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Empirical Determination of the Harmonic Force Constants in Benzene. 3. The Harmonic Frequencies

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The aim of this work is to present a full set of 34 empirically determined harmonic force constants $F_{i,k}$ for benzene (in symmetrized Whiffen's coordinates), as well as the corresponding set of 20 harmonic normal mode (NM) frequencies for all four D_{6h} isotopomers: C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$. The reliability of the obtained harmonic force constant values is reinforced by their ability to reproduce satisfactorily the experimentally measured fundamental vibrational frequencies of the four D_{6h} benzene isotopomers. A specific combined LM (local mode)/SM (symmetrized modes) complex symmetrized nonperturbative vibrational model, developed in our previous work, has been employed for calculations on the vibrational energy levels in benzene, using the harmonic force constants $F_{i,k}$ and a few diagonal anharmonic parameters, as input data. A set of local (valence) harmonic force constants has also been derived from the empirically determined symmetrized force constants $F_{i,k}$, and their physical meaning was discussed. The set of 20 harmonic NM frequencies ω_k for all four D_{6h} benzene isotopomers, calculated in the present work using the empirically determined set of $F_{i,k}$ values, have been analyzed and compared to previous empirical and ab initio determinations by other authors.

I. Introduction

The ground electronic state potential surface of benzene has been established as a benchmark molecular potential surface, suitable for calibration of molecular vibrational models in general. This surface has been the target of massive analytical research, both empirical and semiempirical, as well as ab initio calculations.[1−16] A considerable amount of work over the years has been spent on the reliable determination of the harmonic force constants $F_{i,k}$,[1−13,15] whose values are of foremost importance for the understanding and realistic description of the potential energy hypersurface and hence of the vibrational motion in ground electronic state benzene. Despite the large number of vibrational degrees of freedom in benzene (30), due to the high molecular symmetry (D_{6h}), the number of independent harmonic force constants $F_{i,k}$ (defined in terms of symmetrized Whiffen's coordinates S_k) is only 34. The isotopically invariant symmetrized force constants $F_{i,k}$, are rigorously related to the 20 harmonic NM molecular frequencies ω_k, which are, however, isotopically dependent, because the relevant relations (the Wilson **F−G** analysis) involve the atomic masses.[1,8]

For benzene and for some of its isotopomers, there exists a rich database of experimental spectroscopic evidence.[17−37,48−55] The status of the fundamentals has recently been refined and summarized by Trombetti and coauthors.[16,28] Despite the numerous experimental studies, however, the values of several fundamental frequencies remain unclear.

An exhaustive account of the work done on the empirical determinations of the harmonic force constants $F_{i,k}$ in benzene can be found in the Feature Article by Goodman, Ozkabak, and Thakur (GOT),[8] where the best set of empirically determined $F_{i,k}$ values available by 1991 has been listed. In this work,[8] two sets of harmonic frequencies ω_{exp} for benzene C_6H_6 were derived: the one is related rigorously to the empirically determined harmonic force constants $F_{i,k}$ (through Wilson's **F−G** analysis), and the second one follows more closely the experimentally observable frequencies ν_k. In fact, the two sets of ω_{exp} are rather close to each other, except for some of the (strongly anharmonic) C−H stretch frequencies, which were obviously not satisfactorily described by the empirically determined set of $F_{i,k}$ values. Since 1991, there have practically been no further attempts for an empirical refinement of the harmonic force constants and harmonic frequencies of benzene. In those years there has been, however, considerable activity, aimed at the theoretical (both ab initio and density functional) computational determination of the harmonic frequencies, ω_{calc} (and hence of the harmonic force constants),[9−16] or even some anharmonic (cubic and quartic) force constants.[9,11,16] So far, the most accurate ab initio harmonic force field for benzene has been obtained by Martin, Taylor, and Lee (MTL).[13] The harmonic frequencies ω_{calc} calculated by MTL[13] exceed significantly the harmonic frequencies ω_{exp} empirically determined by GOT. The same is true, as a rule, for the results obtained from density functional calculations.[12,15,16] At present it is difficult to judge, in general, which values for the harmonic frequencies are closer to reality: the lower set of values (ω_{exp}) obtained empirically or the theoretically derived (higher) ones (ω_{calc}). Of course, the only reliable test for the quality of a given

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set of harmonic frequencies ω_k is that against the experimentally measured fundamentals ν_k. However, there is no easy and straightforward way to check the harmonic frequencies (and the related set of harmonic force constants $F_{i,k}$) against the fundamental frequencies in benzene. The anharmonic corrections $\nu_k - \omega_k$ involve two main possible sources of error: (i) the uncertainties, inherent to the vibrational method, employed for calculation of the anharmonic corrections, as functions of the harmonic and anharmonic force constants; (ii) uncertainties in the values of the (theoretically calculated) anharmonic force constants themselves. The authors[11,14,16] have assumed that these two sources of error should be negligible, as compared to the error coming from the direct theoretical calculation of the harmonic frequencies ω_{calc}; so they have derived a set of harmonic frequencies ω_{est} by combining the experimentally measured fundamentals with the calculated anharmonic corrections, obtained using theoretically calculated anharmonic force constants as input data. Two such sets of ω_{est} values have been obtained in this way.[11,16] Again, in either case, the estimated ω_{est} values were obtained as a rule much larger than the empirically determined ω_{exp} values, although not so large as the directly calculated ω_{calc} values. Thus, at present, it remains unclear which set of harmonic frequencies are closer to reality: those derived empirically by GOT (ω_{exp}) or those obtained theoretically (ω_{calc}, ω_{est}).

Taking all this into account, it is clear that a reliable set of empirically determined values of the harmonic force constants $F_{i,k}$ and the harmonic frequencies ω_k in benzene should be very valuable as a guide for the quality of theoretically obtained results. An inherent part of the empirical procedure for determination of the harmonic force constants $F_{i,k}$ and the related harmonic frequencies ω_k is the vibrational method employed for calculation of the fundamentals ν_k from the harmonic force constants (and some anharmonic constants), as input data. It has been our main purpose in the last years to develop a reliable vibrational procedure, capable of establishing a sound correspondence between the harmonic force constants and the fundamental vibrational frequencies in benzene. Such a method should necessarily be nonperturbative, because of the considerable congestion of vibrational levels, even at the energies of the fundamental frequencies, in a molecule the size of benzene. This work is the third in a series,[38,40] aimed at the development and elaboration of a specific, fully symmetrized, nonperturbative model approach for the treatment of benzene vibrations. Our approach will be schematically outlined in section II. In section III, using our vibrational procedure, all 34 symmetrized harmonic force constants $F_{i,k}$ for benzene will be empirically determined, from a very good fit of the calculated fundamental frequencies to the experimentally measured values, for benzene and its D_{6h} isotopomers. The presently obtained $F_{i,k}$ values will be analytically compared to other sets of both empirically derived and theoretically calculated sets of values, by other authors. In section IV the local bond (valence) harmonic force constants are derived from the set of empirically determined symmetrized harmonic force constants $F_{i,k}$. Our values for the local (valence) force constants are compared to those obtained by other authors and their physical meaning is discussed. In section V the harmonic NM frequencies ω_k are calculated for each of the 4 D_{6h} benzene isotopic species (C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$), using Wilson's **F**−**G** analysis. Our results are compared to other determinations of ω_k, both empirical and ab initio or semiempirical methods, and some peculiarities concerning these data are pointed out and discussed in detail. In section VI we summarize the main results and conclusions.

