RESEARCH ARTICLE | AUGUST 01 1969

Infrared Spectrum of Anthracene-d_{10}

A. Bree; R. A. Kydd

J. Chem. Phys. 51, 989–995 (1969)
https://doi.org/10.1063/1.1672168

Infrared Spectrum of Anthracene-d_{10}*

A. BREE AND R. A. KYDD†
Chemistry Department, University of British Columbia, Vancouver 8, British Columbia, Canada
(Received 26 September 1968)

The infrared spectrum of anthracene-d_{10} is reported with the electric vector of the plane-polarized incident light parallel to all three crystal axes; thus the c-polarized spectrum is recorded for the first time. The measurements extend from 2000 to ~50 cm^{-1}; the single-crystal samples used were too thick to transmit radiation in the strongly absorbing region near 2260 cm^{-1} so that little new data are available concerning the CD stretching fundamentals. However, a fairly complete assignment of the molecular fundamentals at lower energy is presented, based on the criteria of line strength and polarization, and the product rule. A comparison with calculated frequencies and some earlier experimental assignments is given.

INTRODUCTION

In a recent publication[1] (hereafter referred to as I), we have reported the results of a study of the infrared spectrum of anthracene-h_{10} single crystals extending down to 50 cm^{-1}. The use of plane-polarized light parallel to all three crystal axes permitted an assignment to be made of all the infrared-active lattice modes and low-frequency molecular vibrations. In addition, a more tentative assignment of the higher-energy infrared-active fundamentals was proposed.

In this paper the infrared spectrum of anthracene-d_{10} is recorded with the plane of polarization of the incident light along all three crystal axes. The spectrum of the deuterated molecule down to about 400 cm^{-1} has been reported[2,3] with the plane of polarization parallel to the axes a and b of a sublimation flake and, by comparison with the solution spectrum, two rather dissimilar assignments of the molecular fundamentals were made. Both assignments were based on the assumption that c-polarized bands should have a greater relative strength in solution (or KBr pellet) than in the ab spectrum. In a later paper,[4] Califano revised his experimental assignment to make it consistent with the results of a normal-coordinate calculation which applied a simplified valence force field simultaneously to benzene, naphthalene, anthracene, and some deuterated derivatives.

The present work was undertaken with the aim of clarifying the experimental situation by recording the c-polarized spectrum to assign more firmly the B_{2u} bands and by extending the polarized measurements to the low-frequency region for the first time. It was hoped that such a study would permit an assessment of the ability of the unified force field[4] to predict the fundamental frequencies.

EXPERIMENTAL

Single-crystal sections were cut parallel to the ab, ac, and bc' crystal planes[5] from a large ingot kindly supplied by D. F. Williams. The techniques used to prepare the samples and the apparatus used to record the spectra have been described in I.

THE SPECTRA

Polarized spectra were recorded with light incident on the ab, bc', and ac faces; the spectra at energies less than 650 cm^{-1} are shown in Figs. 1, 2, and 3, respectively. Figures 4–6 show the spectra of the same faces at energies between 500 and 1900 cm^{-1}. Because of the higher extinction coefficients associated with the CD stretching vibrations, the crystals were almost opaque in the 2260-cm^{-1} region and the spectra are not included. Attempts to cut thinner bc' and ac crystals were unsuccessful with the limited amount of material available. The ab spectra for the higher-energy region were in good agreement with those already reported by Califano[2] and, to the extent that our ab sample was rather thicker than a sublimation flake, the data shown in Fig. 4 complement his. On the other hand, the resolution exhibited in the spectra of Colombo is not as good and a correspondence between lines of his spectra and those in Fig. 4 is not always obvious.

Table I lists the observed band frequencies and their assignments based on the oriented-gas assumption that B_{1u} lines are most intense along b, B_{2u} along c, and B_{3u} along a. The mean frequency of the two factor-group components was entered in Table I. Lines that show a significant factor-group splitting (with components parallel and perpendicular to b in parentheses) occur at 102 (100, 103), 397 (393, 401), 560 (564, 557), 722 (724, 720), and perhaps 784 (785, 782). That these are all out-of-plane modes is consistent with the similar

* This work was supported by a grant received from the National Research Council of Canada.
† Supported by a Studentship awarded by the National Research Council of Canada.
[1] A. Bree and R. A. Kydd, J. Chem. Phys. **48**, 5319 (1968).
[2] S. Califano, J. Chem. Phys. **36**, 903 (1962).
[3] L. Colombo, Spectrochim. Acta **20**, 547 (1964).
[4] N. Neto, M. Scrocco, and S. Califano, Spectrochim. Acta **22**, 1981 (1966).
[5] Paper I contains definitions of the crystal directions a' and c' and also describes the molecular axis convention used. Note that before making comparisons with the results of other workers, the axis conventions they used were changed (if necessary) to conform with the internationally recommended one used here and in I.

