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

“Additional” Absorption Spectrum at Low Temperature in Monocrystalline Anthracene

Michèle Vial [a] & Michel Martin-bouyer [a]

[a] Laboratoire de Spectroscopie Moléculaire, Centre Universitaire de Savoie Faculté des Sciences et des Techniques de Chambéry, B.P. 143, 73011, Chambery Cedex

To cite this article: Michèle Vial & Michel Martin-bouyer (1978): “Additional” Absorption Spectrum at Low Temperature in Monocrystalline Anthracene, Molecular Crystals and Liquid Crystals, 47:1-2, 29-38

To link to this article: http://dx.doi.org/10.1080/00268947808083729

Mol. Cryst. Liq. Cryst., 1978, Vol. 47, pp. 29-38

Printed in Holland

"Additional" Absorption Spectrum at Low Temperature in Monocrystalline Anthracene

MICHÈLE VIAL and MICHEL MARTIN-BOUYER

Laboratoire de Spectroscopie Moléculaire, Centre Universitaire de Savoie, Faculté des Sciences et des Techniques de Chambéry, B.P. 143, 73011 Chambery Cedex

(*Received January 11, 1978; in final form March 28, 1978*)

Low temperature absorption spectra of anthracene monocrystals 1 to 2 mm thick show a set of narrow lines below the first singlet band of anthracene. By comparison with the emission spectra observed by other authors, we associate these lines with the energy levels of chemical or physical traps. We find there are 9 distinct traps each with a vibrational structure formed either by lattice modes only, or by lattice modes combined with vibrational frequencies of anthracene.

INTRODUCTION

Previous studies of absorption, reflection and emission spectra at very low temperature have proved the existence of many energy levels below the first singlet absorption band edge of monocrystalline anthracene which is generally assumed to be located at 25103 cm^{-1}. This frequency is close to that measured for an isolated molecule. Sidman[1] has observed a weak $\vec{b}$ polarised absorption between 24800 cm^{-1} and the band edge in very thin crystals. Using crystals 1 mm thick, Berry *et al.*[2] have seen an absorption spectrum beginning at 23900 cm^{-1} which they assigned to anthraquinon on the basis of comparison with an anthraquinon thin plate spectrum. This conclusion is questioned by Morris *et al.*[3] who, although they see in reflection a spectrum very similar to Berry's, explain its origin by physical defects in the crystal possibly induced by impurities. Helfrich *et al.*[4] have shown the existence of fluorescence for exciting radiation wavenumbers less than the crystalline anthracene O–O band wavenumber. Later, Lyons *et al.*[5] and Brillante *et al.*[6,7] confirmed the presence of trapping centres. Brillante *et al.* showed that these traps are either chemical impurities with excitation energies less than that of the host molecules, or host molecules with excitation energies lowered by the presence of a surface or a crystal dislocation, a perturbation or electronic displacement due to chemical impurities (X-traps), or a local lattice deformation following electronic excitation (self-trapping). The energy levels of the "X-traps" depend on the impurity and its site in the crystalline cell. Such traps emit a fluorescence which, from its vibrational analysis, may be ascribed to host molecules rather than impurity molecules. Other workers, e.g. Davydov,[8] attribute the narrow lines occurring below the O–O band in the absorption spectra of crystalline anthracene to free excitons.

The purpose of this work was to obtain absorption spectra by transmission of these traps, in thick oriented samples at 4.2 K, permitting a comparison with the reflection and emission spectra in the literature, thus obtaining new information on the trap levels in anthracene monocrystals.

EXPERIMENTAL

1 Samples

Using KODAK PE 362 anthracene, purified by fractioned codistillation in ethylene-glycol and series crystallisations in the purest grade ethanol (Merck), anthracene monocrystals were grown by the Bridgman method, under Argon atmosphere. These bulk grown monocrystals easily yield crystals one to two millimeters thick along the cleavage (001) plane. The crystal orientation is obtained by X-ray diffractometry and classical optical methods.

2 Optical appliance

The spectrophotometer is a Monospek 1000 used as a spectrograph (Rank Precision Industries) with a 600 lines per mm diffraction grating, blazed to 3000 Å and operated in the first order with a 15 μm entrance slit. The sample is put in the liquid helium cryostat and oriented so that the $\vec{a}$ and $\vec{b}$ axes are respectively parallel to the two polarisation directions of a Wollaston prism placed in the light beam. The light source is a XBO Osram 250 Watts lamp.