TABLE 1: Tranfsormation Table for the Complex Symmetry Species of Point Group D_{6h}[a]

D_{6h}	c_6	$c_2'(\Psi\rightarrow\Psi^*)$	$c_2''(\Psi\rightarrow\Psi^*)$	i
$A_g = A_{1g} \pm iA_{2g}$	1	1	1	1
$A_u = A_{2u} \pm iA_{1u}$	1	−1	−1	−1
$B_g = B_{1g} \pm iB_{2g}$	−1	1	−1	1
$B_u = B_{2u} \pm iB_{1u}$	−1	−1	1	−1
E_{1ga}	F	1	−1	1
E_{1gb}	F^*	1	−1	1
E_{1ua}	F	−1	1	−1
E_{1ub}	F^*	−1	1	−1
E_{2ga}	F^2	1	1	1
E_{2gb}	F^{-2}	1	1	1
E_{2ua}	F^2	−1	−1	−1
E_{2ub}	F^{-2}	−1	−1	−1

[a] The notation ($\Psi\rightarrow\Psi^*$) attached to the symmetry operations c_2', c_2'' means that in addition to multiplying by the indicated factor, complex conjugation must also be performed (i = space inversion; c_6 = rotation about the top axis of the molecule by $\pi/3$; c_2', c_2'' = rotations by π about two axes, perpendicular to the top axis of the molecule, and perpendicular to each other. $F = e^{i\pi/3}$, $F^* = e^{-i\pi/3}$. $S \times A = S$, $E_{1a,b} \times B = E_{2b,a}$, $E_{2a,b} \times B = E_{1b,a}$, $E_{1b,a} \times E_{1b,a} = E_{2a,b}$, $E_{1a,b} \times E_{1b,a} = A$, $E_{2a,b} \times E_{2b,a} = A$, $E_{1a,b} \times E_{2a,b} = B$, $E_{1a,b} \times E_{2b,a} = E_{1b,a}$, $g \times u = u$, $u \times u = g$.

II. Vibrational Model and Computational Approach, Used for Studying Benzene Vibrational Levels

Our vibrational model approach to an empirical determination of the harmonic force constants in benzene[38−40] is based on three main points. First is the well-known fact that anharmonicity in benzene, although extremely strong, is almost entirely localized on each of the (six) equivalent C−H bond stretches.[41−44] The C−H stretch system in benzene is most adequately and economically (with a minimum number of parameters) described in terms of the local mode, Morse oscillator formalism.[41−45] Thus for the vibrational characterization of the C−H stretch system in benzene, only a single (diagonal) cubic force constant f_{sss} is required, besides the four harmonic force constants f_{ss}, $f_{1,2}$, $f_{1,3}$, $f_{1,4}$, replacing the symmetrized force constants $F_{2,2}$, $F_{20,20}$, $F_{7,7}$, $F_{13,13}$. The remaining (non C−H stretch) vibrations in benzene are described as nonlocal, symmetrized modes (SM). Second, we are making full use of the high molecular symmetry (D_{6h}), by employing a specific complex symmetrized vibrational model approach (and basis set).[39,40] This approach is based on the introduction of complex symmetry species (CSS) for the symmetric top point group D_{6h}, as described in our previous work.[39,40] Table 1 displays the CSS of the benzene point group D_{6h}, replacing the conventional character table for this group.[1] This table was published in our preceding paper[40] but is displayed here again because of some errors in the previous version. We note that such CSS can be readily introduced for all remaining symmetric top point groups. The main advantage of using CSS instead of conventional real symmetry species[1] is the product of any two CSS is a well-defined CSS again, which is not true for real symmetry species, in the case when 2-D species are involved.[38−40,46,47] It is this quality for product reproducibility of the CSS that is crucial for the construction of a fully symmetrized vibrational (or electronic) basis set in product form for molecules, belonging to symmetric top point groups. For the description of vibrational motion in benzene, a set of curvilinear complex symmetrized vibrational coordinates has been introduced (transforming according to the CSS of D_{6h}, displayed in Table 1), which can be expressed as simple linear combinations of Whiffen's symmetrized curvilinear coordinates.[4] Table 2 contains the full description of these coordinates in terms of the local bond stretches and angle distortions and is published again here, in corrected form. In terms of the complex

TABLE 2: Complex Symmetrized Vibrational Coordinates q_i for Benzene[a]

	s_1	s_2	s_3	s_4	s_5	s_6
q_2 ($A_g = A_{1g}$)	g	g	g	g	g	g
q_{7a} (E_{2ga})	g	gG^*	$g(G^*)^2$	$g(G^*)^3$	$g(G^*)^4$	$g(G^*)^5$
q_{7b} (E_{2gb})	g	gG	gG^2	gG^3	gG^4	gG^5
q_{20a} (E_{1ua})	ig	igF^*	$ig(F^*)^2$	$ig(F^*)^3$	$ig(F^*)^4$	$ig(F^*)^5$
q_{20b} (E_{1ub})	$-ig$	$-igF$	$-igF^2$	$-igF^3$	$-igF^4$	$-igF^5$
q_{13} ($B_u = iB_{1u}$)	ig	$-ig$	ig	$-ig$	ig	$-ig$
	t_1	t_2	t_3	t_4	t_5	t_6
q_1 ($A_g = A_{1g}$)	g	g	g	g	g	g
q_{8a} (E_{2ga})	gF^*	gF^*G^*	$gF^*(G^*)^2$	$gF^*(G^*)^3$	$gF^*(G^*)^4$	$gF^*(G^*)^5$
q_{8b} (E_{2gb})	gF	gFG	gFG^2	gFG^3	gFG^4	gFG^5
q_{14} ($B_u = B_{2u}$)	g	$-g$	g	$-g$	g	$-g$
q_{19a} (E_{1ua})	gF	g	gF^*	$g(F^*)^2$	$g(F^*)^3$	$g(F^*)^4$
q_{19b} (E_{1ub})	gF^*	g	gF	gF^2	gF^3	gF^4
	$\alpha_1 \times t_0$	$\alpha_2 \times t_0$	$\alpha_3 \times t_0$	$\alpha_4 \times t_0$	$\alpha_5 \times t_0$	$\alpha_6 \times t_0$
q_{6a} (E_{2ga})	g	gG^*	$g(G^*)^2$	$g(G^*)^3$	$g(G^*)^4$	$g(G^*)^5$
q_{6b} (E_{2gb})	g	gG	gG^2	gG^3	gG^4	gG^5
q_{12} ($B_u = iB_{1u}$)	ig	$-ig$	ig	$-ig$	ig	$-ig$
	$\beta_1 \times s_0$	$\beta_2 \times s_0$	$\beta_3 \times s_0$	$\beta_4 \times s_0$	$\beta_5 \times s_0$	$\beta_6 \times s_0$
q_3 ($A_g = iA_{2g}$)	ig	ig	ig	ig	ig	ig
q_{9a} (E_{2ga})	ig	igG^*	$ig(G^*)^2$	$ig(G^*)^3$	$ig(G^*)^4$	$ig(G^*)^5$
q_{9b} (E_{2gb})	$-ig$	$-igG$	$-igG^2$	$-igG^3$	$-igG^4$	$-igG^5$
q_{15} ($B_u = B_{2u}$)	g	$-g$	g	$-g$	g	$-g$
q_{18a} (E_{1ua})	g	gF^*	$g(F^*)^2$	$g(F^*)^3$	$g(F^*)^4$	$g(F^*)^5$
q_{18b} (E_{1ub})	g	gF	gF^2	gF^3	gF^4	gF^5
	$\delta_1 \times t_0$	$\delta_2 \times t_0$	$\delta_3 \times t_0$	$\delta_4 \times t_0$	$\delta_5 \times t_0$	$\delta_6 \times t_0$
q_{16a} (E_{2ua})	$-igG$	$-ig$	$-igG^*$	$-ig(G^*)^2$	$-ig(G^*)^3$	$-ig(G^*)^4$
q_{16b} (E_{2ub})	igG^*	ig	igG	igG^2	igG^3	igG^4
q_4 ($B_g = iB_{2g}$)	ig	$-ig$	ig	$-ig$	ig	$-ig$
	$\gamma_1 \times s_0$	$\gamma_2 \times s_0$	$\gamma_3 \times s_0$	$\gamma_4 \times s_0$	$\gamma_5 \times s_0$	$\gamma_6 \times s_0$
q_5 ($B_g = iB_{2g}$)	ig	$-ig$	ig	$-ig$	ig	$-ig$
q_{10a} (E_{1ga})	ig	igF^*	$ig(F^*)^2$	$ig(F^*)^3$	$ig(F^*)^4$	$ig(F^*)^5$
q_{10b} (E_{1gb})	$-ig$	$-igF$	$-igF^2$	$-igF^3$	$-igF^4$	$-igF^5$
q_{11} ($A_u = A_{2u}$)	g	g	G	g	g	g
q_{17a} (E_{2ua})	g	gG^*	$g(G^*)^2$	$g(G^*)^3$	$g(G^*)^4$	$g(G^*)^5$
q_{17b} (E_{2ub})	g	gG	gG^2	gG^3	gG^4	gG^5

