

Condensed Aromatics. Part VI

Force-Field Approximation for the Out-of-Plane Molecular Vibrations

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The out-of-plane vibrations of aromatic molecules are studied. Theoretical considerations are based on the “classical” Whiffen force field. The new approximation contains five numerical parameters and is considerably simpler than the one of Whiffen with seven parameters and substantially more interaction terms. The five-parameter approximation is applied with success to benzene and naphthalene.

Introduction

The *in-plane* vibrations of condensed aromatics have been studied by many researchers. The major part of the previous papers in this series [1–5] deal with this problem. Numerous additional works are cited therein. Quite recently the same problem has also been taken up by Ohno [6, 7].

In comparison to this large amount of work the *out-of-plane* vibrations of condensed aromatics have been offered much less attention. It suggests that the problem may be more difficult (as also is our experience), in spite of the fact that the number of out-of-plane modes, i.e. $N - 3$, in a planar (non-linear N -atomic) molecule invariably is smaller than the number of the in-plane modes, which is $2N - 3$.

Two “classical” works on the out-of-plane vibrations of conjugated systems have appeared, both in 1955 [8, 9]. In the paper of Coulson and Senent [8] the out-of-plane vibrations of ethylene, benzene and naphthalene are treated. The developed force field contains only two force constants. We agree that a small number of parameters is an essential virtue of the force field approximation. A critical examination of the Coulson-Senent force field shows, however, that it does not meet the modern standards of accuracy in view of more recent experimental evidence. Whiffen [9] developed a seven-parameter force field with numerical force constants adjusted to the out-of-plane frequencies for benzene. This method of approximation has been applied to naphthalene

by Scully and Whiffen [10, 11], and later to anthracene [12] and pyrene [13] by others. The Whiffen force field reproduces satisfactorily the experimental frequencies in the relatively few cases where it has been applied. However, it has some deficiencies of a principal nature: (a) The number of parameters should be decreased and the force field should be simplified, if possible, within a reasonable approximation. (b) The rules for application to an arbitrary condensed aromatic should be more definite. In the existing applications [9–13] it seems necessary to introduce special conventions in each case.

Another attempt to produce a force field approximation for the out-of-plane vibrations of aromatic molecules is reported in the first part of this paper series [1]. It is the out-of-plane part of the approximation with seven parameters (three out-of-plane parameters). The numerical values were adjusted to experimental frequencies for naphthalene and seemed to be applicable to certain other condensed aromatics. The approximation failed for benzene [1], however, and further investigations showed it to be unsatisfactory in general [2].

Tables 1 and 2 show the application of the three approximations discussed above for benzene and naphthalene, respectively.

In view of this discussion it seems highly warranted to seek for a new approximation of a force field for the out-of-plane vibrations of aromatic molecules. Such a force field should fulfil the following conditions. It should (a) be simple and contain as few parameters as possible, (b) be transferable to any condensed aromatic according to strict rules, (c) reproduce modern experimental

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Table 1. Previous attempts of force field approximations for the out-of-plane vibrations of benzene; frequencies in cm^{-1} .

Species	a	b	c	Observed [14]
B_{2g}	1110	992.2	1238	990
	638	705.9	438	707
E_{1g}	850	851.1	741	846
A_{2u}	671	673.0	686	673
E_{2u}	1049	984.0	981	967
	413	404.2	319	398

^a Two parameters; Coulson-Senent [8].

^b Seven parameters; Whiffen [9].

^c Seven-parameter approximation [1] with three out-of-plane parameters; two of them are effective in benzene.

Table 2. Previous attempts of force field approximations for the out-of-plane vibrations of naphthalene; frequencies in cm^{-1} .

Species	a	b	c	Observed [1]/[11]
B_{1g}	1040	920	934	943
	722	704	702	717
	365	365	312	386
B_{2g}	1107	971	1305	980
	937	881	952	876
	687	770	679	846/778
	436	485	379	461
A_u	1143	1022	1150	970
	917	807	776	841
	549	594	417	581
	222	207	185	195
B_{3u}	1053	962	999	958
	776	759	714	782
	422	445	429	476
	183	177	139	176

^a Two parameters; Coulson-Senent [8].