The spectra are recorded on photographic Ilford HP4 plate, with, as reference, the iron arc emission spectrum. The densitogram of these plates is recorded with an automatic microdensitometer Joyce Loebl recorder. The precision of the measurements is ± 3 cm^{-1}.

RESULTS AND DISCUSSION

As can be seen from Figure 1, the absorption spectrum is strongly polarized along the $\vec{b}$ axis. Above 24910 cm^{-1}, the $\vec{b}$ polarized absorption is very strong

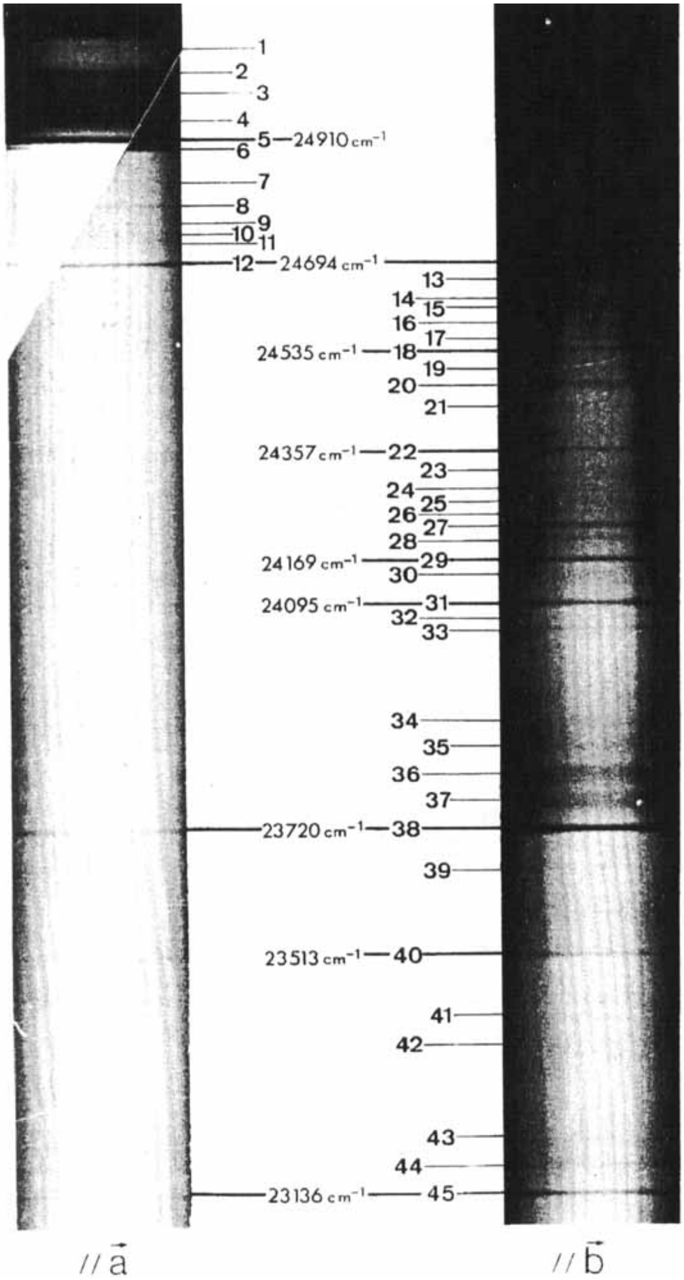

FIGURE 1a Absorption spectrum at 4 K of an anthracene single crystal about 2 mm thick along the $\vec{b}$ and $\vec{a}$ axis.

