Condensed Aromatics. Part VII

The Five-Parameter Approximation of the Out-of-Plane Force Field Applied to Anthracene and Pyrene

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A simple, five-parameter force field approximation for the out-of-plane vibrations of aromatic molecules is applied to anthracene and pyrene. The calculated frequencies are remarkably well compatible with previous calculations and observed data. Among the given experimental frequencies are new data recorded in infrared for anthracene and both in Raman and infrared for pyrene.

Introduction

In the previous part [1] of this paper series a simple force-field approximation for the out-of-plane vibrations of aromatic molecules was developed. The benzene and naphthalene molecules were analysed. In the present work the force field is applied to anthracene and pyrene.

A force-constant matrix is based on a set of conventional valence coordinates including redundancies. Specifically two "boat" torsions are defined for every CC bond and one out-of-plane bending for every C atom. The nonvanishing force constants are all given by the following five parameters; values in mdyne/Å:

$$f_\gamma = 0.20\,, \quad f_\gamma^* = 0.15$$

for the CH and CC out-of-plane bendings, respectively;

$$f_\delta = 0.05$$

for every torsion. The only nonvanishing interaction terms occur for every pair of torsions pertaining to the same CC bond;

$$f_{\delta\delta} = 0.07\,, \quad f_{\delta\delta}^* = 0.02\,,$$

where $f_{\delta\delta}$ pertains to the HCCH/CCCC and HCCC/CCCC types and $f_{\delta\delta}^*$ to CCCC/CCCC. These numerical values were developed during the analysis of benzene and naphthalene [1]. No additional parameters are included in the present extension of the application of the force field.

Anthracene

Calculated Frequencies

An analysis of the in-plane vibrations of anthracene is reported in Part II [2] of the series. Part I [3] gives reference to the applied structural parameters, which are adopted also in the present work. A complete set of independent symmetry coordinates is given elsewhere [4].

In the construction of the out-of-plane force field 10 parameters f_γ were needed, 4 of f_γ^*, 32 of f_δ, 14 of $f_{\delta\delta}$ and 2 of $f_{\delta\delta}^*$.

Table 1 shows three sets of calculated out-of-plane frequencies for anthracene. The sets are due to: (1) Krainov [5], who performed an elaborate force-constant analysis involving many interaction terms. Details from the analysis are not reported. (2) Evans and Scully [6], who applied the seven-parameter approximation of Whiffen et al. [9, 10]. (3) The present results of the five-parameter approximation [1].

Experimental Raman Frequencies

The assignments of recorded Raman lines for anthracene have been very uncertain and contra-

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Table 1. Calculated and observed frequencies (cm^{-1}) for the out-of-plane vibrations of anthracene.

Species	Calculated			Observed
	Krainov [5]	Evans and Scully [6]	Present	
B_{1g}	949	936	956	956
	754	739	761	760
	437	466	444	479
	215	235	255	244
B_{2g}	977	960	981	977
	929	909	930	916
	858	871	869	896^a
	840	754	755	773
	552	617	572	580
	270	321	293	287
A_u	975	966	979	988
	848	876	874	858
	774	826	704	743
	488	552	505	—
	133	137	142	—
B_{3u}	959	952	969	956
	916	892	922	883
	743	732	758	737/725
	484	504	428	474/464
	378	383	396	380^b
	98	96	102	106

[a] From Ref. [7]. The other Raman (B_{1g} and B_{2g}) frequencies are from Ref. [2].

[b] From Ref. [8]. All other infrared (A_u and B_{3u}) frequencies are present values (cf. Tables 3 and 4).

dictory until recently. Some experimental Raman frequencies from 1964 [11] are quoted in the work on the infrared spectrum by Bree and Kydd [8]. Assignments from 1968 [12] and 1969 [13] are quoted elsewhere [7].

In Table 1 we were able to produce an almost complete assignment in Species B_{1g} and B_{2g} using Raman data recorded in our laboratory [2]. None of these bands has been used in the previous assignment of inplane frequencies for anthracene [2]. Only one fundamental in the B_{2g} species is unobserved.

Krainov [5] used 852 cm^{-1} in place of our unobserved frequency, making reference to Landolt-Börnstein tables from 1951. He has assigned a very weak band of 852 cm^{-1} to both A_g (in-plane) and B_{2g} (out-of-plane; our notation). Otherwise the three quoted Landolt-Börnstein values (745, 474 and 577 cm^{-1}) assigned to out-of-plane vibrations by Krainov [5] are fairly compatible with the Klaeboe values.

