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

Experimental Study Of The Davydov Splitting Of Trikplet Excition In Pyrene At Room Temperature

J. L. Fave [a] & M. Schot [a]
[a] Groupe de Physiquedes Solides, Universtié Paris VII, Tour 23, 2 oplace Jussieu, 75 221, Paris Cedex 05, France
Version of record first published: 28 Mar 2007.

To cite this article: J. L. Fave & M. Schot (1976): Experimental Study Of The Davydov Splitting Of Trikplet Excition In Pyrene At Room Temperature, Molecular Crystals and Liquid Crystals, 34:2, 47-56

To link to this article: http://dx.doi.org/10.1080/15421407608083883

Mol. Cryst. Liq. Cryst., Vol. 34 (Letters), pp. 47-56

Printed in U.S.A.

EXPERIMENTAL STUDY OF THE DAVYDOV SPLITTING OF TRIPLET EXCITONS IN PYRENE AT ROOM TEMPERATURE

J.L. FAVE and M. SCHOTT
Groupe de Physique des Solides*, Université Paris VII,
Tour 23, 2 place Jussieu, 75 221 Paris, Cedex 05, France

Submitted for Publication May 14, 1976

Abstract - The 0-0 line of the $S_0 \rightarrow T_1$ absorption in crystalline pyrene has been studied as the action spectrum of delayed fluorescence in polarized light at 295 K, at 0.4 cm^{-1} resolution. The centroid for the b polarized line lies at an energy 2.8 ± 2 cm^{-1} higher than the one for the a polarized line. The polarization ratio is $\varepsilon_b/\varepsilon_a = 1.1 \pm 0.1$. A discussion of spin-orbit coupling processes shows that in this case the factor group (Davydov) splitting, is much larger than the energy difference of the centroids, and hence also larger than the splittings reported before. The most probable value of the Davydov splitting is in the range 13 ± 9 cm^{-1}.

I. INTRODUCTION

The transport properties of triplet excitons in crystalline pyrene have been the subject of a number of recent investigations. Triplet exciton transfer integrals have been calculated[1,2], from which, according to the reported band structure[3] essentially two-dimensional, follows a very small bandwidth along the c* direction[1]. On the other hand, the directly measured triplet exciton diffusivity tensor is essentially three-dimensional at 295 K, the anisotropy being less than a factor of four[4]. Other properties are also in accord with this three-dimensional motion of the triplet[5].

* Laboratoire associé au C.N.R.S. et à l'Ecole Normale Supér.

The pyrene triplet exciton band structure has just been reinvestigated[6], and is in fact different from the, erroneous, previously published one in Ref. (3). In this note, we present some experimental information related to the band structure, which may be useful to improve our understanding of triplet transport properties in pyrene.

The room-temperature phase of pyrene crystal is monoclinic, space group $P\,2_{1/a}$ or C_{2h}^5, with four molecules per unit cell occupying general positions[7]. The site group is trivial and does not contain inversion - as it does in anthracene for instance. The interchange group[8] is isomorphous to the point group C_{2h} and the four molecules of the unit cell are related by the operations of C_{2h}. Any molecular energy level, for instance the lowest triplet is split, at the center of the Brillouin zone, into four levels having symmetry A_u, B_u, A_g, and B_g, the irreducible representations of C_{2h}

The center of symmetry of the reference molecule is at a general position with coordinates χ, γ, z along crystal axis $\underline{a}$, $\underline{b}$, $\underline{c}$, respectively, with $z \neq 0$ - unlike anthracene again -. Using the transfer integrals calculated in (1), a simple band structure is found. Only two integrals are important: that between the molecules related by inversion A(i) - 141 cm^{-1} and that between the molecules related by C_2^b screw-rotation ($A(C_2^b)$ = - 2.2 cm^{-1}. At the center of the BZ (Fig. 1), the splitting between A_u and B_u, or A_g and B_g, is - $4A(C_2^b)$, and the splitting between A_u and A_g, or B_u and B_g is $2A(i)$[3,6]. In the correct structure[6], the leading term in the dispersion relations $\varepsilon(\underset{\sim}{k})$, in all directions, is $A(i)\cos 2\underset{\sim}{k}\cdot(\underset{\sim}{\chi}+\underset{\sim}{\gamma}+\underset{\sim}{z})$, hence a three-dimensional band structure as χ, γ, z are of comparable magnitudes[9].

If the relative orders of magnitudes of the calculated transfer integrals[1] are correct, the band structure is known if A(i) and $A(C_2^b)$ are known.