TABLE I. The polarized infrared spectrum of anthracene-d_{10}.

$\nu_{crystal}$	Assignment			$\nu_{crystal}$	Assignment		
	Present work	Reference 2	Reference 3		Present work	Reference 2	Reference 3
60 m	b_u			941 m	B_{2u}		
71 vw ?	a_u ?			982 ms	B_{2u}	B_{2u}	
100 w	b_u			998 vw	B_{3u} ?		
102 s	B_{3u}			1038 w	B_{2u}		
118 ms	a_u			1046 mw	B_{3u}		B_{3u}
153 m	B_{3u}			1062 vw	B_{2u}		B_{1u}
220 s	B_{1u}			1070 vw	B_{1u}		
336 mw	B_{1u}			1120 mw	B_{2u}	B_{2u}	B_{1u}
349 vw	B_{3u}			1175 ms	B_{2u}		
363 sh	B_{3u} ?			1195 vw	B_{2u}		
374 w	B_{2u}			1210 vw	B_{2u}		B_{1u}
393 m	B_{2u}			1220 ms	B_{1u}	B_{1u}	B_{1u}
397 vs	B_{3u}	B_{3u}	B_{3u}	1245 sh	B_{3u} ?	B_{1u}	B_{1u}
424 s	B_{3u} ?		B_{1u}	1258 vs	B_{1u}	B_{1u}	B_{1u}
435 w	B_{1u} ?		B_{3u}	1298 s	B_{2u}		
451 vw	B_{2u}			1312 ms	B_{2u}		B_{1u}
477 vvw	B_{3u} ?			1335 s	B_{2u}		B_{2u}
500 w	B_{2u}			1348 vw	B_{1u}	B_{2u}	
513 mw	B_{3u}	?		1380 ms	B_{1u}	B_{2u}	
531 vw	B_{2u}			1386 ms	B_{3u}	B_{1u}	B_{2u}
548 vw	B_{2u}			1401 s	B_{2u}		
560 vs	B_{3u}	B_{3u}	B_{3u}	1406 ms	B_{1u}		B_{1u}
575 vs	B_{2u}	B_{3u}	B_{3u}	1416 ms	B_{2u}		B_{3u}
601 vw	B_{3u}		B_{2u}	1430 m	B_{1u}		B_{3u}
619 w	B_{2u}		?	1455 sh	B_{2u}		
633 m	B_{3u}		B_{3u}	1468 ms	B_{2u}		
665 vw	B_{3u}		B_{1u}	1493 s	B_{2u}	B_{2u}	B_{2u}
689 ms	B_{3u}	B_{3u}	B_{3u}	1512 mw	B_{1u}		B_{1u}
703 ms	B_{2u}		A_u	1530 ms	B_{2u}		
722 vs	B_{3u}	B_{3u}	B_{3u}	1537 vw	B_{1u}		B_{1u}
755 m	B_{3u}	B_{3u}	B_{3u}	1556 w	B_{1u}		B_{1u}
784 vs	B_{3u}	B_{3u}	B_{3u}	1584 s	B_{1u}	B_{1u}	
805 m	B_{3u}	B_{3u}	B_{3u}	1597 vs	B_{2u}	B_{2u}	B_{2u}
824 vs	B_{2u}	B_{1u}	B_{3u}	1606 vw	B_{1u}		B_{1u}
830 sh	B_{3u} ?	B_{2u}	B_{2u}	1628 m	B_{1u}		
860 sh	B_{1u}	B_{1u}	B_{1u}	1647 m	B_{2u}		B_{1u}
879 vs	B_{1u}	B_{1u}	B_{1u}	1670 mw	B_{2u} ?		?
892 s	B_{3u}	B_{3u}	B_{3u}	1749 w	B_{1u}		
904 ms	B_{3u}		B_{2u}	1785 vw	B_{1u}		B_{2u}
913 s	B_{3u}	B_{3u}	B_{3u}	1808 vw	B_{1u}		B_{1u}
918 w	B_{2u} ?		B_{2u}	1824 ms	B_{2u}		B_{2u}