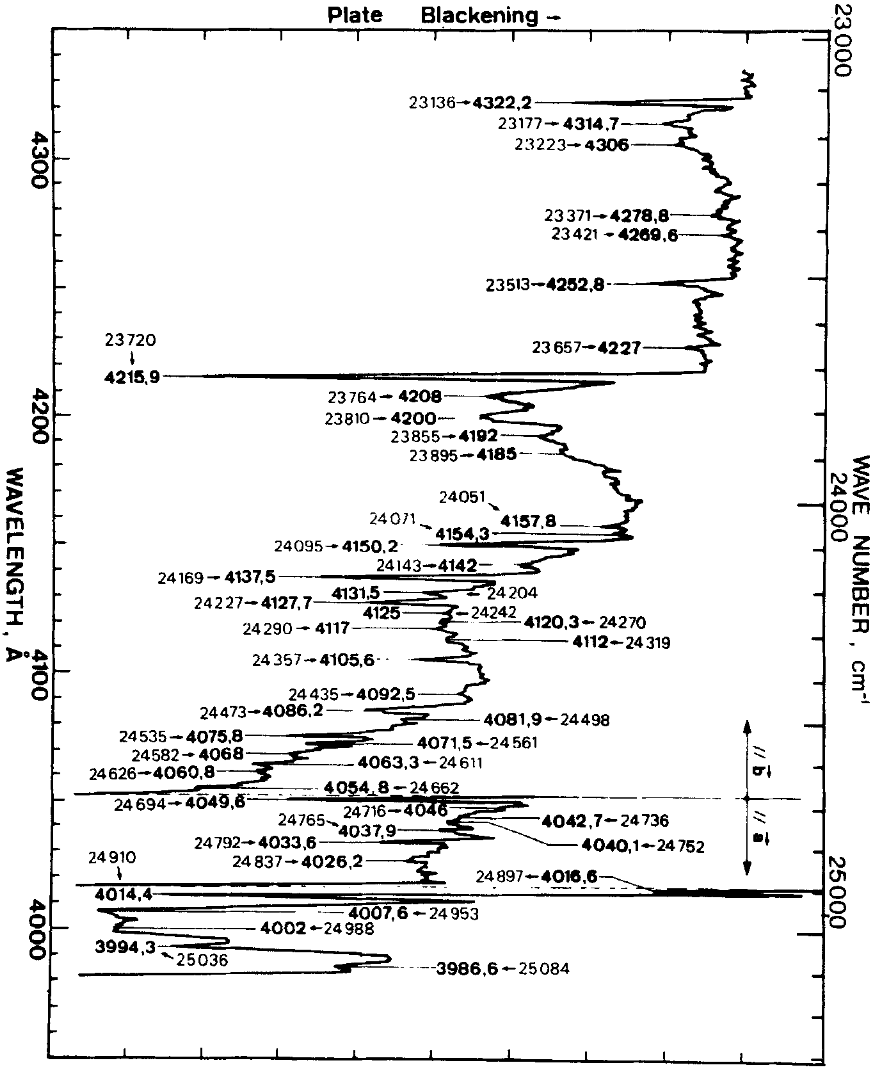

FIGURE 1b Densitometer traces of the absorption spectrum along the $\vec{b}$ and $\vec{a}$ axis.

and no resolved structure can be detected. But in the $\vec{a}$ axis polarization direction where the absorption is weaker, we are able to observe a sharp structure by using time-exposures of about 15 minutes. (Elsewhere other parts of the spectrum, the time-exposures are a few seconds.) With these experimental conditions, it is possible to record a narrow line spectrum from 23136 cm^{-1} to 25084 cm^{-1}. At higher wavenumbers, the absorption is much too strong in the two polarization directions to detect a sharp structure. This confirms that the origin of the anthracene O–O band is at 25100 cm^{-1} in good agreement with the literature. The absorption lines occurring below 25100 cm^{-1} are generally narrow but of unequal intensities and are observed only at very low temperatures. Moreover, we verified experimentally that these lines were absent from absorption spectra of thin (ca. 1 μm) plates prepared by sublimation under Argon atmosphere. To obtain the spectrum shown in Figure 1, we used a crystal more than a millimeter thick. A previous observation on a thinner crystal (about $\frac{2}{3}$ mm) gave us a less intense spectrum in which the weakest lines did not appear. We may therefore conclude that the intensities of these absorption lines are related to the bulk crystal and that the observed phenomena are due neither to surface effects, nor to interference effects such as have been reported for 1 μm thick crystals.[9]

Certain lines which we observe in thick samples coincide with the "antireflection" lines recorded by Morris *et al.*[3] in reflection spectra of anthracene crystals at 4 K (Table I). In this table we list those emission lines, not belonging to the usual fluorescence of anthracene which were recorded by Glockner and Wolf[10] and by Lyons and Warren[4] in low temperature fluorescence spectra. Comparing all the spectra, we note that:

1) the lines designed O_3, O_5, O_8, O_9 by Lyons and Warren are observed in absorption as well as emission with comparable intensities.