Only A_u and B_u states are accessible from the A_g ground state. A spectroscopic measurement of A(i) was not possible in our samples[10] and was not attempted. $A(C_2^b)$ can be determined through the measurement of the factor group (Davydov) splitting between A_u and B_u states at k=0 which is here[1-3,6].

$$\Delta \simeq \varepsilon(B_u) - \varepsilon(A_u) = -4A(C_2^b)$$

A value Δ = 2.4 cm^{-1} was reported previously[3]. But the measurement was performed at a resolution of 100 cm^{-1}, about the absorption line halfwidth at 300 K[13], hence much larger than the inferred splitting. A much better resolution is possible now using tunable dye lasers. In addition, it will

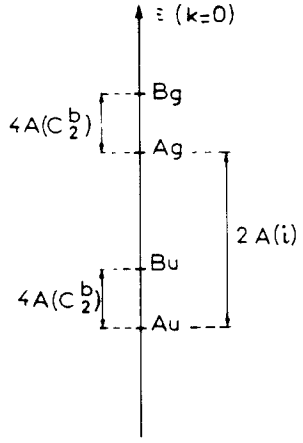

Figure 1 - Relative positions of the four crystal k = 0 sublevels corresponding to the lowest excited molecular triplet in pyrene. A(i) and A(C_2^b) are triplet exciton transfer integrals (see text).

be shown below that the absorption data do not yield Δ directly, a fact which was not taken properly into account in (3). It was therefore decided to perform new measurements under improved conditions, in conjunction with an analysis of the possible spin-orbit routes, according to Hochstrasser's theory[14], of the first triplet absorption.

II. EXPERIMENTAL METHOD AND RESULTS

The spectroscopic determination of Δ rests upon the measurement of the $S_o \rightarrow T_1$ absorption in polarized light. As the direct absorption is too small in pyrene[15], the spectrum was obtained as the action spectrum of delayed fluorescence. Exciting light was incident normal to (a,b) cleavage planes and polarized either along a or b crystallographic axis. Crystals were oriented conoscopically.

The experimental method was similar to that described in (13), the resolution was 0.4 cm^{-1}. The only change was that the square root of the absorption coefficient squared $\varepsilon^2(\lambda)$ was electronically obtained before data accumulation in the Didac 4000 multiscaler.

The moments' theorem[16] was used to calculate the positions of the controïds of the lines in the two polarizations. No specific lineshapes has to be assumed. This method, however, requires an accurate knowledge of the whole absorption line, including the wings, and the choice of a consistent truncation procedure. The absorption in the wings cannot be obtained accurately at the same time as the maximum absorption:

a change of ε by a factor of 10 means a change in the fluorescence light intensity ϕ by a factor of 100 if ε is to remain proportional to the incident light intensity squared L^2. On the other hand, the accuracy of the electronic operations is poor at low signal levels. To measure more accurately in the wings, L was increased 3 times, hence ϕ 9 times and the wing regions were recorded at these conditions, where one has no more $\varepsilon \propto L^2$ near the maximum of the line. The connection which the central portion of the line is not always correct (Fig. 2), but it was checked that, even in such cases the centroid position was not affected within the resolution of the experiment. Similarly, different tuncation procedures were tried, and it was found that, although the absolute positions of the centroids may be displaced by up to .5 Å, the separation D of the centroids in the two polarizations was not affected. Indeed, the shapes of the two lines appear to be identical.

Three crystals of different origins were studied. The centroids are at 5936.2 $\pm$ 1 Å in the b polarization and 5937.2 $\pm$ 1 Å in the a polarization. But as a large part of the uncertainty affects both numbers in the same way, their difference is known to a higher accuracy, D $\{E(//b)-E(//a)\}$ = 2.8 ± 2 cm^{-1}.

These results are in good accord with previous works in which the maximum absorption was found at 5935 Å [17], 5928 $\pm$ 16 Å [3] and 16851 $\pm$ 5 cm^{-1} [18], with the difference D = 2.8 $\pm$ 0.5 cm^{-1} [3].

As discussed below, the factor group splitting Δ can be deduced from D only if information on spin-orbit coupling route is available. The so-called polarization ratio, the ratio of total absorptions for light polarized along b and perpendicular to b (i.e., in the present case, along a), gives some information on the SOC route. As both lines have the same shape, it sufficed to measure the ratios of the maximum absorptions, ε_a and ε_b. To do this, a small--3 mm^2--fraction of the crystal was excited with the most homogeneous part of the expanded laser beam, and the crystal rotated. One finds $\varepsilon_b/\varepsilon_a = 1.1\pm0.1$, which is close to the value 1.2 quoted in (3).

