Condensed Aromatics. Part II
The Five-Parameter Approximation of the In-Plane Force Field of Molecular Vibrations

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An approximate force field for the in-plane vibrations of condensed aromatics with only five parameters is investigated. Calculated frequencies are given for naphthalene, anthracene and coronene. The results are compared with values from other, more elaborate methods, mainly the Califano-Neto force field. The five-parameter approximation is found to be useful as an aid in assignments of experimental frequencies. It appears to give amazingly good results considering its great simplicity and small number of parameters. New experimental infrared and Raman data for anthracene and coronene are given. Especially some new features in the Raman spectrum of anthracene are reported in some details.

Introduction

In the first part of this series [1] a very simple method of normal coordinate analysis for condensed aromatics was described. A force field approximation with seven parameters was proposed. This analysis contains both the in-plane and out-of-plane vibrations; only four of the parameters pertain to the in-plane force field. Further investigations showed certain insufficiencies of the seven-parameter approximation. They are most serious for the out-of-plane vibrations. For the in-plane vibrations, on the other hand, only a slight modification was sufficient to produce a seemingly useful approximation still being very simple. It has been tested for pyrene which is the subject for a forthcoming paper, and will be referred to as the five-parameter approximation. The present paper reports further applications of this approximation to demonstrate its usefulness. We shall in particular compare the results from the five-parameter approximation to those from the celebrated method of Califano and Neto with collaborators [2–5].

The molecules treated are naphthalene and anthracene in the first place. They have been used as test molecules in normal coordinate analyses by several research groups. Finally we report the normal coordinate analysis of the in-plane vibrations of coronene, both by the five-parameter approximation and using the Califano-Neto method.

The Five-Parameter Approximation

The approximate force field is produced by means of a diagonal F matrix in terms of valence coordinates including redundancies. All stretchings and in-plane bendings are contained in the set of the valence coordinates.

(i) The CC stretching parameters are taken around 4.7 mdyne/Å, which is a standard reference obtained as an average value for the naphthalene bonds [1]. Modifications of the CC stretchings were produced by means of the bond order (P) with the result [1]

$$f = 1.793[(0.235\,P + 0.765)/(0.00916\,P + 0.6548)]^3$$

where f is the stretching parameter in mdyne/Å.

(ii) The CH stretching parameters are 5.0 mdyne/Å.

(iii) The value 0.7 mdyne/Å is used for the α-type bendings, viz. the CCC bendings where an H atom is attached to the central C. In naphthalene (see Fig. 1) there are eight bendings of this type.

(iv) The value 0.4 mdyne/Å is used for the β-type CCC bendings where three CC bonds meet. This

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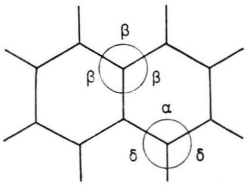

Fig. 1. The valence angle bendings exemplified by naphthalene. The bendings are scaled in the usual way, viz. $(r_{ik} r_{jk})^{1/2} \varphi_{ikj}$.

type also includes the "outer" bendings between bonds belonging to different benzene rings; see Figure 1. Altogether there are six bendings of this type in naphthalene.

(v) Finally δ(CCH) bendings are introduced (see Fig. 1) and given the value of 0.35 mdyne/Å.

Naphthalene and Anthracene

The molecular vibrations of naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$, have been studied by a great number of investigators both experimentally and theoretically. This is not the place for a complete survey of the literature, but the references given in the following may be consulted for more extensive bibliographies.

Naphthalene

Table 1 shows the calculated and observed in-plane vibrational frequencies for naphthalene. The assignment of experimental frequencies from Neto et al. [3] is the only one included in that table. In supplement we wish to quote some very recent far-infrared data, viz. (in cm^{-1}) 359.3 and 619 ± 0.5 for the lowest B_{1u} and B_{2u} frequencies, respectively [6]. The experimental assignment [3] is based on different sources [7, 8]. The final calculated frequencies from Neto et al. [3] (see Table 1) emerged from an adjustment of 34 force constants using 146 weighted observed frequencies for benzene, naphthalene and anthracene along with their completely deuterated species.

An independent computation of the naphthalene frequencies was performed by Krainov [9] as quoted in Table 1. His experimental assignment; see e. g. Ref. [1], was based on several original works, viz. Ref. [7, 10 – 13] as far as the in-plane vibrations are concerned. The mentioned work [9] does not give much details of the normal coordinate analysis. However, 14 diagonal in-plane force-constant values are reported, while a number of interaction terms clearly have been employed in addition.