^b Seven parameters; Scully and Whiffen [11].

^c Three parameters [1].

frequencies satisfactorily and (d) be useful as an aid in the assignments of observed frequencies.

Theoretical Considerations

Cartesian Displacement Coordinates

Both of the pioneering works cited above [8, 9] work with the out-of-plane cartesian displacements [15, 16]. These coordinates are used to construct different internal coordinates by linear combinations. It seems attractive, as a new approach, to assign a force constant directly to every cartesian

displacement along with interaction terms, if necessary. Some theoretical implications of this approach seem to be of interest to be reported here, although the method did not lead to an acceptable approximation of the force field at the present stage.

In order to inspect this possibility we have considered the simplified molecular model of a benzene ring (Figure 1).

Let us assume a two-parameter force field defined by f_z and f_{zz} . Here f_z is the main force constant associated with a cartesian displacement, z_i ($i = 1, \dots, 6$), while f_{zz} designates the interaction term pertaining to two neighbouring (directly bonded) atoms. Hence the potential energy contains the terms with $z_1^2, z_2^2, \dots, z_1 z_2, z_2 z_3, \dots$. We wish to emphasize the validity of defining the force field in terms of *external* displacement coordinates. Nevertheless it is a representation of the usual (*internal*) force field, as is demonstrated in the following. The six-atomic system of Fig. 1 gives rise to three out-of-plane vibrational modes, which are described by the symmetry coordinates (S) [16, 17]

$$S(B_{2g}) = \frac{D}{\sqrt{6}} (\delta_1 - \delta_2 + \delta_3 - \delta_4 + \delta_5 - \delta_6),$$

$$S_a(E_{2u}) = \frac{D}{\sqrt{12}} \cdot (\delta_1 - 2\delta_2 + \delta_3 + \delta_4 - 2\delta_5 + \delta_6),$$

$$S_b(E_{2u}) = \frac{D}{2} (-\delta_1 + \delta_3 - \delta_4 + \delta_6).$$

The six dependent external coordinates z_i , assuming the Eckart conditions [16] to be valid, may be expressed unambiguously by the above three symmetry coordinates through the **A** matrix; in Cyvin's [16] notation:

$$\mathbf{x} = \mathbf{A}\mathbf{S}, \quad \mathbf{A} = \mathbf{m}^{-1}\mathbf{B}'\mathbf{G}^{-1}.$$

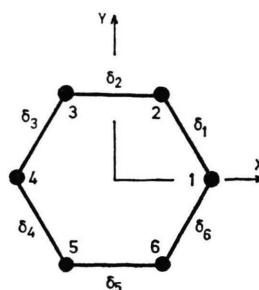


Fig. 1. The six-atomic molecular model. $\delta_1, \dots, \delta_6$ are the torsions of the bonds 1–2, ..., 6–1.

The result is:

$$\begin{aligned}
 z_1 &= \frac{\sqrt{2}}{24} S(B_{2g}) - \frac{1}{4\sqrt{3}} S_b(E_{2u}), \\
 z_2 &= -\frac{\sqrt{2}}{24} S(B_{2g}) - \frac{1}{8} S_a(E_{2u}) \\
 &\quad + \frac{1}{8\sqrt{3}} S_b(E_{2u}), \\
 z_3 &= \frac{\sqrt{2}}{24} S(B_{2g}) + \frac{1}{8} S_a(E_{2u}) \\
 &\quad + \frac{1}{8\sqrt{3}} S_b(E_{2u}), \\
 z_4 &= -\frac{\sqrt{2}}{24} S(B_{2g}) - \frac{1}{4\sqrt{3}} S_b(E_{2u}), \\
 z_5 &= \frac{\sqrt{2}}{24} S(B_{2g}) - \frac{1}{8} S_a(E_{2u}) \\
 &\quad + \frac{1}{8\sqrt{3}} S_b(E_{2u}), \\
 z_6 &= -\frac{\sqrt{2}}{24} S(B_{2g}) + \frac{1}{8} S_a(E_{2u}) \\
 &\quad + \frac{1}{8\sqrt{3}} S_b(E_{2u}).
 \end{aligned}$$