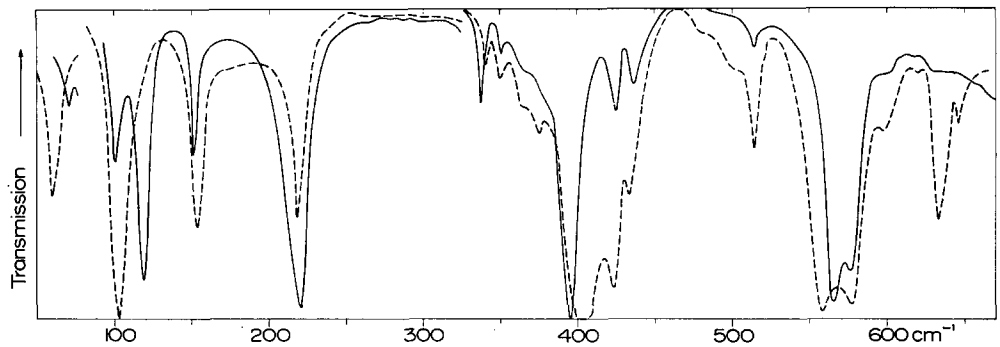

FIG. 1. Anthracene-d_{10} low-frequency infrared spectrum with incident light normal to *ab* face; crystal 0.45 mm thick below 325 cm^{-1}, 0.10 mm thick above 325 cm^{-1}. Solid line || *b*, broken line || *a*.

behavior[6] observed in anthracene-h_{10}. However, it should be noted that Colombo[3] has interpreted the *ab* spectrum as showing no factor-group splittings; in Table I we have accordingly omitted Colombo's assignments of what we take to be less intense factor-group components.

ASSIGNMENT OF FUNDAMENTALS

Excluding the CD stretching region eight B_{1u}, nine B_{2u}, and six B_{3u} fundamentals are expected. An additional three B_{1u} and two B_{2u} CD stretches should be found at about 2250 cm^{-1}. The following assignments are based on the assumption that strong lines mark the presence of molecular fundamentals. At low frequencies an attempt was made to assign all the lines, both weak and strong, in the hope of detecting a few low-energy infrared-inactive fundamentals; it was not considered worthwhile carrying this analysis beyond 500 cm^{-1} because of ambiguities arising from incomplete knowledge of inactive modes. It is clear that the greatest difficulty will rest in locating the last few fundamentals of each symmetry species from the many lines of low intensity.

The Low-Frequency Region

Three translational lattice modes, referred to here and in Table I using lower case symbols, are expected in the infrared spectrum; two are of symmetry a_u polarized along the *b* crystal axis and one of symmetry b_u polarized in the *ac* plane. The two a_u lattice modes are identified with the *b*-polarized lines at 71 and 118 cm^{-1} and the b_u mode with the essentially *a*-polarized line at 60 cm^{-1}. The second b_u line at 100 cm^{-1}, best seen as a *c*-polarized line in the *ac* spectrum, could be assigned as the combination of the b_u mode at 60 cm^{-1} with an a_g mode observed in the Raman spectrum[7] at 38 cm^{-1}. These frequencies, as expected, are somewhat less than the corresponding values[1] in an anthracene-h_{10} crystal where the a_u modes were located at 72 and 126 cm^{-1} and the b_u at 63 cm^{-1}.

In a molecule like anthracene that has a large number of intramolecular fundamentals at low frequency, considerable mixing between inter- and intramolecular modes may occur and any sharp distinction between them is lost. However, we identify the lines at 103 cm^{-1} (polarized in *ac*) and 100 cm^{-1} (polarized along *b*) as the two factor-group components of what was a B_{3u} fundamental in the isolated molecule. Other molecular fundamentals are seen at 153 (B_{3u}) and 220 cm^{-1} (B_{1u}).