[a] Conversion matrixes A_{ik} of complex symmetrized vibrational coordinates q_i in terms of curvilinear internal coordinates x_k (s_i, t_i, α_i, β_i, γ_i, δ_i) and vice versa. Rows: $q_i = \Sigma A_{ik} x_k$. Columns: $x_i = \Sigma A_{ik} q_k$. s_0 and t_0 are equilibrium C−H and C−C bond lengths, respectively; $g = 1/\sqrt{6}$, $F = e^{i\pi/3}$, $F^* = e^{-i\pi/3}$, $G = e^{2i\pi/3}$, $G^* = e^{-2i\pi/3}$.

symmetrized description of the vibrational coordinates and wave functions, in the framework of the combined LM/SM approach, a completely symmetrized, separable (in product form), infinite dimensional vibrational basis set for benzene has been set up, as described in detail in our previous work.[39,40] A wave function, belonging to this basis set, is the product of a C−H stretch part (a symmetrized linear combination of local Morse oscillator eigenfunctions[40]) and a SM part, which in turn is a product of separate eigenfunctions, belonging to each of the SM in benzene. Third, a completely nonperturbative procedure was applied for (i) selection of an appropriate active space of vibrational basis states (all of them belonging to one and the same CSS), (ii) construction of the relevant Hamiltonian matrix (containing the energy levels of the selected basis states as well as the coupling matrix elements among them), and (iii) Lanczos tridiagonalization and subsequent diagonalization, for determination of the molecular vibrational energy levels, which are located in an energy range of interest. A specific vibrational code has been written, on the basis of these theoretical principles, that allows for the automatic calculation of the vibrational level energies (belonging to a defined symmetry species), of all four D_{6h} benzene isotopomers, and is related to an initially chosen basis state of interest.

In the following, we shall summarize briefly the recipe employed for construction of a fully symmetrized, multiplicative, infinite dimensional vibrational basis set for benzene. Because part of the benzene vibrations (the C−H stretches) will be considered as LM, and the remaining part as SM, the conventional NM treatment cannot be applied in this case; i.e., the quadratic Hamiltonian interaction terms, coupling various vibrational modes in benzene, cannot be removed. Each of those two vibrational parts (LM and SM) is described in a different way. The complex symmetrized LM wave functions for the C−H stretch part have already been defined in our previous work.[40] On the other hand, each mode belonging to the SM part (e.g., the kth), is defined in the usual way,[1] in terms of a diagonal harmonic force constant, $F_{k,k}$, and a diagonal **G**-matrix element, $G_{k,k}$. The harmonic frequency f_k for such a SM, is given by $f_k = (1/2\pi c)\sqrt{F_{k,k}G_{k,k}}$ [cm^{-1}] (c = the velocity of light). The SM in benzene are of two types: either nondegenerate or doubly degenerate. The eigenstates $|n_k\rangle$ ($n_k = 0, 1, 2, ...$) of a nondegenerate SM are usually described as harmonic oscillator eigenfunctions, whose energy is given by $E_{nk} = f_k(n_k + 1/2)$, and only in a few cases of more strongly anharmonic modes, as Morse oscillator eigenfunctions, are the energy levels $E_{nk} = f_k(n_k + 1/2) - x_k(n_k + 1/2)^2$, where x_k is an anharmonic constant. For the case when k is a doubly degenerate mode, it is described by the eigenfunctions of a 2-D oscillator (taken in complex form, as eigenfunctions of the z-component of the vibrational angular momentum as well). In this case two occupation numbers must be defined (n_{ka}, $n_{kb} = 0, 1, ...$), instead of one n_k, and the 2-D oscillator eigenstates are given by $|n_{ka},n_{kb}\rangle = |n_{ka}\rangle \times |n_{kb}\rangle$.[40] We have shown previously[46,47] that these eigenfunctions belong to well-defined CSS of the molecular point group D_{6h}. Of course the same is true for the eigenfunctions $|n_k\rangle$ of nondegenerate SM. Now, the vibrational function Ψ_a for a group of (both nondegenerate and 2-D) SM is obtained as the product of the eigenfunctions of all modes, $\Psi_a = \prod_k |n_k\rangle$, in completely complex symmetrized form. The energy of Ψ_a is obtained as the simple sum of the energy levels of the participating harmonic or anharmonic oscillators.

A quadratic harmonic nondiagonal (interaction) Hamiltonian H^{int} is next defined as a sum of terms $H_{i,k}$, where i and k are two SM, belonging to one and the same symmetry species (e.g., $i = 4$ and $k = 5$, in Wilson's numbering, both of them of b_{2g} symmetry): $H^{\mathrm{int}} = \sum_{i \neq k} H_{i,k}$. H^{int} is responsible for the couplings between various basis states Ψ_a, as defined above. An interaction Hamiltonian term $H_{i,k}$, has kinetic ($G_{i,k}$) and potential ($F_{i,k}$) parts:

$$H_{i,k} = \frac{1}{2}(F_{i,k} - \hbar^2 G_{i,k})(a_i^+ a_k^- + a_i^- a_k^+) + \frac{1}{2}(F_{i,k} + \hbar^2 G_{i,k})(a_i^+ a_k^+ + a_i^- a_k^-) \quad (1)$$

where $a_k^+|n_k\rangle = \sqrt{n_k+1}|n_k + 1\rangle$ and $a_k^-|n_k\rangle = \sqrt{n_k}|n_k - 1\rangle$. ($H_{i,k}$ is written in analogous form, already detailed in our previous work,[46,47] for the case when i and k are two 2-D, instead of nondegenerate, SM.) Any one of the $H_{i,k}$ terms, and H^{int} in general, can couple only such pairs of basis states Ψ_a and Ψ_b, which belong to one and the same CSS, i.e., $\langle Y_a|H^{\mathrm{int}}|\Psi_b\rangle = 0$, whenever Ψ_a and Ψ_b do not belong to the same CSS of D_{6h}.[39−40,46,47]

In this way a very simple Hamiltonian model for the description of benzene vibrational states is obtained, containing an extremely small number of adjustable parameters: the harmonic force constants $F_{i,k}$, with the addition of a local bond

TABLE 3: Calculated Fundamental Vibrational Frequencies (cm^{-1}) for D_{6h} Symmetry Benzenes, Corresponding to the Empirically Determined Harmonic Force Constants [References in Brackets]