III. ESTIMATION OF THE FACTOR GROUP SPLITTING

In anthracene or naphthalene D $\neq \Delta$, since the absorption to the A_u and B_u states are both almost uniquely polarized[14], but in other crystals the situation can differ. To discuss the polarization of triplet factor group states in pyrene, we assume that only one SOC route is important and consider only intramolecular mixing of singlet states in the excited trip-

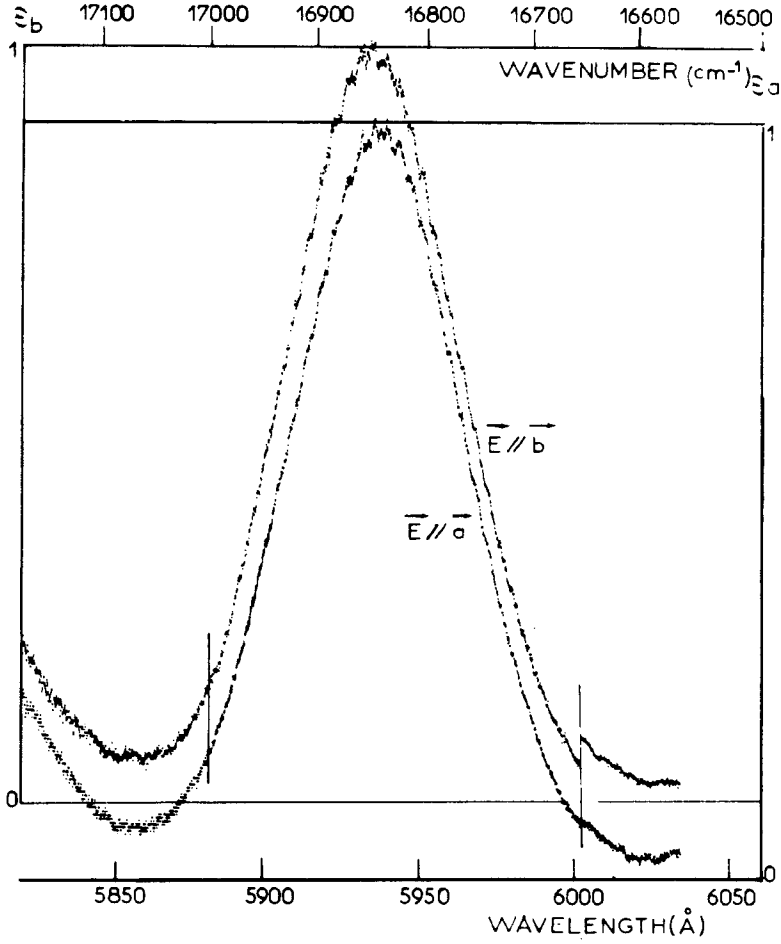

Figure 2 - Polarized absorption of crystalline pyrene at 295 K, 0-0 line of the $S_o \rightarrow T_1$ absorption. Upper curve: b polarization - lower curve - a polarization. The curves are normalized and the zeros are shifted for clarity.

The wings and central part are connected at the positions of the vertical lines. In this particular example, a misfit on the blue side of the b polarized line is clearly visible.

let[19]. One obtains the results displayed on Table I. There are six cases, of which only two are excluded by the experimental polarization ratio. Only two of the four remaining cases correspond, as in anthracene, to almost pure polarization of A_u and B_u transitions.

The lowest triplet state of the pyrene molecule is probably of B_{3u} symmetry[20], so that only cases 4 and 6 of Table I should be considered as most probable. In both cases,

A_u and B_u have comparable intensities in both polarizations. The phosphorescence of pyrene (dimers ?) in benzophenone at 77 K is mainly polarized perpendicular to the molecular plane[22], which favors case 4 [25].

To estimate Δ from D in Table I, the absorption in each polarization was assumed to be the sum of two lorentzians of equal widths, corresponding to A_u and B_u respectively. As any independent experimental information on the relative intensities of the two components was lacking, the heights of these lines were taken from Table I. The ratio of their heights is α/β in one polarization, β/α in the other. Then one has

$$\Delta = \left| \frac{1 + \beta/\alpha}{1 - \beta/\alpha} \right| D. \qquad (1)$$

This result is general for any line shape as long as both lines have the same shape.