2) the lines O_4 and O_{12} were observed in fluorescence by Glockner and Wolf, in reflection by Morris *et al.*, in absorption in this work, but not at all by Lyons and Warren.

3) the line O_6 was observed only in reflection and absorption. It is absent in the fluorescence spectrum.

These observations cast doubt on the conclusions of Lyons and Warren[11], because O_3 cannot be the only origin from which to build the 2-methylanthracene vibrational spectrum with the O_n lines being deduced by a simple combination. The existence of the lines O_3, O_5, O_8 and O_9 in the emission spectra as well as in absorption indicates four origin levels. The O_3 line, very intense in our spectrum, is probably due to 2-methylanthracene as suggested by Lyons and Warren.[11] O_8 and O_9 were associated by Brillante *et al.*[6] with trace of 2-hydroxyanthracene. For O_5, there is no indication in the literature whether it is caused by a trace of chemical impurity or only a crystal defect.

TABLE I

				Fluorescence			
	This work				Ref. 5		
No.	$\|\vec{b}$	$\perp\vec{b}$	Reflection Ref. 3	Ref. 10	$\|\vec{b}$	:	Assignment
1		25084 w		25081	25081 vs	:	(E − 22 ph)
2		25036 s		25043	25042 vs	:	(E − 61 ph)
3		24988 s					
4		24953 s					
5	24910 s	24910 s	24907	24909	24909 s	:	O_3
6	24897	24894 m					
7	24837	24837 vw					
8	24795	24792 w					
9		24765 vw					
10		24752 vw					
11	24740 vw	24736 vw 24716 vw	24728	24732		:	O_4
12	24694 s			24693			
13	24662 vw						
14	24626 vw			24629	24632 w		
15	24611 vw						
16	24582 vw			24581	24583 vw	:	E − 391 − 129 ph
17	24561 vw						
18	24535 m		24535	24539		:	$O_5(O_3 - 370)$
19	24498 vw		24497			:	O_6
20	24473 m			24480	24481 m	:	E − 622
21	24435 vw						
22	24357 m	24362	24354	24357	24357 w	:	$O_8(O_4 - 371)$
23	24319 vw			24317	24318 vw	:	E − 2 × 391 − 3
24	24290 w						
25	24270 vw						
26	24242 vw						
27	24227 m						
28	24204 w						
29	24169 s	24170	24167	24169	24170 m	:	$O_9(O_3 - 2 \times 371)$
30	24143 w						
31	24095 s	24099		24096	24096 m	:	E − 1007
32	24071 vw						
33	24051 w						
34	23895 vw			23896	23896 m	:	E − 1165 − 42
35	23855 w						
36	23810 m large						
37	23764 m large				23764 w	:	E − 1260 − 79
38	23720 vs	23719	23714	23718		:	$O_{12}(O_3 - 1192)$
39	23657 w			23655	23656 m	:	E − 1404 − 43
40	23513 m	23509					
41	23421 vw						
42	23371 vw						
43	23223 w						
44	23177 w						
45	23136 s						

Since the O_{12} line is very strong on our spectrum, and Glockner *et al.*[10] observed it clearly also in emission, we assume it to be the origin of an other trap, in spite of the fact that it does not appear in the spectra of Lyons and Warren.

On the other hand, the frequency gap between the weak line located 24740 cm^{-1} and that recorded in emission by Glockner *et al.*, designated O_4 by Lyons *et al.*,[5] is much greater than the differences found for the other above-mentioned lines: we deduce that this line is unrelated to the O_4 emission line and is only a vibrational component of an other trap level absorption spectrum. O_6 was not observed in emission and its very weak intensity leads us to class it among vibrational lines.