		C_6H_6		C_6D_6		$^{13}C_6H_6$		$^{13}C_6D_6$	
symmetry	frequency	calc	exp	calc	exp	calc	exp	calc	exp
A_{1g}	ν_1	993.0	993.071 [51]	945.7	945.583 [24]	957.4	957.4 [29]	915.6	916.6 [8]
	ν_2	3076.1	3073.942 [51]	2300.3	2303.44 [24]	3064.9	3049.8 [29]	2283.6	2283.9 [8]
A_{2g}	ν_3	1349.9	1350^a [17]	1046.2	1059^a [17]	1338.8		1031.9	
B_{2g}	ν_4	702.1	702.24 [28]	599.6	599^a [17]	679.4		592.6	
	ν_5	991.7	992.93 [28]	822.1	829^a [17]	984.3		799.0	
E_{2g}	ν_6	608.9	608.13 [50]	579.0	580.2 [32]	587.1	584.2 [33]	560.8	561.3 [8]
	ν_7	3059.1	3057.04 [28]	2285.8	2272.5 [24]	3049.2		2267.3	
	ν_8	1603.2	1600.9764^b [34]	1554.5	1558.3 [24]	1550.7		1497.5	
	ν_9	1177.3	1177.776 [50]	864.5	867.00 [24]	1169.1		861.3	
E_{1g}	ν_{10}	847.3	847.1062 [52]	659.1	660^a [17]	840.4		650.2	
A_{2u}	ν_{11}	674.2	673.97465 [35]	495.0	496.2136 [36]	672.2		492.3	
B_{1u}	ν_{12}	1013.7	1013.74 [28]	964.6	970^a [17]	977.3		934.0	
	ν_{13}	3027.2	3028^a [15]	2249.4	2285^a [17]	3019.6		2234.1	
B_{2u}	ν_{14}	1309.4	1309.4 [37]	1286.2	1286.3 [37]	1270.1	1270.1 [37]	1236.3	1236.3 [37]
	ν_{15}	1150.0	1147.6751 [52]	828.1	823.677^a [18]	1138.9	1138.4 [37]	827.7	823.762^a [31]
E_{2u}	ν_{16}	398.5	398.1330 [53]	346.0	346.8^a [49]	387.1		339.4	
	ν_{17}	967.7	967.98 [28]	787.7	787^a [17]	956.8		772.5	
E_{1u}	ν_{18}	1038.4	1038.2670 [54]	814.1	814.2969 [18]	1018.6	1018.3798 [18]	808.1	808.5479 [31]
	ν_{19}	1484.0	1483.9854 [55]	1336.8	1335.2212 [18]	1453.3	1454.2576 [18]	1295.3	1295.7564 [31]
	ν_{20}	3064.8	3064.3674^b [18]	2285.7	2284.9524 [48]	3055.3	3065.4540 [18]	2268.8	2266.0796 [31]

[a] Estimated from IR combinations or from rotational perturbations. [b] Strongly perturbed by Fermi resonance.

C−H stretch cubic force constant f_{sss} and several anharmonic constants x_k, pertaining to the few anharmonic SM (with $k = 1, 3, 8, 9, 18$, in Wilson's numbering). We note that the anharmonic constants introduced in the present work are related to the symmetrized modes, and therefore they are different from the usual definition of anharmonic constants x_k, attached to normal modes. The introduced anharmonic constants x_k for some of the symmetrized modes in benzene C_6H_6 are transformed into "effective" cubic force constants $F'_{k,k,k}$, which are isotopically independent and allow for appropriate anharmonic constants x_k to be readily calculated for each of the remaining three D_{6h} isotopomers C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$. The only one of these "effective" cubic force constants, which was not given in our previous work,[40] is $F'_{3,3,3} = -1.678$. The "effective" cubic force constants do not have direct physical meaning. Such true cubic force constants $F_{k,k,k}$ do not exist, because of symmetry considerations, except for the totally symmetric mode 1. In fact, the quantities $F'_{k,k,k}$ characterize, in simplified (isotope invariant) form, the cumulative effect of a large number of nondiagonal anharmonic (cubic and quartic) force constants, on the Morse potential curve along the kth symmetrized coordinate, and hence on the energy levels of the kth SM. In practice, these diagonal anharmonicities, attached to some of the SM, are rather small and do not have a strong effect on the quality of the overall vibrational description.

Using the basis set schematically defined above, the computation of vibrational levels proceeds as follows. The search procedure is started with a suitably chosen initial basis state of the required CSS. On this state, all quadratic Hamiltonian terms in operator form (1) are consequtively applied, which leads to the generation of new basis states, which are coupled to the initial state. The $H_{i,k}$ terms (1) are next applied on these states, and as a result, more basis states arise. The search goes on by continuously repeating this procedure. All basis states, which can be generated in this way (which form the active space), necessarily belong to one and the same CSS, that of the initially chosen state for the search. The energy levels of the selected basis states and their mutual coupling matrix elements form the Hamiltonian matrix for the particular vibrational problem explored, whose dimensionality may amount to several hundred thousand. The Hamiltonian matrix obtained in this way has to be diagonalized (using Lanczos tridiagonalization techniques) to obtain the required benzene vibrational energy levels. The calculated energy levels can be compared to experimentally measured values.

In our recent work,[40] we have carried out large scale calculations, involving each of the four mode blocks in benzene that contain a C−H stretch vibration and whose symmetries are A_{1g}, E_{2g}, B_{1u}, and E_{1u}. As a result of these calculations, we have been able to achieve a satisfactory fit of the calculated fundamentals of benzene (and its D_{6h} isotopomers), belonging to these four mode blocks, with the experimentally measured values. Thus we have empirically obtained an improved set of force constant values f_{ss}, f_{sss}, $f_{1,2}$, $f_{1,3}$, $f_{1,4}$, pertaining to the C−H stretch system, as well as the relevant set of SM harmonic force constants: $F_{1,1}$, $F_{1,2}$, $F_{6,6}$, $F_{6,7}$, $F_{6,8}$, $F_{6,9}$, $F_{7,8}$, $F_{7,7}$, $F_{8,8}$, $F_{8,9}$, $F_{9,9}$, $F_{12,12}$, $F_{12,13}$, $F_{18,18}$, $F_{18,19}$, $F_{18,20}$, $F_{19,19}$, and $F_{19,20}$.[40] In the present work we shall employ the described approach to the determination of the remaining harmonic force constants in benzene: $F_{3,3}$, $F_{4,4}$, $F_{4,5}$, $F_{5,5}$, $F_{10,10}$, $F_{11,11}$, $F_{14,14}$, $F_{14,15}$, $F_{15,15}$, $F_{16,16}$, $F_{16,17}$, $F_{17,17}$. Thus a full set of 34 harmonic force constants for benzene will be derived empirically. It is noteworthy that a very good fit could be achieved for almost all theoretically calculated fundamentals ν_k with the experimentally measured values (where available), for all four benzene D_{6h} isotopomers: C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$. A full set of the best fit fundamentals for benzene and its isotopomers corresponding to the set of harmonic force constant values, empirically determined in this work, together with the available experimentally measured values of ν_k, are summarized in Table 3.

III. A Full Set of 34 Harmonic Force Constants $F_{i,k}$ for Benzene

A full set of 34 empirically determined harmonic force constants $F_{i,k}$ for benzene is displayed in Table 4, column 3. The $F_{i,k}$ values, pertaining to the four C−H stretch containing mode blocks have already been published in our recent work.[40] Here, the $F_{i,k}$ values for the E_{2g} block have been slightly modified to achieve better conformity of the relevant calculated fundamentals with experiment. The remaining $F_{i,k}$ values, pertaining to the non-C−H stretch containing modes blocks,

TABLE 4: Symmetrized Harmonic Force Constants for Benzene (mdyn and Å), Empirically Determined in This Work, and in Ref 8, and Theoretically Calculated in Refs 12 and 13