The conventional symmetrized force-constant matrix, \mathbf{F} , is obtained by

$$\mathbf{F} = \mathbf{A}' \mathbf{f}_x \mathbf{A},$$

where \mathbf{f}_x is based on the z_i coordinates. The analytical solution of the problem yields

$$F(B_{2g}) = \frac{1}{48} (f_z - 2f_{zz}),$$

$$F(E_{2u}) = \frac{1}{16} (f_z - f_{zz}).$$

The normal coordinate analysis is easily accomplished in this case since we know the corresponding \mathbf{G} matrix elements [16]: $G(B_{2g}) = 48 \mu$, $G(E_{2u}) = 16 \mu$.

If we assume a one-parameter force field approximation putting $f_{zz} = 0$, we obtain $\omega(B_{2g}) = \omega(E_{2u})$ for the frequencies from the above equations, remembering that [15, 16] $\mathbf{GF} = 4\pi^2 c^2 \omega^2$. This accidental degeneracy seems not to be reasonable. We know it is wrong if we can assume the skeletal frequencies of benzene as appropriate to the model in question. They are (in cm^{-1}) [14]: $\omega(B_{2g}) = 707$, $\omega(E_{2u}) = 398$. Consequently we should at least

have one nonvanishing interaction force constant. The attempt to adjust the two parameters f_z and f_{zz} to the above numerical frequencies failed completely. It led to negative values for both of the parameters.

Internal Valence Coordinates

A different theoretical analysis was performed, taking advantage of the work of Whiffen et al. [9, 10], but using the modern formalism in terms of the T matrix [18]. The analysis was found to add to the understanding of the main features of the Whiffen force field.

We have adopted the numbering of atoms in a six-atomic fragment of an aromatic molecule from the cited work [10]; for the sake of convenience it is reproduced in Figure 2. For the sake of simplicity we assume all the interatomic distances to be the same, say D . Following Whiffen et al. [9, 10] also all interbond angles are assumed to be equal, viz. 120° . Under these conditions we can define two out-of-plane bendings [15] (cf. Fig. 2) as

$$\gamma = \frac{1}{D} (-3z_1 + z_2 + z_3 + z_4),$$

$$\gamma' = \frac{1}{D} (z_1 - 3z_4 + z_5 + z_6),$$

and two torsions:

$$\delta = \frac{2}{D\sqrt{3}} (-2z_1 + z_2 + 2z_4 - z_5),$$

$$\delta' = \frac{2}{D\sqrt{3}} (2z_1 - z_3 - 2z_4 + z_6).$$

Here the coordinates are expressed in terms of the out-of-plane cartesian displacements [17]. Scully and Whiffen [10] introduce the two types of out-of-plane coordinates (i) deformation and (ii) twisting.

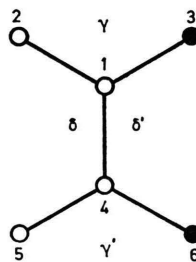


Fig. 2. Numbering of atoms, and valence coordinates for out-of-plane vibrations of a six-atomic fragment of an aromatic molecule.

(i) The two deformation coordinates in the six-atomic fragment (Fig. 2) appear to be identical to the out-of-plane bendings [15] γ and γ' when equal interbond angles (120°) are assumed, even if the bond lengths are different. Notice that the distinction between "anchor" and "end" atom [15] disappears in this case.

(ii) Define the combination of torsions

$$\varepsilon = (1/\sqrt{2})(\delta + \delta').$$

Under the assumptions we have made one has

$$\varepsilon = \frac{1}{D} \sqrt{\frac{2}{3}} (z_2 - z_3 - z_5 + z_6).$$

This coordinate appears to be proportional to Whiffen's twisting.