Besides these O_n determined by Lyons *et al.*,[5] we note some further coincidences between absorption and emission spectra, particularly for the lines: 24694, 24626, 24582, 24473, 24319, 24095, 23895, 23764 and 23657 cm^{-1} (Table I). These lines are distinct from the anthracene vibrational spectrum, because the vibrational components which, in emission, obey the relationship $E-\bar{v}_{vib}$, must give, in absorption, $E+\bar{v}_{vib}$, which is not the case. Thus, either all these lines correspond to same transitions in absorption and emission and therefore the assignments given by Lyons *et al.* are improper, or these assignments are correct for emission and no comparison is possible between emission and absorption spectra. Our conclusion is intermediate to these two extreme solutions. Indeed, a comparison between emission and absorption intensity of each line and its shape suggests that the lines 24694 cm^{-1} and 24095 cm^{-1} correspond to origin levels like the O_n, while the others are only vibrational components. As for 24740 cm^{-1} line, there is an accidental coincidence in the numerical values of the emission and absorption wavenumbers. Among the lines seen only in absorption, two seem to be spectrum edges: 23136 cm^{-1} and 23513 cm^{-1}. These observations suggest the existence of 9 spectrum origins each corresponding to a trap level absorption band. In Table II, we group all these results and calculate Δv from each origin.

In each range, we find the lattice vibration modes recorded by Brigodiot[12] in anthracene Raman spectra. We observe an additional mode at 24 cm^{-1}, seen by Durocher *et al.*[13] in a phosphorescence spectrum and by Lacey and Lyons[14] in a fluorescence spectrum. It was described by Morris *et al.*[15] as a transverse polariton. In the range (a), 41 and 89 cm^{-1} are lattice modes. 235 cm^{-1} and 286 cm^{-1} may be anthracene B_{1g} and B_{2g} vibrations. In the range (b), 144 cm^{-1} may be a combination of phonons modes, for example 123 cm^{-1} +21 cm^{-1}. In the range (c), 44, 93, 135 and 175 cm^{-1} are phonon wavenumbers or frequency combinations. 331 cm^{-1} and 351 cm^{-1} are not anthracene fundamental frequencies but may be deduced from combinations 286 + 45 ph and 286 + 65 ph. In the other ranges, there are only fundamental or combined phonon modes. Whatever the nature of the trap (chemical

TABLE II

Series	ν	$\Delta\nu$	Assignment	Ref. 12	Ref. 14
(a)	23136				
	23177	41	41 ph	36 or 45	
	23225	89	79 ph or 64 ph + 25 ph	79	81
	23371	235	B_{1g}	236	
	23422	286	B_{2g}	288	
(b)	23513				
	23657	144	123 ph + 21 ph	123	27
(c)	23720		O_{12}		
	23764	44	44 ph	45	45
	23813	93	64 ph + 29 ph	64	27
	23855	135	135 ph		137
	23895	175	123 ph + 42 ph		
	24051	331	286 B_{1g} + 45 ph		
	24071	351	286 B_{1g} + 65 ph		
(d)	24095				
	24143	48	48 ph	45	45
(e)	24169		O_9	39	
	24204	35	35 ph		
	24227	58	58 ph	64	67
	24242	83	83 ph	79	81
	24270	101	64 ph + 39 ph		
	24290	121	121 ph	123	
	24319	150	121 ph + 29 ph	123	27
(f)	24357		O_8		
	24435	78	78 ph	79	81
	24473	116	116 ph	123	
	24498	141	123 ph + 19 ph		137
(g)	24535		O_5		
	24561	24	24 ph		27
	24582	47	47 ph	45	45
	24611	76	76 ph	79	81
	24627	91	64 ph + 27 ph		
	24662	127	127 ph		
(h)	24694				
	24716	22	22 ph		27
	24736	42	42 ph	45	45
	24752	58	64 ph		
	24765	71	71 ph	79	81
	24792	98	71 ph + 27 ph	79	27
	24837	143	143 ph		137
	24897	203	123 ph + 80 ph		
(i)	24910		O_3		
	24953	43	43 ph	45	45
	24988	78	78 ph	79	81
	25036	126	126 ph	123	
	25084	174	125 ph + 45 ph		