Another difficulty arises in the interpretation of lines that appear only weakly in the spectrum. Crystal forces may induce mixing of free-molecule states resulting in transfers of intensity amongst the absorption lines of the

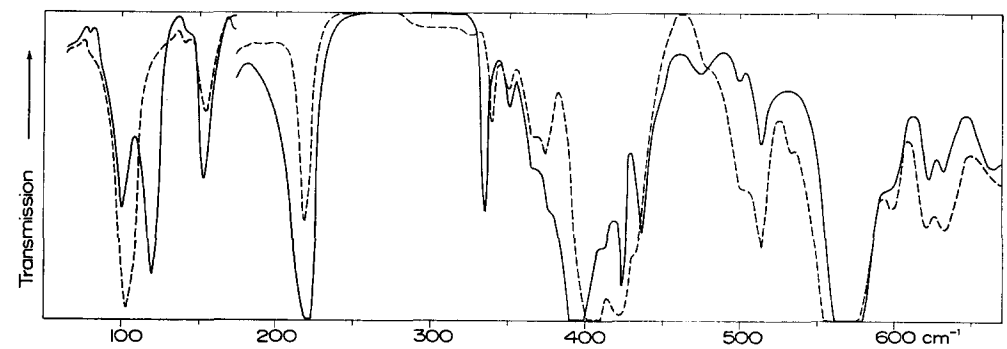

FIG. 2. Anthracene-d_{10} low-frequency infrared spectrum with incident light normal to *bc'* face; crystal 0.45 mm thick. Solid line || *b*, broken line || *c'*.

[6] S. Califano, Mol. Phys. **5**, 601 (1962).
[7] A. Bree and R. A. Kydd, Chem. Phys. Letters (to be published).

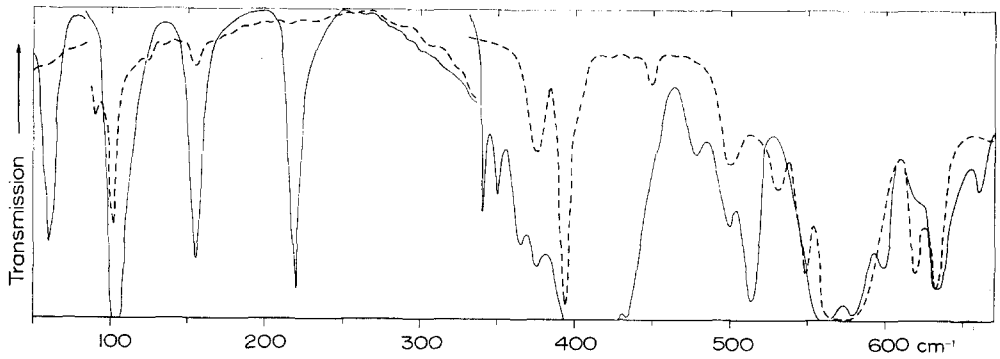

FIG. 3. Anthracene-d_{10} low-frequency infrared spectrum with incident light normal to ac face; crystal 0.95 mm thick below 85 cm^{-1} 0.47 mm thick above 85 cm^{-1}. Solid line || a', broken line || c.

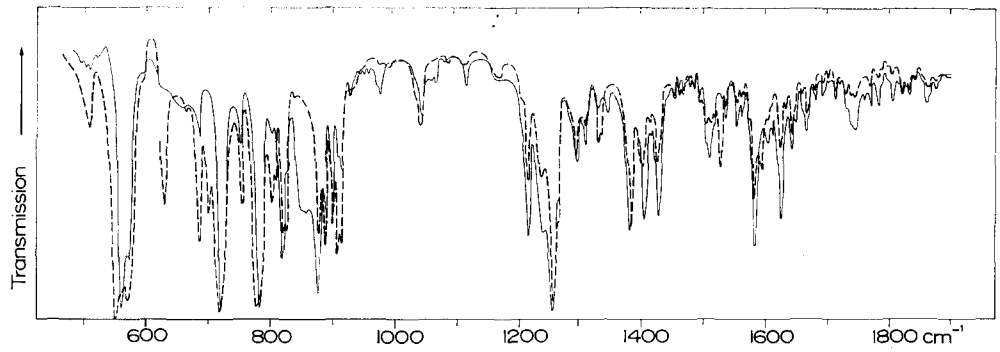

FIG. 4. Anthracene-d_{10} infrared spectrum, 500–1900 cm^{-1}, with incident light normal to ab face. Solid line || b, broken line || a.