At the same time it is natural to define another combination of the torsions, viz.

$$\begin{aligned} \varepsilon' &= \frac{1}{\sqrt{2}} (\delta - \delta') = \sqrt{\frac{2}{3}} (\gamma - \gamma') \\ &= \frac{1}{D} \sqrt{\frac{2}{3}} (-4z_1 + z_2 + z_3 + 4z_4 - z_5 - z_6). \end{aligned}$$

In the following we are going to consider the set of independent coordinates

$$S = \{\gamma, \gamma', \varepsilon\}$$

referred to as Whiffen's coordinates on one hand and two alternatives on the other:

$$(a) S_a = \{\gamma, \gamma', \delta\},$$

$$(b) S_b = \{\gamma, \gamma', \delta, \delta'\}.$$

The S_a and S_b sets contain conventional types of coordinates (out-of-plane bendings and torsions) only. In case (a) the coordinates are independent while a redundancy occurs in the set (b).

Scully and Whiffen [10] argue, with reference to previous works [9, 19], that the interaction term between γ and ε is much smaller than between γ and δ . We shall find a sound theoretical basis for the validity of this statement.

The simplest force field in terms of Whiffen's coordinates, S is given by

$$F = \begin{bmatrix} F_\gamma & 0 & 0 \\ & F_{\gamma'} & 0 \\ & & F_\varepsilon \end{bmatrix},$$

where we have assumed $F_{\gamma\gamma} = 0$ in addition to $F_{\gamma\varepsilon} = 0$. The γ and γ' coordinates are assumed to be symmetrically equivalent for the sake of simplicity.

(a) The S_a coordinates are applicable in such fragments where δ and δ' are not symmetrically equivalent; observe the black and white circles in Fig. 2. The torsional coordinates in benzene is an example. The most general harmonic force field based on the S_a coordinates is

$$f_a = \begin{bmatrix} f_\gamma & f_{\gamma\gamma} & f_{\gamma\delta} \\ & f_\gamma & -f_{\gamma\delta} \\ & & f_\delta \end{bmatrix},$$

when we adhere to the assumption that γ and γ' are symmetrically equivalent. The T matrix method [18] was used to transfer this force constant matrix to the basis of Whiffen's coordinates. On introducing the approximations involved in the form of the F matrix it was found

$$f_{\gamma\delta} = -\frac{1}{\sqrt{3}} f_\delta, \quad f_{\gamma\gamma} = -\frac{1}{3} f_\delta.$$

The equations show clearly that none of the interaction force constants in f_a can be neglected under the present conditions. The result obtained for the force constants of F is

$$F_\gamma = f_\gamma - \frac{1}{3} f_\delta, \quad F_\varepsilon = \frac{1}{2} f_\delta.$$

(b) The alternative choice of valence coordinates as S_b leads to a still more interesting analysis and shall be treated in more details. The additional coordinate δ' must necessarily be included when δ and δ' are symmetrically equivalent. The torsional coordinates around the central bond of naphthalene provide a good example. The most general harmonic force field on the basis of f_b reads

$$f_b = \begin{bmatrix} f_\gamma & f_{\gamma\gamma} & f_{\gamma\delta} & -f_{\gamma\delta'} \\ & f_\gamma & -f_{\gamma\delta} & f_{\gamma\delta'} \\ & & f_\delta & f_{\delta\delta'} \\ & & & f_{\delta'} \end{bmatrix},$$

where we have assumed that δ and δ' are symmetrically equivalent as well as γ and γ' . The transformation matrix of

$$S_b = TS$$

is found to be

$$\mathbf{T} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1/\sqrt{3} & -1/\sqrt{3} & 1/\sqrt{2} \\ -1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{2} \end{bmatrix}.$$

The connection between the two sets of force constants of \mathbf{F} and \mathbf{f}_b is found from [18]

$$\mathbf{F} = \mathbf{T}' \mathbf{f}_b \mathbf{T}.$$

The result is

$$\mathbf{F} = \begin{bmatrix} A & B & 0 \\ & A & 0 \\ & & C \end{bmatrix},$$

where

$$\begin{aligned} A &= f_\gamma + \frac{4}{\sqrt{3}} f_{\gamma\delta} + \frac{2}{3} (f_\delta - f_{\delta\delta}) \\ B &= f_{\gamma\gamma} - \frac{4}{\sqrt{3}} f_{\gamma\delta} - \frac{2}{3} (f_\delta - f_{\delta\delta}), \\ C &= f_\delta + f_{\delta\delta}. \end{aligned}$$

The zero's in the \mathbf{F} matrix above are not additional approximations, but emerge as a consequence of the symmetry restrictions. The result, $F_{\gamma\epsilon} = 0$, is actually deducible from the assumption that δ and δ' are symmetrically equivalent. This part of the analysis constitutes a theoretical basis of the statement of Scully and Whiffen [10] referred to above.