impurities, "X" trap near by an impurity, physical defect owing to a distortion, etc.), one expects to find the host crystal lattice modes in the vibrational structures of the trap levels. On the other hand, the 236 cm^{-1} and 288 cm^{-1} vibrations which are in good agreement with the anthracene crystal (C- C) deformation modes[12] are not found in any chemical impurity likely to be present in this crystal (see Bridge and Vincent[16]). For this reason, the (a) and (c) spectra are probably due to the excitation of two energy levels induced by physical defects. The range (i) has its origin at 24910 cm^{-1}. This wavenumber is assigned by Bridge *et al.*[16] and Lyons *et al.*[11] to the 2-methylanthracene fluorescence origin. These molecules are impurities in anthracene. For the range (e) and (f), O_8 and O_9 are caused, according to Brillante *et al.*,[6] by 2-hydroxyanthracene molecules. Bridge and Vincent have found the 2-hydroxyanthracene fluorescence origin 24159 cm^{-1}. Thus we assume O_9 is a chemical trap like O_3. If O_8 (24357 cm^{-1}) is also attributed to 2-hydroxyanthracene,[6] it must be a crystal defect level induced by the impurity molecule. But, on the other hand, O_8 may also be the spectrum origin of 2-carboxylic acid anthracene (24364 cm^{-1}) produced by 2-methylanthracene oxidation during the crystal growth.

For the ranges (b), (d), (g) and (h), we have no clues to allow a classification either as chemical traps, or as physical defects inducing energy traps.

CONCLUSION

We have observed and were able roughly to classify the additional lines in anthracene spectrum in the following groups:

a) a first group composed of strong narrow lines in which the wavelengths completely coincide with those seen in emission and which can be assigned to origin levels of traps in the crystal. These traps are either chemical impurities or physical defects.

b) a second group including less intense lines of which the wavelengths coincide only approximately with the emission wavelengths, but which can be assigned to vibrational spectra constructed from the origins of the trap levels of the previous group.

c) a third set of lines which have been seen only in absorption and which we assign also to the presence of trap levels.

A few traps seem to be chemical impurities which absorb light in their O–O band, while others are physical defects whose exact nature is unknown.

References

1. J. W. Sidman, *Phys Rev.*, **102**, No. 1, 96–101 (1956).
2. R. S. Berry, J. Jortner, J. C. Mackie, E. S. Pysh, and S. A. Rice, *J. Chem. Phys.*, **42**, No. 5, 1535–1540 (1965).
3. G. C. Morris, S. A. Rice, and A. E. Martin, *J. Chem. Phys.*, **52**, No. 10, 5149–5158 (1970).
4. W. Helfrich and F. R. Lipsett, *J. Chem. Phys.*, **43**, No. 12, 4368–4376 (1965).
5. L. E. Lyons and L. J. Warren, *Aust. J. Chem.*, **25**, 1411–25 (1972).
6. A. Brillante, D. P. Craig, A. W.-H. Mau, and J. Rajikan, *Chem. Phys. Letters, Netherl.*, **31**, No. 2, 215–219 (1975).
7. A. Brillante, D. P. Craig, A. W.-H. Mau, and J. Rajikan, *Chem. Phys. Letters, Netherl.*, **30**, No. 1, 5–10 (1975).
8. Davydov, *Theory of Molecular Excitons*, McGraw-Hill.
9. P. Pesteil, *C.R. Acad. Sc. Paris*, **263**, B, 1250 (1966).
10. E. Glockner and H. C. Wolf, *Z. Naturf.* (*A.*), **24**, 943 (1969).
11. L. E. Lyons and L. J. Warren, *Aust. J. Chem.*, **25**, 1427–41 (1972).
12. M. Brigodiot and J. M. Lebas, *C.R. Acad. Sci. Paris*, **268**, B, 51–54 (1969).
13. G. Durocher and D. F. Williams, *J. Chem. Phys.*, **51**, No. 12, 5405–5414 (1969).
14. Lacey and Lyons, *J. Chem. Soc.*, 5393 (1964).
15. G. C. Morris, S. A. Rice, M. G. Sceats, and A. E. Martin, *J. Chem. Phys.*, **55**, No. 12, 5610–5621 (1971).
16. N. J. Bridge and D. Vincent, *Chem. Soc. Faraday, II*, **68**, 1522 (1972).