Among the Raman frequencies observed by Colombo and Mathieu [14], quoted by Evans and Scully [6] and assigned to in-plane vibrations, the 475 cm^{-1} band evidently corresponds to one of our B_{1g} (out-of-plane) fundamentals.

A modern re-investigation of the Raman spectrum of anthracene is due to Räsänen et al. [7]. This excellent work is a continuation of a similar investigation of naphthalene by Stenman [15]. It is interesting to notice the extremely good agreement of the experimental assignment of Raman inplane (A_g and B_{3g}) frequencies of Räsänen et al. [7] with our independent assignment of the frequencies [2]. Also for the out-of-plane frequencies we find a close correspondence (cf. Table 2). For the missing frequency in Species B_{2g} we have adopted the very weak band (896 cm^{-1}) reported by Räsänen et al. [7].

Experimental Infrared Frequencies

Table 3 gives a survey of modern infrared records of anthracene frequencies assigned to out-of-plane vibrations. All the quoted data pertain to the crystalline phase; hence some inactive A_u frequencies may also be observed. Three of the works [16—18] have given almost identical assignments for the infrared-active B_{3u} frequencies. The later work of Bree and Kydd [8] represents an interesting innovation. Their 600 cm^{-1} band is assigned as the lowest B_{2u} (in-plane) frequency. This interpretation was also adopted in our analysis of the in-plane vibrations of anthracene [2]. The lowest B_{3u} fundamental as 110 cm^{-1} [8] is confirmed by all the calculations reported in Table 1, but neither 166 cm^{-1} [8] or 278 cm^{-1} [16, 18] are compatible with the calculations. We should look for a frequency around 396 cm^{-1} (our calculated value). Unfortunately we

Table 2. Observed Raman frequencies (cm^{-1}) assigned to out-of-plane vibrations of anthracene^a.

Species	Ref. [7]	Ref. [2]
B_{1g}	956 (15)	956 m
	747 (9)	760 m, sh
	477 (40)	479 m
	242 (81)	244 m
B_{2g}	975 (5)	977 w
	916 (7)	916 m
	896 (1)	—
	771 (5.5)	773 w
	577 (3)	580 vw
	284 (22)	287 m

[a] Relative intensities in parentheses. Abbreviations: m medium; w weak; v very; sh shoulder.

Table 3. Observed infrared frequencies (cm^{-1}) assigned to out-of-plane vibrations of anthracene[a].

Species	Califano [16]	Mecke et al. [17]	Colombo [18]	Bree and Kydd [8]	Present
A_u	979 w	980	—	(977 m)	988 w
	860 w	860	870	(856 m)	858 w
	778 vw	743	—	(775 w)	743 m
B_{3u}	956 s	953	955 vs	954 s	956 s
	884 vs	880	880 vs	883 vs	883 vs
	727 vs	726	725 vs	730 vs	737 s/ 725 vs
	603 w(m)	600	600 vs	(600 s)	(601 m)
	475 vs	468	474 vs	469 vs	474 s/ 464 m
	—	—	(384 w)	(380 w)	—
	278 s	—	278 m	—	—
	—	—	—	166 s	—
	—	—	—	110 s	106 s

[a] Parenthesized values are assigned differently in the cited works. Abbreviations: s strong; m medium; w weak; v very.

cannot use 392 cm^{-1} from a misquotation of Bree and Kydd [8]. It appears from the original work [17] that this frequency pertains to 9, 10-dibromo-anthracene. But Bree and Kydd [8] have reported a weak band at 380 cm^{-1} and Colombo [18] at 384 cm^{-1}. They have assigned them as combination bands. We suggest these bands to be B_{3u} fundamentals. This opinion is strongly supported by all the calculations reported in Table 1.

Table 4 shows details below 1000 cm^{-1} of the infrared spectrum from Klaeboe's laboratory. They have not been published previously. The experimental conditions and bands assigned to in-plane vibrations (B_{1u} and B_{2u}) are reported elsewhere [2]. For the sake of comparison also the details from the infrared spectrum of Bree and Kydd [8] are shown (Table 4). Finally we have included the recently reported observations of Vodehnal et al. [19]. These workers have not indicated a precise assignment of their frequencies, but suggested characteristic regions and approximate modes.