Next we introduce as an approximation $F_{\gamma\gamma} = B = 0$. This requirement may be fulfilled in infinitely many ways because of the presence of redundancy in the \mathbf{S}_b coordinates. Perhaps the simplest way to meet the requirement is to put

$$f_{\gamma\gamma} = f_{\gamma\delta} = 0, \quad f_{\delta\delta} = f_\delta.$$

The force constants of the \mathbf{F} matrix now read

$$F_\gamma = f_\gamma, \quad F_\epsilon = 2f_\delta.$$

The alternative (b) is more general than (a) and is going to be exploited as a guide for a simple force field approximation.

In conclusion we can formulate the following recipe for producing a force field approximation of the out-of-plane vibrations in aromatic molecules.

(1) Define two torsions for every CC bond, corresponding to δ and δ' . This requirement implies the definition of "outer" torsions of the types HCCH

and HCCC in addition to the "inner" CCCC. All the torsions are of the "boat" form.

(2) Assume a considerable interaction term between two such torsions, in fact of the same order of magnitude as the main torsional force constant.

(3) All other interaction terms may tentatively be neglected.

(4) Main force constants are also attributed to CH and CC out-of-plane bendings. We adopt the convention to include one out-of-plane bending for every C atom. In every case the three surrounding atoms (of which one may be an H) move in one direction while the given central atom, C, moves in the opposite direction. If all interbond angles are assumed to be equal (120°) this convention gives a prescription for an unambiguous selection of coordinates of this type. Even if we use accurate structural data with angles slightly deviating from 120° we may assume that the ambiguities in the construction of the approximate force field are insignificant.

New Out-of-plane Force Field Approximation

The benzene and naphthalene molecules were used to fix the numerical values of the parameters of a new force-field approximation for the out-of-plane vibrations of conjugated systems. The principles outlined in the above theoretical part were followed.

The units of mdyne/Å are used throughout for the force constants. Hence the parameters are based on torsions and out-of-plane bendings scaled by factors with the dimension of length. The adopted conventions are given by $(D_{12}D_{45})^{1/2}\delta$ and $[(D_{12}D_{13})^{1/2}D_{14}]^{1/2}\gamma$, where the numbering of atoms refers to Figure 2.

It has been mentioned that the previously proposed approximation [1] failed in general. Nevertheless it was found possible to repair its deficiencies relatively easy, maintaining a substantial part of it. Thus the numerical values for out-of-plane bendings are unchanged; in mdyne/Å:

$$f_\gamma(\text{C}_3\text{H}) = 0.20, \quad f_\gamma^*(\text{C}_4) = 0.15.$$

A scrutiny of the analysis of benzene made it clear that the invalidity of the simple approximation [1] can be traced back to the lack of interaction force constants. Not only are all interactions in terms of the valence coordinates neglected; also the

Table 3. Symmetrized F matrix (mdyne/Å) for the out-of-plane vibrations of benzene from three approximations.

Species	Two param- eters [1]	Three param- eters	Whiffen [9]
B _{2g}	$\begin{bmatrix} 0.10 \\ 0.00 \ 0.20 \end{bmatrix}$	$\begin{bmatrix} 0.189 \\ 0.221 \ 0.407 \end{bmatrix}$	$\begin{bmatrix} 0.197 \\ 0.210 \ 0.392 \end{bmatrix}$
E _{1g}	[0.20]	[0.252]	[0.260]
A _{2u}	[0.20]	[0.200]	[0.192]
E _{2u}	$\begin{bmatrix} 0.10 \\ 0.00 \ 0.20 \end{bmatrix}$	$\begin{bmatrix} 0.189 \\ 0.192 \ 0.355 \end{bmatrix}$	$\begin{bmatrix} 0.157 \\ 0.136 \ 0.321 \end{bmatrix}$