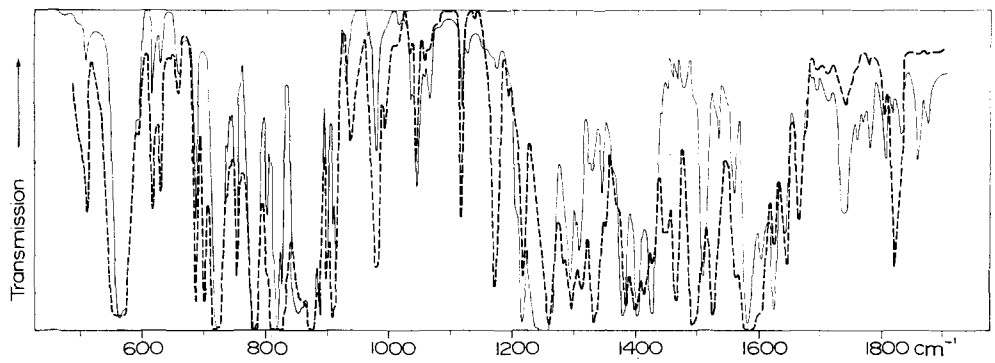

FIG. 5. Anthracene-d_{10} infrared spectrum, 500–1900 cm^{-1}, with incident light normal to bc' face. Solid line || b, broken line || c'.

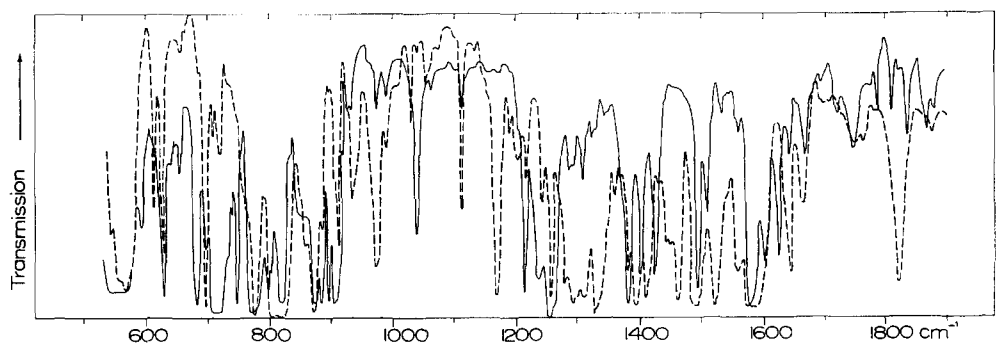

FIG. 6. Anthracene-d_{10} infrared spectrum, 500–1900 cm^{-1}, with incident light normal to ac face. Solid line || a', broken line || c.

gas-phase spectrum. However, the transferred intensity retains the characteristics of the line it originated from so that lines of mixed symmetry (in D_{2h}) may be found. These effects are usually most obvious in weak lines (combinations) when the mixed-in contribution may outweigh the original, or in forbidden lines (A_u fundamentals or combinations) that gain all their strength in this manner.

Lines that showed mixed B_{1u} and B_{3u} character were observed at 349, 363, 424, and 435 cm^{-1}. Presumably the B_{3u} intensity was stolen from the very strong B_{3u} fundamental at 397 cm^{-1} that dominates this region of the spectrum. B_{1u} intensity may be derived from the more distant strong line at 220 cm^{-1} although this process would probably be relatively inefficient unless the combination itself was of B_{1u} symmetry. The following tentative analysis of the remaining low-frequency lines may then be made:

$$336(B_{1u}) = 125(A_u) + 216(B_{1g}) - 5,$$

$$349(B_{3u}) = A_u \text{ fundamental},$$

$$363(B_{3u}?) \equiv 363(B_{1u}) = 102(B_{3u}) + 270(B_{2g}) - 9,$$

$$374(B_{2u}) = 153(B_{3u}) + 216(B_{1g}) + 5,$$

$$393(B_{2u}) = 125(A_u) + 270(B_{2g}) - 2,$$

$$397(B_{3u}) = B_{3u} \text{ fundamental},$$

$$424(B_{3u}) \equiv 424(B_{1u}) = 153(B_{3u}) + 270(B_{2g}) + 1,$$

$$435(B_{1u}?) \equiv 435(A_u) = 216(B_{1g}) + 220(B_{1u}) - 1,$$

$$451(B_{2u}) = 102(B_{3u}) + 349(B_{1g}),$$

$$477(B_{3u}) = 102(B_{3u}) + 381(A_g) - 6,$$

$$500(B_{2u}) = 153(B_{3u}) + 349(B_{1g}) - 2.$$

In the above analysis we have postulated the presence of five fundamentals at 125(A_u), 216(B_{1g}), 270(B_{2g}), 349(A_u), and 349 cm^{-1}(B_{1g}) and there is very little experimental information available concerning the low-frequency g fundamentals to check these assumptions. Two very weak lines at 221 and 280 cm^{-1} and a strong line at 381 cm^{-1} were observed[8] in the fluorescence spectrum of anthracene-d_{10} in a fluorene matrix. All three lines were polarized in the same sense as the electronic origin indicating that they were either A_g, B_{1u}, B_{2g}, or B_{3u}. The strong line formed a progression and was assigned A_g while the two weak lines were presumed to be either B_{1u}, B_{2g}, or B_{3u} molecular vibrations arising through crystal forces. The lower line coincides with the 220-cm^{-1} B_{1u} line we have identified so that the line at 280 cm^{-1} marks the position of the lowest B_{2g} fundamental in the fluorene matrix. Recently, the lowest B_{1g} and B_{2g} fundamentals of anthracene-h_{10} were located[9] at 243 and 290 cm^{-1}, respectively, so that corresponding values near 216 and 270 cm^{-1} for the deuterated molecule are very reasonable.

The above analysis parallels assignment II for anthracene-h_{10} presented in Paper I and suggests that the recent Raman spectrum of the solid[9] on which it was based is more reliable at low-frequency intervals than the solution Raman spectrum,[10] since no reasonable analogy to assignment I was possible for anthracene-d_{10}. Although the analysis given above was not unique others tried seemed less plausible in at least one respect, e.g., the prediction of an A_u molecular fundamental with a frequency less than 100 cm^{-1}, a B_{3g} fundamental less than 250 cm^{-1}, or an anthracene-d_{10} frequency rather greater than or very much less than the corresponding anthracene-h_{10} value.

B_{1u} Fundamentals

There are three CD stretching fundamentals having B_{1u} symmetry. A very intense b-polarized line centered at 2264 cm^{-1} dominates this region of the spectrum and is assigned as one B_{1u} CD stretching fundamental. This line is flanked by lines at 2248 and 2283 cm^{-1} of lesser strength and these are taken as the other CD stretching fundamentals in agreement with the previous workers.[2,3]

The eight B_{1u} fundamentals expected below 2000 cm^{-1} are difficult to identify. Only four fairly certain assignments can be made corresponding to the lines at 220, 879, 1258, and 1584 cm^{-1}. The line of medium strength at 1220 cm^{-1} and at least one of the trio of lines at 1380, 1406, and 1430 cm^{-1} may also mark the positions of fundamentals. We have rather arbitrarily taken the fundamental at 1406 cm^{-1} since it probably has the greatest B_{1u} intensity; certainly the strength of the line at 1380 cm^{-1} is exaggerated by the overlap with the B_{3u} line at 1386 cm^{-1}. The presence of four fundamentals above 1200 cm^{-1} suggests there are four ring modes (see Table II for a correlation between modes of the isotopic molecules) where only three are expected. However, the approximation that ring modes and CH in-plane bends do not strongly interact may not be warranted for a molecule as large as anthracene and the 1220 cm^{-1} assignment is retained especially since there seems to be no reasonable alternative.

In an attempt to locate the remaining two fundamentals below 2000 cm^{-1} we have been guided by product rule calculations. The expected value for the product rule ratio is 0.182. If the 11 fundamentals proposed for anthracene-h_{10} and the nine so far assigned for anthracene-d_{10} are accepted as correct, then we conclude that *both* of the unassigned fundamentals must lie between 500 and 800 cm^{-1}. However, it is evident from Table I and Figs. 4–6 that any B_{1u} lines that may be present in

[8] A. Bree, S. Katagiri, and S. R. Suart, J. Chem. Phys. **44**, 1788 (1966).

[9] M. Suzuki, T. Yokoyama, and M. Ito, Spectrochim. Acta **24A**, 1091 (1968).

[10] N. Abasbegovic, N. Vukotic, and L. Colombo, J. Chem. Phys. **41**, 2575 (1964).