The three sets of calculated frequencies (Table 1) are seen to be very nicely compatible with each other. In many instances our simple approximation tends to confirm the results of Krainov [5] from his elaborate analysis rather than the results of Evans and Scully [6] from the Whiffen approximation [10].

Table 4. Observed infrared frequencies (cm^{-1}) below 1000 cm^{-1} for anthracene[a].

Bree and Kydd [8]	Vodehnal et al. [19]	Present[b]	
998 s	998 s	998 m	(B_{2u})
977 m	979 w	988 w	(A_u)
954 s	957 s	956 s	(B_{3u})
930 ?		930 vw	
915 ?			
903 s	906 m	906 w	(B_{1u})
883 vs	886 vs	883 vs	(B_{3u})
856 m	859 w	858 w	(A_u)
		823 vw	
808 w	810 vw	809 vw	(B_{2u})
775 w	775 m	775 vw	
	757 w	751 w, sh	
744 m	743 m	743 m	(A_u)
	737 m	737 s	(B_{3u})
730 vs	729 vs	725 vs	
706 ?			
689 vw			
650 m	655 w	653 w	(B_{1u})
621 vw	613 m		
600 s	602 s	601 m	(B_{2u})
536 vw	574 vw	567 vw	
515 vw			
493 w			
469 vs	476 vs	474 s	(B_{3u})
464 w	466 s	464 m	
456 sh	452 w		
431 sh	440 sh	431 vw	
423 sh			
380 w			
361 vw			
235 s		234 w	(B_{1u})
166 s		165 vw	
126 s		121 vw	
107 w			
110 s		106 w	(B_{3u})
104 m			
72 w			
63 m			

[a] Abbreviations: See footnotes to Tables 2 and 3.

[b] Tentative assignments given in parentheses. Notice that B_{1u} and B_{2u} are in-plane modes.

Pyrene

Calculated Frequencies

The in-plane vibrations of pyrene are treated in Part III [20]. That paper also includes the reference to structural data and a complete set of independent symmetry coordinates.

In our five-parameter approximation the different parameters enter into the force-constant matrix in the following way. There are 10 parameters f_γ, 6 of f_γ^*, 38 of f_δ, 14 of $f_{\delta\delta}$ and 5 of $f_{\delta\delta}^*$.

Table 5. Calculated and observed frequencies (cm^{-1}) for the out-of-plane vibrations of pyrene.

Species	Calculated		Observed	
	Bree et al. [21]	Present	[21]	Present
B_{1g}	899	932	—	—
	811	837	—	842
	512	497	—	—
	251	272	263	221
B_{2g}	963	986	971 ?	1003 ?
	947	960	—	970
	764	943	780 ?	—
	755	792	—	799
	579	566	530 ?	581
	469	495	—	—
	272	280	227	268
A_u	942	968	—	973 ?/966
	897	922	—	910
	660	622	—	589
	391	425	319 ?	—
	179	172	164	—
B_{3u}	957	977	963	963
	816	855	845	839
	753	783	748	747
	717	732	710	708
	483	500	484	483
	195	210	219	218
	113	118	126	—

Observed Frequencies

The assignment of infrared and Raman frequencies to the out-of-plane fundamentals of pyrene due to Bree et al. [21] is shown in Table 5. The last column of this table shows our frequency values. They have not been published previously, but the experimental conditions and an assignment to in-plane fundamentals is given elsewhere [20]. In Table 6 we give the observed frequencies below 1010 cm^{-1} from this work along with a tentative assignment of fundamentals to the different species. Notice that A_g, B_{3g}, B_{1u} and B_{2u} are the species of in-plane modes. Our experimental assignment for the out-of-plane modes (Table 5) basically confirms the one of Bree et al. [21]. There are some hardly significant discrepancies for the highest frequencies of B_{2g}; our calculation indicates that three of them should be above 900 cm^{-1}. We have assigned rather arbitrarily 221 and 268 cm^{-1} to B_{1g} and B_{2g}, respectively, because it fits somewhat better the calculations than the opposite choice. Bree et al. [21] have chosen the opposite assignments, viz. 227 cm^{-1} (B_{2g}) and 263 cm^{-1} (B_{1g}).