Now we turn to the computed results from our simple five-parameter approximation; cf. the first column of Table 1. It is at once amazing how closely the general picture of the different assignments is reproduced by this very simple method and few parameters. Furthermore, in several instances, the agreement with observed frequencies is even better than the one from the more elaborate methods. In other instances of more pronounced disagreement with the results from the Califano-Neto method the trends are often supported by Krainov's computation. In the lower part of the B_{2u} frequencies one finds the largest discrepancies when comparing with the experimental assignment of Neto et al. [3]; cf.

Table 1. Calculated and observed in-plane vibrational frequencies (cm^{-1}) of naphthalene.

Species	Calculated			Observed [d]
	a	*b*	*c*	
A_g	3037	3085	3057	3055
	3031	3038	3041	3025
	1610	1577	1564	1579
	1480	1445	1452	1460
	1457	1368	1405	1379
	1123	1173	1125	1144
	898	1013	981	1025
	667	767	778	763
	438	504	491	512
B_{3g}	3040	3062	3072	3055
	3031	3019	3056	2980
	1663	1625	1631	1624
	1452	1442	1462	1436
	1237	1253	1226	1240
	1083	1117	1145	1099
	963	938	961	936
	481	488	499	506
B_{1u}	3041	3064	3063	3065
	3033	3020	3052	3029
	1563	1597	1593	1595
	1411	1379	1372	1389
	1255	1258	1271	1265
	1047	1125	1136	1125
	803	795	777	810
	343	369	329	362
B_{2u}	3035	3084	3066	3056
	3030	3037	3042	3029
	1587	1529	1533	1509
	1535	1357	1360	1361
	1143	1186	1218	1209
	1082	1136	1141	1144
	863	1007	1016	1008
	693	628	606	618

[a] Five-parameter approximation; present work.
[b] Califano-Neto method; Ref. [3]. [c] Krainov [9]. [d] Ref. [3].

Table 1. In this part, however, these authors have chosen the assignment of Scully and Whiffen [8] rather than the one of Freeman and Ross [7]. In the latter assignment the four lowest B_{2u} frequencies read (in cm^{-1}) 1144, 1008, 823 and 618, thus representing a strong support to our computation. Only one serious discrepancy remains, namely for our calculated B_{2u} frequency of 1535 cm^{-1}.

Anthracene

Sets of calculated and observed in-plane vibrational frequencies for anthracene are found in Table 2. The assignment of experimental frequencies from Neto et al. [3] is included. It is based on several original works [2, 14 – 17]. Results from a more recent infrared work on anthracene by Bree and Kydd [18] are included in Table 2; the same authors have also investigated anthracene-d_{10} [19].

The computation of Krainov [20] (see Table 2) is based on his force-constant values deduced for naphthalene [9]. Concerning the experimental data he quotes the early values from Landolt-Börnstein (1951) along with those of Califano [16]. In addition to a sufficiently good agreement with experimental vibrational frequencies Krainov [20] succeeded in completely interpreting the fluorescence spectrum of a frozen solution of anthracene [21]. His assignment of this fluorescence spectrum reads (in cm^{-1}): (A_g) 390, 1165, 1265, 1407 and (B_{3g}) 1567, 1645.

Neto et al. [3] state: "The discussion of the assignment of anthracene offers the greatest difficulty since for several fundamentals there is a serious disagreement among the various authors." More recently Bree and Kydd [18] have discussed in details the infrared bands and produced another assignment, which again contradicts the previous proposals on several points. Even after their significant contribution to the problem there still remain many uncertainties in the experimental assignment.

We have re-investigated the infrared and Raman spectra of anthracene among other condensed aromatics, for which the interpretation of the spectra is in progress. In Table 2 a possible assignment from our new data is included. We do not wish to go into details of this experimental work because it did not reveal many substantially new features in addition to the previous works. Nevertheless the Raman data seem to be the most complete ones produced so far (see Table 3), while our infrared spectrum basically confirms the findings of Bree and Kydd [18]. The experimental conditions are briefly described in the last section.

The calculated frequencies from the five-parameter approximation again demonstrate the usefulness of

Table 2. Calculated and observed in-plane vibrational frequencies (cm^{-1}) of anthracene.