resulting symmetrized F matrix is entirely diagonal; cf. Table 3. The deficiency was repaired by introducing the two types of torsions, viz. $\delta(\text{CCCC})$ and $\delta'(\text{HCCH})$, and an interaction force constant between each pair pertaining to the same CC bond. The final numerical values (in mdyne/Å),

$$f_{\delta} = f_{\delta'} = 0.05, \quad f_{\delta\delta} = 0.07,$$

were fixed after a number of trials. Some of these test runs included different values for f_{δ} and $f_{\delta'}$.

In naphthalene some substantially new valence coordinates occur, which are not found in benzene. The force-constant value for the CC out-of-plane bending (0.15) is given above. It was found that all types of the "boat" torsions could be given the force constant value 0.05 as in benzene. The value of $f_{\delta\delta}$ could be applied to the CCCH/CCCC torsional interactions as well as the HCCH/CCCC; in mdyne/Å:

$$f_{\delta\delta}(\text{HCCH/CCCC}) = f_{\delta\delta}(\text{CCCH/CCCC}) = 0.07.$$

Finally one has the interaction for the two "boat" torsions associated with the middle bond in naph-

thalene. Some trial computations resulted in the following numerical value (in mdyne/Å):

$$f_{\delta\delta}^*(\text{CCCC/CCCC}) = 0.02.$$

In conclusion we have arrived at a simple force-field approximation with five parameters, which is the actual number of different numerical values. The same value is not counted twice when it applies to different types of torsions and interactions.

Benzene

The new force-field approximation applied to the out-of-plane vibrations of benzene imply three parameters: (1) f_{γ} for the 6 CH out-of-plane bendings, (2) f_{δ} for the 6 CCCC and 6 HCCH torsions, and (3) $f_{\delta\delta}$ for 6 torsion/torsion interaction terms. The force field was expressed in terms of the symmetrized F matrix based on standard symmetry coordinates [17] with the result of Table 3.

It is interesting to compare the present results with those from Whiffen's approximation [9], which we have reproduced. The symmetrized F matrix is included in Table 3. Its elements display the same orders of magnitude as the corresponding ones of our new approximation with three parameters. The considerable interaction force constants are noticed in particular. These two approximations contrast dramatically the unsatisfactory approximation [1] with two parameters and a diagonal F matrix; cf. Table 3.

The five parameters of interaction in Whiffen's approximation give rise to 33 interaction force constants in the matrix based on valence coordinates (twistings and deformations). The matrix is shown in Table 4. It is found to be considerably

Table 4. Force-constant matrix in the Whiffen approximation*.

	Φ_{12}	Φ_{23}	Φ_{34}	Φ_{45}	Φ_{56}	Φ_{61}	γ_1	γ_2	γ_3	γ_4	γ_5	γ_6
Φ_{12}	Q	q_0	0	0	0	q_0	t_0	$-t_0$	0	0	0	0
Φ_{23}		Q	q_0	0	0	0	0	t_0	$-t_0$	0	0	0
Φ_{34}			Q	q_0	0	0	0	0	t_0	$-t_0$	0	0
Φ_{45}				Q	q_0	0	0	0	0	t_0	$-t_0$	0
Φ_{56}					Q	q_0	0	0	0	0	t_0	$-t_0$
Φ_{61}						Q	$-t_0$	0	0	0	0	t_0
γ_1							P	p_0	p_m	p_p	p_m	p_0
γ_2								P	p_0	p_m	p_p	p_m
γ_3									P	p_0	p_m	p_p
γ_4										P	p_0	p_m
γ_5											P	p_0
γ_6												P

* Φ_{ij} are the twistings and γ_i the deformations in the terminology of Scully and Whiffen [10].

more complicated than the corresponding one in our new approximation (6 interactions versus 33). The numerical values used by Whiffen [9] for benzene were found to be slightly different from those reported as being applicable to aromatics in general [10, 12]. Here we give the values applied in our recalculation for benzene; they are extracted from Whiffen's work [9] and converted to the units of mdyne/Å by removing the scaling factors.

$$\begin{aligned} Q &= 0.0568, & q_0 &= -0.0196, \\ t_0 &= 0.0212, & P &= 0.3336, & p_0 &= 0.0140, \\ p_m &= -0.0257, & p_p &= -0.0198. \end{aligned}$$

Some of the differences from the values reported in the later works [10, 12] are slightly more than round-off errors. In one of the works [10] the factor $\cos(\pi/6)$ in the definition of the twisting coordinate should be reversed to $1/\cos(\pi/6)$; it is given correctly in [12].