TABLE II. Summary of the infrared-active fundamentals of anthracene-d_{10} and anthracene-h_{10}.[a]

Symmetry type	Experimental					Calculated		
	Present work	Reference 2	Reference 4	Reference 3	$C_{14}H_{10}$	Reference 4	Reference 11	$C_{14}H_{10}$
B_{1u}	220	...	...	283	235	199	195	210
	?	(720)	592	592	650?	617	599	627
	?	822	822	730	903	825	840	922
	879	881	881	882	1145	861	891	1147
	1220?	981	...	1235	1270	1041	1035	1246
	1258	1264	1264	1259	1315	1275	1215	1266
	1406?	1389	1389	1400	1447	1380	1357	1450
	1584	1583	1583	1515	1616	1582	1603	1623
	2248?	2247	2247	2250	3024?	2246	2276	3051
	2264	2262	2262	2260	3050	2271	2291	3062
	2283?	2297	2288	2288	3108?	2280	2303	3073
B_{2u}	575	580	580	388	600	588	570	591
	703	706	706	562	808?	701	660	808
	824	831	...	830	998	811	824	1011
	879?	901	831	903	1068	840	847	1114
	982	...	920	920	1163	943	1007	1181
	1175	1125	...	1325	1392	1267	1291	1345
	1335	1342	1325	1390	1495	1315	1317	1387
	1493	1384	1384	1503	1533	1392	1351	1457
	1597	1500	1500	1595	1690?	1487	1506	1534
	...	2238	2238	2225	3050	2257	2261	3040
	2267	2273	2275	2275	3093?	2294	2294	3062
B_{3u}	102	236		260	110		93	98
	153	407		403	166		333	378
	397	563		566	469		416	484
	560	577		584	730		571	743
	722	726		690	883		753	916
	784	790		758	954		804	959

[a] Entered in the columns headed $C_{14}H_{10}$ are experimental data from Paper I and calculated values from Ref. 11.

this region are hidden by very intense B_{3u} and B_{2u} bands. If the fundamental corresponding to the 650-cm^{-1} vibration of anthracene-h_{10} is assumed to be hidden under the complex system at 560–570 cm^{-1} then the other is predicted by the product rule to appear near 740 cm^{-1} and may be part of the strong absorption at 722 cm^{-1} as suggested by Colombo[3] and in an early work[2] by Califano, or it may be hidden in the strong band at 784 cm^{-1} or even in the strong B_{2u} band at 824 cm^{-1} as suggested by Neto, Scrocco, and Califano in a recent paper.[4] We tentatively assign the final fundamental at about 724 cm^{-1} (the frequency of the *b*-polarized component) although we note that both the 722- and 784-cm^{-1} lines are nearly depolarized in the *ab* spectra.

B_{2u} Fundamentals

Eleven B_{2u} fundamentals are expected, two of these appearing above 2000 cm^{-1}. A very intense *c*-polarized line centered at about 2267 cm^{-1} must mark the presence of at least one of these two CD stretching fundamentals. The second was probably also contained in this strong absorption region (efforts to reduce the thickness of the samples led to breakage) and for the

purpose of product rule calculations we accept the value 2238 cm^{-1} suggested by previous authors.[2-4]

From the *c*-polarized spectrum, eight of the nine fundamentals below 2000 cm^{-1} can be chosen immediately at 575, 703, 824, 982, 1175, 1335, 1493, and 1597 cm^{-1}. There has been no previous experimental evidence to establish that the lines at 703 and 1175 cm^{-1} have B_{2u} symmetry. From product rule calculations (using anthracene-h_{10} frequencies from Paper I) it can be shown that the remaining fundamental must lie near 900 cm^{-1}. Colombo[3] has assigned two B_{2u} fundamentals in this region at 903 and 920 cm^{-1}. Califano[2] has named 901 cm^{-1} and Neto, Scrocco, and Califano[4] have chosen 920 cm^{-1}. From the *ac* and *bc'* spectra, it is clear that the 901-cm^{-1} line is not of B_{2u} symmetry, belonging instead to the B_{3u} species, as does the line at 913 cm^{-1}. The line at 918 cm^{-1} may be of B_{2u} symmetry but in any event is rather weak. We suspect that the strong B_{1u} line at 879 cm^{-1} may also contain the missing B_{2u} fundamental since, in both the *bc'* and *ac* spectra, this line shows unexpected *c*-polarized strength. Inclusion of the 879-cm^{-1} assignment yields a product ratio of 0.179 (theoretical 0.182). As an alternative assignment of the last fundamental, the line at 1120 cm^{-1} of moderate strength (some of which was probably gained from the stronger line at 1175 cm^{-1}) leads to product rule difficulties.

B_{3u} Fundamentals

As for anthracene-h_{10}, the choice of the six infrared-active out-of-plane fundamentals of anthracene-d_{10} is automatic. Strong lines were observed at 102, 153, 397, 560, 722, and 784 cm^{-1} and these correlate very well with the anthracene-h_{10} frequencies. The observed product ratio is 0.372 which compares well with the predicted 0.364.