Species	Calculated			Observed		
	a	*b*	*c*	*d*	*e*	*f*
A_g	3036	3085	3062	3088	—	3072 w
	3033	3053	3041	—	—	3048 s
	3030	3037	3040	—	—	3027 m
	1610	1584	1590	1561	—	1556 s
	1532	1476	1499	1481	—	1480 s
	1501	1398	1396	1403	—	1412 s/1400 vs
	1145	1240	1258	1261	—	1264 vs
	1093	1169	1127	1165	—	1164 s
	881	1007	1029	1007	—	1007 vs
	708	735	826	745	—	754 vs
	645	658	623	652	—	625 w
	320	369	376	—	—	397 vs
B_{3g}	3040	3063	3068	—	—	3054 m, sh
	3032	3019	3055	3006	—	3017 vw/3005 vw
	1681	1612	1633	1631	—	1632 s/1627 s
	1533	1563	1569	1596	—	1574 w
	1413	1389	1396	—	—	1433 w
	1237	1273	1279	—	—	1273 w
	1170	1206	1202	1188	—	1187 vs
	1023	1093	1112	—	—	1102 ? w
	892	912	894	—	—	903 w
	513	517	504	522	—	521 vs
	373	388	364	400	—	397 (A_g ?)
B_{1u}	3040	3063	3073	3100	3108 ?	3084 vw
	3034	3053	3062	3049	3050	3053 m, sh
	3031	3019	3051	3022	3024 ?	3007 w, sh
	1619	1616	1623	1620	1616	1620 m
	1449	1446	1450	1448	1447	1448 m
	1288	1341	1266	1316	1314	1317 m
	1272	1277	1246	1274	1270	1272 m
	1063	1123	1147	1150	1145	1147 s
	953	921	922	907	903	906 w
	617	647	627	651	650 ?	653 w
	210	214	210	244	235	234 w
B_{2u}	3036	3085	3062	3079	3093 ?	3048 m
	3030	3037	3040	3048	3050	3021 w, sh
	1600	1532	1534	1533	1695 ?	1690 w, bd
	1563	1441	1457	1462	1533	1534 m
	1456	1394	1387	1398	1495	1495 vw, bd
	1440	1377	1345	1346	1392	1397 w
	1138	1169	1181	1169	1163	1167 m
	1106	1127	1114	1125	1068	1124 w
	891	1007	1011	999	998	998 m
	692	812	808	—	808 ?	809 ? vw
	597	609	591	615	600	601 m

[a] Five-parameter approximation; present work.
[b] Califano-Neto method; Ref. [3].
[c] Krainov [20]. [d] Ref. [3]. [e] Ref. [18].
[f] Present work. Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad.

Table 3. Raman spectral data for crystalline anthracene *.

3072 w	1412 s	903 w
3054 m, sh	1400 vs	773 w
3048 s	1384 m	760 m, sh
3040 vw	1375 m	754 vs
3027 m	1351 w	677 ? vvw
3017 vw	1346 w	625 w
3005 vw	1317 vw	580 vw
1670 w	1273 w	527 m, sh
1632 s	1264 vs	521 vs
1627 s	1187 vs	491 vw
1601 vw	1171 m	479 m
1574 w	1164 s	397 vs
1556 s	1144 vw	287 m
1552 w, sh	1125 vw	267 w
1530 vw	1102 w	244 m
1524 vw	1007 vs	219 m
1504 m	992 w	194 w
1495 m	988 w	125 m
1480 s	977 w	95 w
1469 w	956 m	73 vw
1440 w, sh	916 m	58 w
1433 w		

* Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

this method in a striking way. In Table 2 the results may be compared to those from the methods of Neto et al. [3] and Krainov [20]. In some instances of discrepancies between the five-parameter and Califano-Neto methods one finds that the former method tends to confirm the new assignment of Bree and Kydd [18].

General Discussion

In conclusion there seem to be no doubt about the usefulness of the five-parameter approximation for the in-plane force field of condensed aromatics. It is clearly an improvement of the simple method with four in-plane parameters [1]. The most striking improvement is the removal of bands around 1700 cm^{-1} in B_{3g}: 1721 cm^{-1} for naphthalene and 1767 cm^{-1} for anthracene [1].

We do not claim that the five-parameter method gives more accurate or reliable results than the more elaborate method of Califano and Neto with collaborators. However, the former method has a clear advantage by virtue of its simplicity and the small number of parameters. Still the simple method seems to be useful as an aid in the interpretation of experimental spectra. One should have in mind that the experimental assignments of such large molecules as condensed aromatics hardly can be reliable without the support of a normal coordinate analysis. A

Table 4. Calculated and observed in-plane vibrational frequencies (cm^{-1}) of coronene.

