^{-1}. Such a spectrum is indeed observed in naphthalene[1] and anthracene[2, 3] crystals where the intense system is L-polarized.

The thinnest crystals studied (0.6 μ) were in fact opaque in this region, indicating an extinction coefficient greater than 8000 (cm mole/l)$^{-1}$ between the cutoff at 37,500 cm^{-1} and at least 45,000 cm^{-1} where the intensity of the hydrogen discharge lamp falls off. The 2500 Å system must therefore be, at least substantially, M-polarized, recording an A_1—A_1 transition. An intense M-polarized transition in this region is consistent with the occurrence of vibrationally induced M-polarized bands in the weak 3400 Å system.[4]

It does not follow, however, that all the intensity observed near 2500 Å is due to an *M*-polarized transition. Luminescence polarization experiments[12] indicate the presence of an *L*-polarized transition in this region, and theoretical studies[13] predict transitions of both in-plane polarizations near 2500 Å. The 2500 Å absorption may possibly record two differently polarized, closely spaced transitions. There is evidence for a similar situation in the crystal spectra of other aromatic hydrocarbons.[1, 3]

The Moderately Weak 3000 *Å System*

The measured intensity in the crystal at room temperature is plotted in Fig. 2, along with oriented gas predictions for the 3000 Å system. The observed intensity, especially in the *b*-polarized spectrum, is much lower than expected for an *M*-polarized, and much higher than expected for an *L*-polarized transition. It is improbable that crystal-induced intensity transfer could reduce the strong absorption predicted for an *M*-polarized transition to the much lower values observed. Table 5 shows that dipole–dipole effects would in fact lead to an increase.

It has already been noted, however, that the 3000 Å system appears to overlap considerably with the tail of the intense *M*-polarized 2500 Å system. If the 3000 Å system were *L*-polarized, such overlapping would lead to a large increase in total intensity, since the projection of the *M* molecular axis on the *ab* crystal plane is much greater than that of the *L* axis. The background absorption would be stronger in the *b*- than in the *a*-polarized spectrum and would increase towards higher energies as is observed.

The 3000 Å system is thus assigned to an *L*-polarized, B_2—A_1 transition, in agreement with theory[13, 14] and luminescence polarization experiments.[12] A large part of the total absorption in the 33,000–37,000 cm^{-1} region is assumed to be due to the tail of the 2500 Å system. Since it is difficult to estimate how large this background actually is, it is difficult to assess the extent to which the free molecule intensity is altered by intermolecular interactions. However, in the *a*-polarized origin band, where background absorption should be least, the observed intensity is close to the oriented gas value, but much lower than predicted by a dipole–dipole treatment.

Discussion and Conclusions

The intense absorption near 2500 Å in phenanthrene records an M-polarized transition, although the possibility of an additional L-polarized transition in the same region cannot be ruled out. The moderately weak 3000 Å system is L-polarized, has a very small Davydov splitting, and is artificially enhanced in intensity by overlapping with the tail of the 2500 Å system.

Several important differences make the interpretation of the phenanthrene crystal spectrum more difficult than that of naphthalene and anthracene. In the latter two molecules the intense ($f > 1$) transition is L-polarized, and hence its intensity in the crystal is sufficiently low to permit direct observation. In phenanthrene the intense system is substantially, if not completely, M-polarized, and thus so strong that only its onset can be observed directly in the crystal absorption spectrum.

Second, the much closer spacing in phenanthrene between the moderately weak and the intense systems (6480 cm^{-1} in the free molecule, compared to 10,800 and 12,600 cm^{-1} in naphthalene and anthracene respectively) permits substantial overlapping of the two systems, making it difficult to estimate the true intensity of the former.

Partly because of these limitations to the experimental data, no attempt has been made to carry out a more refined theoretical treatment as has been done for naphthalene and anthracene.[10, 11] Such a treatment would be more complicated for phenanthrene since the interactions between transition quadrupole moments, which vanish in the centrosymmetrical hydrocarbons, may be important. The closer spacing of the molecular electronic states in phenanthrene would also complicate the treatment of mixing between states.

There is no reason to doubt that the dipole–dipole approximation gives at least a good qualitative picture of the crystal spectrum of the intense 2500 Å system; however, it has proved to be quite inadequate to predict the spectrum of the weaker 3000 Å system.

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