In conclusion we find the application of our five-parameter approximation to the out-of-plane vibrations of pyrene to be very successful.

Future Prospects

The developed force-field approximation is simple enough to be extended to larger condensed aromatic molecules. Applications to triphenylene, naphthacene and pentacene are in progress. Out-of-plane force fields for these molecules have not been developed previously, as far as we know, although in-plane force-field analyses have been reported [22, 23].

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Table 6. Observed frequencies (cm^{-1}) below 1010 cm^{-1} for pyrene[a].

Raman			Infrared			
1003 w	(B_{2g} ?)	203 vw	1000 vw		708 vs	(B_{3u})
970 w, bd	(B_{2g})	186 w, sh	989 vw		692 w, sh	
842 w	(B_{1g})	174 vw	973 w, sh	(A_u ?)	674 vw	(B_{1u})
805 w	(A_g)	160 w	966 w, sh	(A_u)	589 w	(A_u)
799 vw, sh	(B_{2g})	139 w	963 w	(B_{3u})	578 vw	
775 vw	(B_{3g})	127 w, sh	959 w, sh		540 w	(B_{2u})
594 s	(A_g)	118 m	910 w	(A_u)	528 w	
581 vw	(B_{2g})	95 w, bd	891 w	(B_{2u})	496 w	(B_{1u})
505 m	(B_{3g})	79 m	850 w, sh		483 w	(B_{3u})
450 m	(B_{3g})	68 w	839 vs	(B_{3u})	454 vw	
408 s	(A_g)	59 m	819 w	(B_{1u})	351 m	(B_{2u})
268 m	(B_{2g})	55 s	804 vw		268 w	
221 vw	(B_{1g})	50 m	800 vw		260 w	
210 vw, sh		47 w	777 w		218 m	(B_{3u})
			747 s	(B_{3u})	204 sh	
			734 w, sh			

[a] Abbreviations: bd broad; otherwise see footnotes to Tables 2 and 3.

[1] B. N. Cyvin, G. Neerland, J. Brunvoll, and S. J. Cyvin, Z. Naturforsch. (in press).

[2] A. Bakke, B. N. Cyvin, J. C. Whitmer, S. J. Cyvin, J. E. Gustavsen, and P. Klaeboe, Z. Naturforsch. **34a**, 579 (1979).

[3] J. C. Whitmer, S. J. Cyvin, and B. N. Cyvin, Z. Naturforsch. **33a**, 45 (1978).

[4] B. N. Cyvin and S. J. Cyvin, J. Phys. Chem. **73**, 1430 (1969).

[5] E. P. Krainov, Opt. Spektrosk. **16**, 984 (1964).

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

[7] J. Räsänen, F. Stenman, and E. Penttinen, Spectrochim. Acta **29 A**, 395 (1973).

[8] A. Bree and R. A. Kydd, J. Chem. Phys. **48**, 5319 (1968).

[9] D. H. Whiffen, Phil. Trans. Roy. Soc. London **A 248**, 131 (1955).

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

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

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

[13] M. Brigodiot and J.-M. Lebas, C. R. Acad. Sci. Paris **268**, 51 (1969).

[14] L. Colombo and J. P. Mathieu, Bull. Soc. Franc. Minér. Crist. **83**, 250 (1960).

[15] F. Stenman, J. Chem. Phys. **54**, 4217 (1971).

[16] S. Califano, J. Chem. Phys. **36**, 903 (1962).

[17] R. Mecke, W. Bruhn, and A. Chafik, Z. Naturforsch. **19a**, 41 (1964).

[18] L. Colombo, Spectrochim. Acta **20**, 547 (1964).

[19] J. Vodehnal and V. Štěpán, Coll. Czechoslov. Chem. Commun. **36**, 3980 (1971).

[20] S. J. Cyvin, B. N. Cyvin, J. Brunvoll, J. C. Whitmer, P. Klaeboe, and J. E. Gustavsen, Z. Naturforsch. **34a**, 876 (1979).

[21] A. Bree, R. A. Kydd, T. N. Misra, and V. V. B. Vilkos, Spectrochim. Acta **27 A**, 2315 (1971).

[22] V. Schettino, J. Mol. Spectry. **34**, 78 (1970).

[23] K. Ohno, J. Mol. Spectry. **77**, 329 (1979).