Species	Calculated				Observed [e]
	a	*b*	*c*	*d*	
A_{1g}	3031	3032	3052	3060	–
	1404	1550	1607	1590	1683/1584
	1397	1421	1341	1360	1370/1350
	936	1086	1180	1250	1250
	759	946	1029	1084	1084
	374	379	451	486	485
A_{2g}	3034	3036	3049	–	–
	1554	1555	1484	–	–
	1050	1200	1200	–	–
	906	984	905	–	–
	691	652	604	–	–
E_{2g}	3035	3038	3052	3074	–
	3031	3031	3050	3051	–
	1811	1672	1561	1633	1631
	1556	1563	1443	1441	1434
	1361	1459	1408	1405	–
	1171	1383	1375	1295	1292
	941	1163	1210	1230	1232
	899	1017	1147	995	993
	781	912	996	904	905
	677	653	667	847	846
	426	460	494	596	–
	341	305	328	367	365
B_{1u}	3035	3038	3050	–	–
	1649	1551	1527	–	–
	1276	1427	1383	–	–
	952	1173	1117	–	–
	566	559	631	–	–
	470	528	528	–	–
B_{2u}	3031	3031	3052	–	–
	1699	1654	1509	–	–
	1438	1446	1413	–	–
	1059	1176	1229	–	–
	776	987	1143	–	–
	507	448	466	–	–
E_{1u}	3035	3037	3052	–	3053 w, sh
	3031	3032	3050	–	3045 w
	1679	1619	1594	–	1606 w
	1456	1495	1470	–	1497 vw
	1321	1464	1360	–	1314 s
	1217	1289	1282	–	1310 m, sh/ 1297 ? vw, sh
	895	1110	1170	–	1136 ? w, sh/ 1184 vw
	816	1060	1136	–	1133 w
	752	835	801	–	849 vs
	702	678	791	–	769 m
	307	324	360	–	379 m

[a] Four in-plane parameters [1]; present calculation.

[b] Five-parameter approximation; present work.

[c] Califano-Neto method [3]; present calculation.

[d] Babkov et al. [22].

[e] Raman $A_{1g} + E_{2g}$ data from Ref. [22]. Infrared E_{1u} data from present work; abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

demonstration of the validity of a force field by means of an experimental assignment should therefore in general be considered with great criticism.

Coronene

A complete normal coordinate analysis of coronene, $C_{24}H_{12}$, has not been published so far to our knowledge. In Table 4 we give the in-plane vibrational frequencies computed according to (a) the method with four in-plane parameters [1], (b) the five-parameter method, which is the main subject of this paper, and (c) the Califano-Neto method [3], which in the present work is applied to the largest molecule so far. Also included are the $A_{1g}+E_{2g}$ frequencies calculated by Babkov et al. [22]. It seems clear that the five-parameter approximation is appreciably superior to the original simple force field [1] with four in-plane parameters. The statement is based on a comparison with our results from the Califano-Neto method (see Table 4), which presumably are the most reliable ones. One finds specifically improvements for the too high frequencies (in cm^{-1}) 1811 and 1649 in E_{2g} and B_{1u}, respectively, and for the too low frequencies of 1404 and 952 in A_{1g} and B_{1u}, respectively. Otherwise there are substantial improvements for the middle ranges ($\sim 750 - \sim 1400$) in general. The comparatively large differences between the two simple approximations may be explained by the presence of many (viz. thirty-six) β-type bendings (where three CC bonds meet) in coronene.

The available suggestions for assignments of experimental frequencies are far from complete for coronene. Babkov et al. [22] have reported a fairly good Raman spectrum (see Table 4) along with less extensive infrared data. In the course of our systematic experimental studies of condensed aromatics we have obtained several supplementary features in the infrared spectrum. A detailed interpretation of the coronene spectra is postponed for later considerations. Here we only give a list of observed bands (see Table 4) interpreted as fundamentals and representing a tentative assignment of E_{1u} frequencies.

Experimental

Infrared spectra of the samples in the region $4000 - 200\ \text{cm}^{-1}$ were recorded with a Perkin-Elmer model 225 spectrometer. Far infrared data in the $800 - 40\ \text{cm}^{-1}$ region were obtained on a fast scan, evacuable Fourier transform spectrometer from Bruker. The samples were investigated as crystalline films between KBr plates, as Nujol mulls and as pressed discs in KBr, KI or polyethylene matrices.

Raman spectra were recorded on Cary 81 spectrometer, using a helium-neon laser (Spectraphysics 125 A) and an argon ion laser (CRL model 52 G) for excitation. The helium neon line 6328 Å was used in the 180° backscattering geometry while the 5145 Å argon laser line excited the sample at 90° [23]. Good Raman spectra were recorded of freshly sublimed samples of anthracene using the argon ion laser. The wave numbers are listed in Table 3. The strong fluorescence of coronene prevented a complete Raman spectrum from being obtained, the best results were achieved for the red laser line (5145 Å). Under these conditions the following wave numbers were recorded (in cm^{-1}): 1357 w, 1340 w, 480 vw and 366 vw.

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