IV. SUMMARY AND CONCLUSIONS

It is clear from the above that a precise determination from spectroscopic data of the splitting Δ of the two A_u and B_u triplet sublevels, at $\underset{\sim}{k} = 0$ in pyrene will be difficult. Even if no precise value of Δ can be given now, it may at least be said that the most probable value is $\Delta = 13 \pm 9$ cm^{-1}, but that values as large as 25 cm^{-1} cannot be strictly excluded[26]. Although the uncertainty on this value of Δ is large, some preliminary conclusions are possible.

Δ is larger than the value quoted previously[1-3], the difference is due to the unwarranted assumption $\Delta = D$ (not to the results of the measurements). Δ is also larger than the values calculated in (1), (2) which is of the order of 2 cm^{-1}. As pointed out in (2), this value is small because of the near cancellation of two large terms. Such calculations are not expected to be very accurate, and an uncertainty of 20% on each term would certainly be considered as a satisfactory result. The uncertainty on Δ is certainly larger in pyrene. It is also possible that the calculations are affected by the use of slightly incorrect atomic positions in the crystal[7]. At present, it is only possible to conclude that the calculated transfer integrals, hence also the big value of A(i), cannot be uncritically accepted and used in a band structure calculation.

Acknowledgements - The crystals used in this study were kindly given to us by Dr. N. Karl, Kristallabor Stuttgart, and Dr. W. Whitten, Queens College of the City University of New York. We are very much indebted to them. We also gratefully acknowledge fruitful discussions with Dr. V. Ern.

Case n°		1	2	3	4	5	6
Triplet symmetry		B_{1u}	B_{2u}	B_{1u}	B_{3u}	B_{2u}	B_{3u}
Mixing singlet symmetry		B_{2u}	B_{1u}	B_{3u}	B_{1u}	B_{3u}	B_{2u}
SOC route		L = B_{3u}		M = B_{2u}		N = B_{1u}	
//a	A_u	100	100	100	100	100	100
	B_u	5	5	65.1	65.1	126	126
//b	A_u	5.5	6.7	13.4	87.8	26	138
	B_u	109.2	135	20.6	135	20.6	109
Allmann (7b) Total abs//b		1.09	1.35	0.206	1.35	0.206	1.09
Total abs//a Robertson (7a)		1.00	1.49	0.192	1.49	0.192	1.00
Δ from Eq. (1)					4.7D		8.7D

Table I - Relative Absorption of A_u and B_u States

The six cases leading, in Hochstrasser's theory, to orbitally allowed transitions between the ground state and the lowest triplet state, are displayed. Relative absorptions are given, the a polarized A_u absorption intensity being taken as 100 in each case. Such relative values depend only on geometrical factors[14]. The ratio of total b polarized absorption to total a polarized absorption, which is experimentally measured, is also given. Refined crystal structure parameters (7b) have been used. Although they differ only slightly from older data (7a) which have been used in other work[1] the polarization ratios change by about 10% as seen in the two last lines.

Symmetry conventions as in (1). Note that different conventions are used elsewhere[24].

REFERENCES

1. A. Tiberghien and G. Delacôte, Chem. Phys. Lett. 14, 184 (1972).
2. S.W. Harrison, C.R. Fischer and S. Arnold, J. Chem. Phys. 57, 1102 (1972.
3. S. Arnold, W.B. Whitten and A.C. Damask, Phys. Rev. B 3, 3452 (1971).
4. S. Arnold, J.L. Fave and M. Schott, Chem. Phys. Lett. 28, 412 (1974).
5. H. Bouchriha, M. Schott, J.L. Fave, J. Phys. (Paris) 36, 399 (1975).
6. V. Ern, to be published.
7. The room temperature crystal structure of pyrene was first studied by
a) J.M. Robertson and J.G. White, J. Chem. Soc. (1947) 358 whose results were used in all previous work. It has been more recently reinvestigated by
b) R. Allmann, Z. Kristallogr. 132, 129 (1970) and, using neutron diffraction by
c) A.C. Hazell, F.K. Larsen and M.S. Lehmann, Acta Cryst. B 28, 2977 (1972).
The more recent results are only slightly different from the earlier ones, but, as discussed in text, this makes a non-negligible difference for some crystal properties. Allmann's data are used in this note.
8. R. Kopelman, J. Chem. Phys. 47, 2631 (1967).
9. In naphthalene or anthracene, the two subbands (corresponding to A_u and B_u at $k = 0$) are degenerate for $k = \pi/a$ or π/b, and the DS is of the order of the total triplet bandwidth. The situation is different in pyrene[6], and A(i), not $A(C_2^b)$, is the main factor in determining the widths.
10. Several spectroscopic methods of measurement of A(i) are possible. In perdeuterated pyrene crystals doped with perprotonated pyrene, pairs of $C_{16}H_{10}$ molecules substituted at sites related by inversion form dimers, whose orbitally allowed optical transition will be redshifted from the monomer transition by an energy A(i) in the $C_{16}D_{10}$ crystal structure. Such measurements were performed, for instance, in naphthalene at 4 K[11,12]. In pyrene, A(i) may be large enough to make the experiment possible at higher temperature, but the samples needed are not available to us. However, as the $C_{16}H_{10}$ crystal lattice is not very stable--there is a phase transition near 120 K--, the identity of $C_{16}D_{10}$ and $C_{16}H_{10}$ crystal structures should be checked first. Another possibility,