D_{6h} symmetry	force constants	this work	GOT[8]	MTL[13]	ref 12
A_{1g}	$F_{1,1}$	7.630	7.616	7.755	7.767
	$F_{1,2}$	0.030	0.157	0.112	0167
	$F_{2,2}$	5.540	5.554	5.612	5.241
A_{2g}	$F_{3,3}$	0.877	0.877	0.894	0.808
B_{2g}	$F_{4,4}$	0.202	0.202	0.209	0.209
	$F_{4,5}$	0.252	0.249	0.263	0.255
	$F_{5,5}$	0.524	0.519	0.545	0.519
E_{2g}	$F_{6,6}$	0.671	0.644	0.651	0.627
	$F_{6,7}$	0.020	−0.136	−0.124	−0.128
	$F_{6,8}$	0.388	0.308	0.314	0.311
	$F_{6,9}$	−0.235	−0.140	−0.143	−0.124
	$F_{7,7}$	5.495	5.510	5.573	5.208
	$F_{7,8}$	0.054	0.054	0.072	0.080
	$F_{7,9}$	−0.066	−0.066	−0.033	0.038
	$F_{8,8}$	6.670	6.690	7.029	6.956
	$F_{8,9}$	−0.030	−0.398	−0.427	−0.409
	$F_{9,9}$	0.918	0.895	0.905	0.822
E_{1g}	$F_{10,10}$	0.337	0.337	0.351	0.322
A_{2u}	$F_{11,11}$	0.249	0.249	0.259	0.241
B_{1u}	$F_{12,12}$	0.661	0.658	0.664	0.629
	$F_{12,13}$	−0.010	−0.237	−0.189	−0.200
	$F_{13,13}$	5.522	5.571	5.569	5.206
B_{2u}	$F_{14,14}$	3.939	3.939	4.142	4.550
	$F_{14,15}$	0.298	0.298	0.329	0.318
	$F_{15,15}$	0.828	0.828	0.830	0.760
E_{2u}	$F_{16,16}$	0.160	0.160	0.168	0.162
	$F_{16,17}$	−0.168	−0.168	−0.178	−0.167
	$F_{17,17}$	0.420	0.420	0.438	0.406
E_{1u}	$F_{18,18}$	0.931	0.926	0.943	0.854
	$F_{18,19}$	0.221	0.209	0.226	0.228
	$F_{18,20}$	0.214	0.151	0.004	0.002
	$F_{19,19}$	7.403	7.380	7.612	7.644
	$F_{19,20}$	0.590	0.572	0.167	0.186
	$F_{20,20}$	5.519	5.568	5.592	5.218

have been calculated in the present work for the first time, using our vibrational method.

In Table 4, for comparison, are given the best available set of empirically determined $F_{i,k}$ values by GOT[8] (obtained using the Wilson's **F−G** analysis) (column 4), the best set obtained using an ab initio method by MTL[13] [CCSD(T), atomic natural basis set] (column 5), and in addition, the set calculated earlier by Berces and Ziegler,[12] using a method based on local density functional theory. The comparison between the $F_{i,k}$ values obtained in this work and those of GOT[8] shows several strong distinctions. These are mainly concerned with the four diagonal C−H stretch constants: $F_{2,2}$, $F_{7,7}$, $F_{13,13}$, $F_{20,20}$. Our values are substantially and systematically lower than those of GOT in all four cases (Table 4). Next, some nondiagonal force constants, connecting a C−H stretch to a non C−H stretch, have been dramatically reduced almost to zero: $F_{1,2}$, $F_{6,7}$, $F_{12,13}$ (however, some others, like $F_{18,20}$ and $F_{19,20}$, have increased, as compared to GOT). And last, in our work most $F_{i,k}$ constants, pertaining to the E_{2g} (ν_6, ν_7, ν_8, ν_9) mode block, obtained have been rather different from those of GOT.[8]

The set of $F_{i,k}$ values obtained from ab initio calculations by MTL [13] (Table 4, column 5) are in general substantially different from both our set and that of GOT. In general, our set is definitely closer to the set of values of GOT, than to the MTL set; in fact, there are only 8 of the 34 force constants ($F_{1,2}$, $F_{6,6}$, $F_{6,7}$, $F_{6,8}$, $F_{6,9}$, $F_{12,13}$, $F_{13,13}$, $F_{18,19}$) for which our value is closer to those of MTL than to those of GOT. The values of Berces and Ziegler[12] are in general closer to the MTL[13] results than to those of GOT.[8] Of special interest are the values of the nondiagonal force constants, coupling a C−H stretch with a non C−H stretch mode: $F_{1,2}$, $F_{6,7}$, $F_{7,8}$, $F_{7,9}$, $F_{12,13}$, $F_{18,20}$, $F_{19,20}$. In view of the pronounced local character of the C−H stretch vibrations and their well-known separation from the remaining modes, these force constants should logically be expected to be very small. Indeed, for three of the four C−H stertch containing blocks in benzene (those of A_{1g}, E_{2g}, and B_{1u} symmetry), the relevant nondiagonal force constants ($F_{1,2}$, $F_{6,7}$, $F_{7,8}$, $F_{7,9}$, $F_{12,13}$) were very small in our work. Though $F_{7,8}$ and $F_{7,9}$ were also found to be small by the other authors,[8,12,13] $F_{1,2}$, $F_{12,13}$, and $F_{6,7}$ were small in our work in contrast to all previous determinations. Contrary to this tendency, the two E_{1u} nondiagonal (C−H stretch)/(non C−H stretch) constants $F_{18,20}$ and $F_{19,20}$ were quite large, as determined in the present work, considerably exceeding the values found by the other authors.[8,12,13] It is noteworthy, that the theoretically derived values for these force constants[12,13] (and in particular $F_{18,20}$) are consistently lower than the empirically determined ones.[8,40] However, as seen from Table 3, our values for the E_{1u} block force constants allow for a particularly good fit of the calculated E_{1u} fundamentals to the experimentally measured values for all four benzene isotopomers. Nevertheless, we are still not completely convinced of the feasibility and reliability of the presently determined set of force constant values, pertaining to the E_{1u} block ($F_{18,18}$, $F_{18,19}$, $F_{19,19}$, $F_{20,20}$, $F_{18,20}$, $F_{19,20}$), and are currently looking for another set of values satisfying the condition for smallness of $F_{18,20}$ and $F_{19,20}$.

IV. Calculation of the Local Bond Force Constants

It is important and instructive to calculate the values of the local (valence) force constants in benzene, corresponding to the set of symmetrized harmonic force constants $F_{i,k}$, determined empirically in the present work. The bond specific (valence) force constants have significant physical meaning and can serve as a test for the feasibility of the empirically determined $F_{i,k}$ values. Furthermore, taking into account the serious distinctions in some of the presently obtained $F_{i,k}$ values, as compared to previous determinations, it is necessary to find out whether these changes lead to physically sound and meaningful changes in the local bond (valence) force constants.

The total number of local bond force constants [according to the definition and notation of Wilson, Decius, and Cross (WDC)[1]] is 44. They were defined by WDC in terms of the local bond stretch and angle distortion coordinates, which have the following meaning ($k = 1, ..., 6$): s_k, C−H stretch; t_k, C−C stretch; α_k, in-plane C-ring distortion; β_k, in-plane H-wag; γ_k, out-of-plane H-wag; δ_k, out-of-plane C-ring distortion. Only 34 of the 44 local bond force constants are independent. All force constants are distributed in the following way among 13 groups (blocks) according to the type of local coordinates involved: 4 s-type (F_s^1, F_s^2, F_s^3, F_s^4), 4 t-type (F_t^1, F_t^2, F_t^3, F_t^4), 3 st-type (F_{st}^1, F_{st}^2, F_{st}^3), 4 β-type (F_β^1, F_β^2, F_β^3, F_β^4), 4 α-type (F_α^1, F_α^2, F_α^3, F_α^4, 2 of them independent), 4 $s\alpha$-type ($F_{s\alpha}^1$, $F_{s\alpha}^2$, $F_{s\alpha}^3$, $F_{s\alpha}^4$, 2 of them independent), 2 $s\beta$-type ($F_{s\beta}^1$, $F_{s\beta}^2$), 3 $t\alpha$-type ($F_{t\alpha}^1$, $F_{t\alpha}^2$, $F_{t\alpha}^3$, 1 of them independent), 2 $\alpha\beta$-type ($F_{\alpha\beta}^1$, $F_{\alpha\beta}^2$, 1 of them independent), 3 $t\beta$-type ($F_{t\beta}^1$, $F_{t\beta}^2$, $F_{t\beta}^3$), 4 δ-type (F_δ^1, F_δ^2, F_δ^3, F_δ^4, 2 of them independent), 4 γ-type (F_γ^1, F_γ^2, F_γ^3, F_γ^4), and 3 $\gamma\delta$-type ($F_{\gamma\delta}^1$, $F_{\gamma\delta}^2$, $F_{\gamma\delta}^3$, 2 of them independent). In the notation of WDC F_σ^k, the subscript denotes the type of local coordinates involved, whereas the superscript number indicates whether the two coordinates are located on one and the same center (1), on adjacent centers (2), etc. In general, the symmetrized force constants $F_{i,k}$ are related to the local force constants F_σ^k, through linear equations, which are restricted to the separate blocks, specified above. These equations are easy to derive and can be found, e.g., in ref 1. For each of the blocks containing only nonredundant coordinates (s, t, β, γ), the number of local force constants coincides with the number of relevant symmetrized force constants. For these cases, the transformation from one set to another is straightforward and will not be discussed here. However, for the blocks, containing redundant coordinates (α, δ), the number of independent, empirically determined symmetrized force constants $F_{i,k}$ is smaller than the number of local force constants; therefore the latter cannot be determined from the former unambiguously. For these cases we have adopted here a specific approximate procedure, which will be discussed in the following, for each block separately.