Table 5 shows the calculated frequencies from our new force field and our tentative reproduction of Whiffen's results. The discrepancies with Whiffen's original calculations (see Table 1) are not larger than it might be expected, especially because of the few significant figures (two or three) for the force constant parameters reported in Whiffen's paper [9]. The agreements of the calculated frequencies from our new force field with observed frequencies are seen to be comparable with those from Whiffen's force field; see Table 5. The only discrepancy of some seriousness occurs for our low B_{2g} frequency, but does not violate the good picture in general.

The crucial test for the success of our force field, of course, is the possible transferability of the numerical parameters to other aromatic molecules.

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

Species	Present new approximation	Whiffen's approximation *	Observed [14]
E_{2g}	985 650	986 710	990 707
E_{1g}	831	845	846
A_{2u}	686	672	673
E_{2u}	968 398	977 406	967 398

* Our recalculation.

Naphthalene

The new force field with five parameters was applied to naphthalene. The following terms were accounted for: (1) f_γ for the 8 CH out-of-plane bendings, (2) f_γ^* for the 2 CC out-of-plane bendings of the middle bond, (3) f_δ for 22 torsions, two for each CC bond; they are 6 of the HCCH type, 4 HCCC and 12 CCCC, (4) $f_{\delta\delta}$ 10 torsion/torsion interactions; 6 of the HCCH/CCCC type and 4 of HCCC/CCCC, and finally (5) $f_{\delta\delta}^*$ for one CCCC/CCCC interaction of middle-bond torsions.

Table 6 shows the calculated frequencies from our force field along with an experimental assignment (see also Table 2). The observed frequencies are adopted from the quotations of Krainov [20], which also are quoted elsewhere [1, 21], except for the third frequency of Species B_{2g} ; cf. Table 2. Krainov [20] has selected the observed frequencies from nine different works. Except for the mentioned frequency (846 cm^{-1}) his assignment is compatible with the one of Scully and Whiffen [11]. We have adopted the value 778 cm^{-1} [11] for this frequency because our analysis strongly supports the choice of Scully and Whiffen [11] on this point, in contrast to the calculated value of Krainov [20]. The calculated frequencies of Krainov [20] (see Table 6) reproduce very accurately the observed values of his assignment. They have emerged from an elaborate force field at variance with benzene and con-

Table 6. Calculated and observed frequencies (cm^{-1}) for the out-of-plane vibrations of naphthalene.

Species	Present new approximation	Krainov [20]	Observed * [11, 20]
B_{1g}	941 744 400	946 720 390	943 717 386
B_{2g}	982 889 745 476	979 873 842 459	980 876 778 461
A_u	976 860 596 206	977 841 580 192	970 841 581 195
B_{3u}	967 772 432 196	958 784 471 175	958 782 476 176

* See also Table 2 (which includes calculated frequencies according to Scully and Whiffen [11]) and the text.

taining numerous interaction terms. On comparing the results from our five-parameter approximation (Table 6) with those from Whiffen's seven-parameter approximation (Table 2) we find them to be comparable; they are definitely not worse from our exceedingly simple force field. To be precise, our approximation gives a better agreement with the adopted experimental data for eight frequencies and worse for seven.

Future Prospects

The present approximation has also been applied to anthracene and pyrene, the additional molecules

which have been treated [12, 13] by the method of Whiffen et al. Details of these results are the subject of a future publication. Already now it is clear that the analysis has confirmed the success of our five-parameter approximation. The numerical values were all transferred from benzene and naphthalene without introducing any additional parameter.

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