DISCUSSION

The fundamentals of anthracene-d_{10} are listed in Table II together with those assigned by earlier workers[2-4] for comparison. Experimental assignments for anthracene-h_{10} taken from Paper I and frequencies calculated for anthracene-d_{10}[4,11] and anthracene-h_{10}[11] are also included.

Most of the discrepancies in the experimental assignments occur in the low-frequency region. Thus we find no evidence to confirm the presence of a line at 236 cm^{-1} as suggested by Califano,[2] or of lines at 283 and 260 cm^{-1} as reported by Colombo[3]; our interpretation of the *c*-polarized line at 388 cm^{-1} differs from Colombo's in that we assign it as a B_{2u} combination. Other important differences not already noted occur (a) in the B_{1u} symmetry block where Califano[2] has assigned the B_{2u} line of only medium strength at 981 cm^{-1} as a B_{1u} fundamental and Colombo[3] has selected a fairly weak line at 1515 cm^{-1} as a fundamental in place of the very much stronger line at 1584 cm^{-1}, (b) in the B_{2u} symmetry block where both Califano[2] and Colombo[3] have selected lines that probably correlate with our B_{2u} line at 1401 cm^{-1} as a fundamental in place of the one assigned at 1597 cm^{-1} in the present work, and (c) in the B_{3u} symmetry block where both of the previous workers[2,3] assigned two B_{3u} fundamentals (as well as a B_{1u} and a B_{2u} fundamental) in the complex region around 570 cm^{-1} while our interpretation involves two low-frequency fundamentals at 102 and 153 cm^{-1}.

Essentially the same difficulties arise when a comparison is made with the calculated frequencies (see Table II). For example, the calculations suggest that the 1220-cm^{-1} line may mark a B_{1u} combination acquiring intensity from the very strong line at 1258 cm^{-1} and that the fundamental is located near 1040 cm^{-1} but is accidentally forbidden. Again, the force fields predict the highest-frequency ring-stretching B_{2u} fundamental to be about 100 cm^{-1} less than the measured 1597 cm^{-1} and the B_{3u} fundamental to be about 150 cm^{-1} more than the observed 153 cm^{-1}. However, these last two difficulties also arise in the analysis of the anthracene-h_{10} spectrum.[1] It should be emphasized that the assignment given in Table II was made essentially on the basis of experimental evidence. It is possible to find alternative experimental assignments for the B_{2u} fundamentals that are rather closer to the calculated values[4,11] yet give a reasonable product rule ratio as follows: anthracene-h_{10}, 3093, 3050, 1533, 1495, 1392, 1219, 1163, 1068, 998, 808, and 600 cm^{-1}; anthracene-d_{10}, 2267, 2238, 1493, 1335, 1175, 1120, 982, 941, 824, 703, and 575 cm^{-1}; product rule ratio, 0.186 (theoretical, 0.182). We will refer to this as assignment *B* and the one in Table II as assignment A. The line at 941 cm^{-1} in B has replaced 879 cm^{-1} in A as the last-chosen fundamental of anthracene-d_{10} to give a better product rule fit; either of these two represents a dubious assignment, as mentioned earlier.

The choice of A or B is rather arbitrary with the present evidence and rests on the choice of the highest ring mode. One method of resolving the dilemma would be to attempt to account for the anthracene-h_{10} line at 1690 cm^{-1} and the anthracene-d_{10} line at 1598 cm^{-1} as binary combinations of out-of-plane modes, as was done for similar bands in benzene[12,13] and naphthalene.[14] Evans and Scully[15] and Krainov[11] have calculated the out-of-plane frequencies of anthracene, but the fit with our B_{3u} assignments is not good in either case. We will attempt to repeat these calculations to fit the more recent experimental data and will extend the treatment to include estimates of the relative strengths of the combinations.

[11] E. P. Krainov, Opt. Spektrosk. **16**, 984 (1964) [Opt. Spectrosc. **16**, 532 (1964)].

[12] Y. Kakiuti, J. Chem. Phys. **25**, 777 (1956).

[13] F. E. Dunstan and D. H. Whiffen, J. Chem. Soc. **1960**, 5221.

[14] D. B. Scully and D. H. Whiffen, J. Mol. Spectry. **1**, 257 (1957).

[15] D. J. Evans and D. B. Scully, Spectrochim. Acta **20**, 891 (1964).