The α-type block contains two independent symmetrized force constants, $F_{6,6}$ and $F_{12,12}$, on one hand and four local force constants, F_{α}^{1}, F_{α}^{2}, F_{α}^{3}, and F_{α}^{4} (two of them independent), on the other hand. The equations that relate the former to the latter have the form[1]

$$F_{6,6}(\mathrm{E_{2g}}) = F_{\alpha}^{\ 1} - F_{\alpha}^{\ 2} - F_{\alpha}^{\ 3} + F_{\alpha}^{\ 4} \tag{2a}$$

$$F_{12,12}(\mathrm{B_{1u}}) = F_{\alpha}^{\ 1} - 2F_{\alpha}^{\ 2} + 2F_{\alpha}^{\ 3} - F_{\alpha}^{\ 4} \tag{2b}$$

$$F_{\alpha}(\mathrm{A_{1g}}) = F_{\alpha}^{\ 1} + 2F_{\alpha}^{\ 2} + 2F_{\alpha}^{\ 3} + F_{\alpha}^{\ 4} \tag{2c}$$

$$F_{\alpha}(\mathrm{E_{1u}}) = F_{\alpha}^{\ 1} + F_{\alpha}^{\ 2} - F_{\alpha}^{\ 3} - F_{\alpha}^{\ 4} \tag{2d}$$

Due to the redundancy of the α-coordinates, the symmetrized force constants denoted $F_{\alpha}(\mathrm{A_{1g}})$ and $F_{\alpha}(\mathrm{E_{1u}})$, cannot be determined, because they do not correspond to real vibrational motions. As a result of this, the four local constants F_{α}^{k} cannot be determined unambiguously from the system of eqs 2, because only the first two equations of this system are meaningful. As a way out of this situation, most authors (e.g., refs 8 and 45) use symmetrized constants instead of local ones, for the blocks of redundant coordinates. This approach does not reveal the local coupling mechanisms. Therefore we have decided to use a different recipe, which is based on the following considerations. It is physically reasonable to expect that the one-center force constant F_{α}^{1} should greatly exceed (in absolute values) the remaining three, F_{α}^{2}, F_{α}^{3}, and F_{α}^{4}, of which the last two are expected to be the smallest because they correspond to the maximum displacement of centers. Therefore we expect to make a good approximation by setting these two to zero: $F_{\alpha}^{3} = F_{\alpha}^{4} = 0$. Under this condition, the first two equations (2a,b) can be solved:

$$F_{\alpha}^{\ 1} = 2F_{6,6} - F_{12,12} = 0.681$$
$$F_{\alpha}^{\ 2} = F_{6,6} - F_{12,12} = 0.010 \tag{3}$$

The numerical values for F_{α}^{1} and F_{α}^{2}, obtained by substituting in eqs 3 the presently determined values for $F_{6,6}$ and $F_{12,12}$ (Table 4, column 3), justify the approach employed (because $F_{\alpha}^{1} \gg F_{\alpha}^{2}$). The obtained values of F_{α}^{1}, F_{α}^{2}, F_{α}^{3}, and F_{α}^{4} are therefore expected to be good approximations to their real values.

Next, there are four local force constants of $s\alpha$ type, $F_{s\alpha}^{1}$, $F_{s\alpha}^{2}$, $F_{s\alpha}^{3}$, and $F_{s\alpha}^{4}$, and only two symmetrized force constants of this type, $F_{6,7}(\mathrm{E_{2g}})$ and $F_{12,13}$ $(\mathrm{B_{1u}})$. Therefore, we propose to keep only the one-center $F_{s\alpha}^{1}$ and the nearest neighbor $F_{s\alpha}^{2}$, as presumably the largest ones, and set the other two to zero: $F^{s}{}_{\alpha}{}^{3} = F_{s\alpha}^{4} = 0$. In this way the original system of four equations is reduced to two equations.

$$F_{6,7}(\mathrm{E_{2g}}) = F_{s\alpha}^{\ 1} - F_{s\alpha}^{\ 2} \qquad F_{12,13}(\mathrm{B_{1u}}) = F_{s\alpha}^{\ 1} - 2F_{s\alpha}^{\ 2} \tag{4}$$

which are readily solved:

$$F_{s\alpha}^{\ 1} = 2F_{12,13} - F_{6,7} = -0.040$$
$$F_{s\alpha}^{\ 2} = F_{6,7} - F_{12,13} = 0.030$$

As seen, the obtained values for both $F_{s\alpha}^{1}$ and $F_{s\alpha}^{2}$ are quite small, which implies that the neglect of $F_{s\alpha}^{3}$ and $F_{s\alpha}^{4}$ is probably justified. In an analogous manner we proceed to handle the block of three $t\alpha$-type force constants, $F_{t\alpha}^{1}$, $F_{t\alpha}^{2}$, and $F_{t\alpha}^{3}$, where the empirically determined symmetrized force constant is only one: $F_{6,8}$. In line with the considerations explained above, we have set $F_{t\alpha}^{2} = F_{t\alpha}^{3} = 0$. This reduces the set of three linear equations[1] to only one: $F_{t\alpha}^{1} = F_{6,8} = 0.388$, which (together with $F_{t\alpha}^{2} = F_{t\alpha}^{3} = 0$) is expected to be a reasonable approximation.

Next, for the block of two $\alpha\beta$-type force constants, $F_{\alpha\beta}^{1}$ and $F_{\alpha\beta}^{2}$, there is only one symmetrized force constant, $F_{6,9}$. Therefore we set $F_{\alpha\beta}^{2} = 0$, which reduces the system of two equations[1] to one equation: $F_{\alpha\beta}^{1} = F_{6,9}/\sqrt{3} = -0.136$, which is expected to be a reasonable approximation. For the δ block of four local force constants, F_{δ}^{1}, F_{δ}^{2}, F_{δ}^{3}, and F_{δ}^{4}, there are only two empirically determined symmetrized force constants: $F_{4,4}$ and $F_{16,16}$. We set to zero the presumably smallest local force constants: $F_{\delta}^{3} = F_{\delta}^{4} = 0$. This reduces the system of four linear equations to two, which are readily solved:

$$F_{\delta}^{\ 1} = 2F_{16,16} - F_{4,4} = 0.118$$
$$F_{\delta}^{\ 2} = F_{16,16} - F_{4,4} = -0.042$$

The obtained numerical results ($F_{\delta}^{1} \gg F_{\delta}^{2}$) indicate that this is probably a good approximation. Finally, for the $\gamma\delta$-type block of three local force constants, $F_{\gamma\delta}^{1}$, $F_{\gamma\delta}^{2}$, and $F_{\gamma\delta}^{3}$, only two symmetrized force constants are available: $F_{4,5}$ and $F_{16,17}$. Here we have set $F_{\gamma\delta}^{3} = 0$, thus reducing the original system of three linear equations to only two, which can be readily solved:

$$F_{\gamma\delta}^{\ 1} = F_{16,17}/\sqrt{3} = -0.097$$
$$F_{\gamma\delta}^{\ 2} = F_{16,17}/\sqrt{3} - 0.5F_{4,4} = -0.029$$

Both obtained values are comparatively small, with $F_{\gamma\delta}^{2}$ being several times smaller than $F_{\gamma\delta}^{1}$; so this seems to be a reasonable approximation again.