using pure crystals, would be to study vibronic transitions where an ungerade vibration is excited in the initial or final state.

11. D.M. Hanson, J. Chem. Phys. 52, 3409 (1970).
12. C.L. Braun and H.C. Wolf, Chem. Phys. Lett. 9, 260 (1971).
13. J.L. Fave, M. Schott and V. Ern, Chem. Phys. Lett. 38 149 (1976).
14. R.M. Hochstrasser, J. Chem. Phys. 47, 1015 (1967).
15. For instance at 5145 Å $\varepsilon = 8.10^{-4}$ cm^{-1}: V. Ern. H. Bouchriha, M. Bisceglia, S. Arnold and M. Schott, Phys. Rev. B 8, 6038 (1973).
16. R.E. Merrifield, J. Chem. Phys. 48, 3693 (1968).
17. P. Avakian and E. Abramson, J. Chem. Phys. 43, 821 (1965).
18. K. Mistelberger and H. Port in "Molecular Spectroscopy of Dense Phases", M. Grosmann, S.G. Elkomoss and J. Ringeissen eds. (Elsevier 1975), p. 181.
19. SOC routes are not discussed in details here. Other intramolecular mixing schemes may be of importance. See for example B.R. Henry and W. Siebrand, J. Chem. Phys. 2396 (1969) and W.S. Veeman and J.H. Van der Waals, Mol. Phys. 18, 63 (1970).
In addition, the close proximity of the two molecules related by inversion might introduce intermolecular coupling routes, for instance via charge transfer states.
20. This is the result of quantum chemical calculations[21], and spectroscopic measurements: the same vibronic structure is found in $S_0 \rightarrow T_1$ absorption[17], phosphorescence[22], and in the second, B_{3u}[23] singlet absorption[24].
21. N.S. Ham and K. Ruedenberg, J. Chem. Phys. 25, 13 (1956). M.K. Orloff, J. Chem. Phys. 47, 235 (1967).
22. R.M. Hochstrasser and S.K. Lower, J. Chem. Phys. 40, 1041 (1964).
23. H. Venghaus, Phys. Stat. Sol. (b) 54, 671 (1972).
24. A. Bree and V.V.B. Vilkos, Spectrochim. Acta A 27, 2333 (1971).
25. The polarization ratio found would rather favor case 6. The difference between experimental and calculated value for case 4 cannot be explained by depolarization due to internal scattering: scattering of 20% of incident light decreases the PR from 1.35 to 1.2 only, but as the quality of the crystals was good, actual scattering was much less. The origin of the discrepancy is not clear: more than one SOC routes, or routes different from those considered here, may be operative.
26. A similar, although less careful and detailed, investibation was conducted at 140 K, where the halfwidth of

the lines is only about 40 cm^{-1} [10-14]. If Δ was that large, one would expect the lineshapes in the two polarizations to be strongly non-lorentizian near the maximum. As this is not found, are upper limit of Δ at 140 K is about 30 cm^{-1}. But from 300 to 140 K (which is still above the phase transition temperature at 120 K) the relative positions of the molecules may have slightly changed, and this may be enough to alter significantly the transfer integrals, and hence Δ.
If one succeeds in quenching to 4 K or below the room temperature phase, the individual linewidths may become narrower than the splitting, allowing simultaneous measurement of Δ and the relative intensities of the lines. Such a measurement in the low temperature phase[18] would at least allow the determination of the SOC route, provided the crystal structure becomes known.