Table 5 summarizes all local force constant values, calculated from our set of empirically determined harmonic force constants $F_{i,k}$ (displayed in Table 4, column 3), under the approximations described in detail above. We have also calculated, using the same approximations, a set of local force constants corresponding to the set of empirically determined force constants $F_{i,k}$ by GOT.[8] These calculated values are displayed in column 4 of Table 5, for the sake of comparison. The following observations and conclusions can be made from the comparison of the values of the local force constants corresponding to the presently obtained set of $F_{i,k}$ (Table 5, column 3) and those calculated from the GOT set of $F_{i,k}$ values (Table 5, column 4). The (nonredundant) sets of 4 F_{s}^{k}, 4 F_{t}^{k}, and 3 F_{st}^{k} values are very similar for the present work and GOT, especially the F_{t}^{k} set. Concerning the F_{s}^{k} block (designated f_{ss}, $f_{1,2}$, $f_{1,3}$, $f_{1,4}$ above) it is noteworthy that the presently obtained F_{s}^{1} value is substantially reduced as compared to the GOT value. Furthermore, F_{s}^{4} is also strongly reduced, attaining a value comparable to and even smaller than the F_{s}^{2} and F_{s}^{3} values, which in our view is

TABLE 5: Calculated Local (Valence) Harmonic Force Constants for Benzene, Corresponding to the Empirically Determined Symmetrized Harmonic Force Constants, Empirically Determined in the Present Work (Column 3) and Ref 8 (Column 4)

block	force constant	this work	GOT[8]
(ss)	$F_s^1(s_1s_1)$	5.515	5.547
	$F_s^2(s_1s_2)$	0.007	0.007
	$F_s^3(s_1s_3)$	0.008	0.008
	$F_s^4(s_1s_4)$	−0.005	−0.022
(tt)	$F_t^1(t_1t_1)$	6.619	6.616
	$F_t^2(t_1t_2)$	0.737	0.728
	$F_t^3(t_1t_3)$	−0.417	−0.419
	$F_t^4(t_1t_4)$	0.371	0.383
(st)	$F_{st}^1(s_1t_1)$	0.184	0.200
	$F_{st}^2(s_1t_2)$	−0.013	0.008
	$F_{st}^3(s_1t_3)$	−0.156	−0.130
($\beta\beta$)	$F_\beta^1(\beta_1\beta_1)$	0.901	1.047
	$F_\beta^2(\beta_1\beta_2)$	0.010	0.016
	$F_\beta^3(\beta_1\beta_3)$	−0.024	−0.023
	$F_\beta^4(\beta_1\beta_4)$	0.004	−0.002
($s\beta$)	$F_{s\beta}^1(s_1\beta_2)$	−0.081	−0.068
	$F_{s\beta}^2(s_1\beta_3)$	−0.043	−0.025
($t\alpha$)	$F_{t\alpha}^1(t_1\alpha_1)$	0.388	0.308
	($F_{t\alpha}^2 = F_{t\alpha}^3 = 0$)		
($\alpha\beta$)	$F_{\alpha\beta}^1(\alpha_1\beta_2) = F_{6,9}/\sqrt{3}$	−0.136	−0.081
	($F_{\alpha\beta}^2 = 0$)		
($\alpha\alpha$)	$F_\alpha^1(\alpha_1\alpha_1)$	0.681	0.630
	$F_\alpha^2(\alpha_1\alpha_2)$	0.010	−0.014
	$F_\alpha^3 = F_\alpha^4 = 0$		
($s\alpha$)	$F_{s\alpha}^1(s_1\alpha_1)$	−0.040	−0.338
	$F_{s\alpha}^2(s_1\alpha_2)$	0.030	0.101
	($F_{s\alpha}^3 = F_{s\alpha}^4 = 0$)		
($t\beta$)	$F_{t\beta}^1(t_1\beta_1)$	0.095	0.200
	$F_{t\beta}^2(t_1\beta_6)$	−0.024	−0.020
	$F_{t\beta}^3(t_1\beta_5)$	−0.078	0.030
($\gamma\gamma$)	$F_\gamma^1(\gamma_1\gamma_1)$	0.381	0.381
	$F_\gamma^2(\gamma_1\gamma_2)$	−0.060	−0.060
	$F_\gamma^3(\gamma_1\gamma_3)$	0.003	0.003
	$F_\gamma^4(\gamma_1\gamma_4)$	−0.018	−0.018
($\delta\delta$)	$F_\delta^1(\delta_1\delta_1)$	0.118	0.118
	$F_\delta^2(\delta_1\delta_2)$	−0.042	−0.042
	$F_\delta^3 = F_\delta^4 = 0$		
($\gamma\delta$)	$F_{\gamma\delta}^1(\gamma_1\delta_1)$	−0.097	−0.097
	$F_{\gamma\delta}^2(\gamma_1\delta_2)$	−0.029	−0.029
	$F_{\gamma\delta}^3(\gamma_1\delta_3) = 0$		

the expected behavior, whereas the GOT F_s^4 value substantially exceeds F_s^2 and F_s^3. For the blocks of F_β^k and F_α^k local force constants, the tendencies displayed by both sets of values are very similar. However, in both blocks, the leading (one-center) constant is substantially different, whereas the smallest member of each block changes sign.

A qualitatively different picture is observed for the $s\alpha$ block. Here our data for both $F_{s\alpha}^1$ and $F_{s\alpha}^2$ are consistently much smaller than the relevant GOT values. Furthermore, they are both quite close to zero, which justifies setting $F_{s\alpha}^3$ and $F_{s\alpha}^4$ to zero preliminarily. Concerning the $t\alpha$ block, our value for $F_{t\alpha}^1$ is similar although substantially increased, as compared to the GOT value, calculated under the same approximation ($F_{t\alpha}^2 = F_{t\alpha}^3 = 0$). The obtained value for $F_{t\alpha}^1$ should be a good approximation to its real value, if the two constants $F_{t\alpha}^2$ and $F_{t\alpha}^3$ are indeed as close to zero as assumed above. Concerning the $\alpha\beta$ (degenerate) block, our $F_{\alpha\beta}^1$ value is substantially (about twice) increased as compared to the relevant GOT value. Here again, the estimate for $F_{\alpha\beta}^1$ should be realistic, if the $F_{\alpha\beta}^2$ constant is indeed sufficiently small, as assumed. For the $t\beta$ (nondegenerate) block, our values differ rather strongly from the GOT results. Indeed, the leading $F_{t\beta}^1$ constant is strongly reduced and $F_{t\beta}^1$ is increased. As a result, all three constants $F_{t\beta}^1$, $F_{t\beta}^2$, and $F_{t\beta}^3$ are of comparable (small) magnitude in our case, which is physically feasible. A qualitatively different, however equally realistic, physical picture is observed in the results of GOT, who have obtained $F_{t\beta}^1 \gg F_{t\beta}^2$, $F_{t\beta}^3$. For the three out-of-plane blocks, $\gamma\gamma$ (nonredundant), $\gamma\delta$ (redundant), and $\delta\delta$ (redundant), the local force constant values coincide, because the relevant $F_{i,k}$ values of this work and of GOT, coincide.

TABLE 6: Calculated Harmonic Frequencies for D_{6h} Symmetry Benzenes, Corresponding to the Empirically Determined Harmonic Force Constants in This Work

symmetry	frequency	C_6H_6	C_6D_6	$^{13}C_6H_6$	$^{13}C_6D_6$
A_{1g}	ω_1	993.7	946.3	958.1	916.1
	ω_2	3193.2	2372.2	3181.7	2353.8
A_{2g}	ω_3	1366.9	1063.2	1355.8	1048.9
B_{2g}	ω_4	702.1	599.6	679.4	592.6
	ω_5	991.7	822.1	984.3	799.0
E_{2g}	ω_6	609.0	578.9	587.2	560.7
	ω_7	3176.0	2351.3	3165.2	2334.3
	ω_8	1606.4	1556.9	1553.9	1499.7
	ω_9	1182.3	867.5	1173.8	864.3
E_{1g}	ω_{10}	847.3	659.1	840.4	650.2
A_{2u}	ω_{11}	674.2	495.0	672.2	492.3
B_{1u}	ω_{12}	1013.0	964.2	976.7	933.5
	ω_{13}	3188.5	2370.0	3176.9	2351.3
B_{2u}	ω_{14}	1309.4	1286.2	1270.1	1236.3
	ω_{15}	1150.0	828.1	1138.9	827.7
E_{2u}	ω_{16}	398.5	346.0	387.1	339.4
	ω_{17}	967.7	788.7	956.8	772.5
E_{1u}	ω_{18}	1041.2	816.5	1020.9	810.1
	ω_{19}	1491.6	1338.7	1461.4	1297.7
	ω_{20}	3170.6	2340.0	3160.8	2324.0

In general, our values for the local force constants are substantially decreased as compared to GOT,[8] with very few exceptions. For some of the blocks, this leads to a qualitatively changed physical picture of couplings.

V. Calculation of Harmonic Normal-Mode Frequencies

The set of harmonic force constants $F_{i,k}$ is rigorously related to the set of harmonic frequencies ω_k through the well-known **F**−**G** analysis of Wilson,[1] which can be summarized as follows. As already mentioned in section II, each one of the 20 ($k = 1$, ..., 20) symmetrized modes in benzene is characterized by a diagonal harmonic force constant $F_{k,k}$, a diagonal **G**-matrix element (inverse mass) $G_{k,k}$, from which its frequency f_k can be calculated, using the formula $f_k = (1/2\pi)\sqrt{F_{k,k}G_{k,k}}$. For the case when there is no other symmetrized mode in the molecule with the same symmetry species as k, this coincides with the harmonic NM frequency, $\omega_k = f_k$. In the case when k belongs to a block of n equal symmetry modes (for benzene, possible values are $n = 2-4$), two $n \times n$ symmetric matrices $\mathbf{G} = \{G_{i,k}\}$ and $\mathbf{F} = \{F_{i,k}\}$ (where $i, k = 1, ..., n$) are set up, including the nondiagonal $G_{i,k}$ and $F_{i,k}$ matrix elements, besides the diagonal ones. These two matrices must be multiplied to obtain the (nonsymmetric) matrix $\mathbf{A} = \mathbf{F} \times \mathbf{G}$. The n harmonic frequencies ω_k ($k = 1$, ..., n) for the considered block of modes are then obtained as the square roots of the eigenvalues of **A**. The **F**−**G** formalism can either be employed to calculate the harmonic frequencies ω_k from a given set of $F_{i,k}$ values (as will be done in the present work), or in the opposite direction, to determine the appropriate set of $F_{i,k}$ values, from a set of input ω_k values.

Employing Wilson's **F**−**G** analysis, we have calculated the set of harmonic NM frequencies ω_k for benzene, using as input values the symmetrized harmonic force constant values $F_{i,k}$, empirically determined in the present work (displayed in Table 4, column 3). For this purpose we have employed a self-made algorithm and computer code. Table 6 contains the set of 20

TABLE 7: Calculated Harmonic Frequencies ω_k for Benzene C_6H_6 (cm^{-1}), Corresponding to the Empirically Determined Harmonic Force Constants in This Work in Comparison with the Values Obtained by Other Authors

		ω_{exp} (this work)	ω_{exp}[a] (ref 8)	ω_{exp}[b] (ref 8)	ω_{calc}[c] (ref 13)	ω_{est}[d] (ref 11))
A_{1g}	ω_1	993.7	994.4	994.4	1002.8	1008
	ω_2	3193.2	3191	3191.0	3209.9	3208
A_{2g}	ω_3	1366.9	1367	1367.0	1379.9	1390
B_{2g}	ω_4	702.1	707	707.0	708.8	718
	ω_5	991.7	990	990.0	1008.8	1011
E_{2g}	ω_6	609.0	607.8	607.2	610.8	613
	ω_7	3176.0	3174	3167.5	3183.1	3191
	ω_8	1606.4	1607	1609.9	1637.2	1639
	ω_9	1182.3	1177.8	1178.2	1194.4	1192
E_{1g}	ω_{10}	847.3	847.1	847.1	865.1	866
A_{2u}	ω_{11}	674.2	674.0	674.0	687.2	686
B_{1u}	ω_{12}	1013.0	1010	1014.4	1019.7	1024
	ω_{13}	3188.5	3174	3166.3	3173.1	3172
B_{2u}	ω_{14}	1309.4	1309.4	1309.4	1326.1	1318
	ω_{15}	1150.0	1149.7	1149.7	1163.1	1167
E_{2u}	ω_{16}	398.5	398	398.0	405.8	407
	ω_{17}	967.7	967	967.0	984.8	989
E_{1u}	ω_{18}	1041.2	1038.3	1038.3	1055.5	1058
	ω_{19}	1491.6	1494	1494.4	1509.4	1512
	ω_{20}	3170.6	3181.1	3181.9	3199.7	3191

[a] Experimentally estimated in ref 8. [b] Calculated from the empirically determined $F_{i,k}$ values in ref 8, by the authors. [c] Calculation CCSD(T) ANO4321′ in ref 13. [d] Estimated by Maslen et al., using the experimentally observed fundamentals and the ab initio calculated anharmonic (cubic and quartic) force constants in ref 11.

calculated harmonic frequencies ω_k, for benzene and its D_{6h} isotopomers (C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$). Next, in Table 7, column 2, are displayed again the ω_k values for benzene C_6H_6, together with four other sets of ω_k values, obtained by other authors, for the sake of comparison. Two sets of ω_{exp} values by GOT are presented: one adapted to the experimentally measured fundamentals (column 4) and one rigorously corresponding to their own set of empirically determined $F_{i,k}$ values (column 5). Column 6 presents the best available set of harmonic frequencies ω_{calc}, obtained using ab initio calculations by MTL.[13] And column 7 contains the estimated set of harmonic NM frequencies ω_{est}, obtained by Maslen et al.[11] by way of combining experimentally measured fundamentals with theoretically calculated anharmonic corrections (from ab initio calculated cubic and quartic anharmonic force constants). This last set (together with the set ω_{est}, obtained using a similar, however more sophisticated, procedure in ref 16) has been considered in the literature as possibly the most reliable available set of harmonic frequencies for benzene, that is, appropriate to serve as a test for theoretically calculated harmonic frequencies.

From a survey of the results displayed in Table 7 it is obvious that our presently obtained values for the harmonic frequencies in benzene C_6H_6 are definitely much closer to the GOT set[8] than to the values calculated by MTL[13] or estimated by Maslen et al.,[11] the last two sets of values being much larger, as a rule. This is true for all 20 harmonic frequencies, without exception. The only serious distinctions between our set and the GOT[8] set are connected with two of the C−H stretch frequencies, ω_{13} and ω_{20}. It is noteworthy that for the case of ω_7, our value is in almost perfect accord with the experimentally estimated GOT value (Table 7, column 4), but rather different from the value derived using their own set of $F_{i,k}$ values (column 5).

VI. Conclusion

This work is the third in a series, aimed at the empirical determinination of an improved and reliable set of harmonic force constants $F_{i,k}$ for benzene, in symmetrized (Whiffen's) coordinates. Using the determined harmonic force constants, as well as a limited number of small "effective" anharmonic constants as input values, and employing a specific fully symmetrized, combined LM/SM, nonperturbative vibrational calculation procedure, it has been possible to reproduce very well most of the experimentally measured vibrational fundamental frequencies, for all four benzene D_{6h} species: C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$. This might be considered as a strong indication that the determined $F_{i,k}$ values are close to the real molecular values. Some of the presently determined $F_{i,k}$ values are quite different from the best existing set of empirically determined harmonic force constant values by GOT,[8] obtained using Wilson's **F**−**G** analysis with a set of experimentally estimated harmonic frequencies. However, our values for $F_{i,k}$ are by far more strongly different from the best set of theoretically calculated harmonic force constants by MTL.[13]

Concerning the distinction in some of the $F_{i,k}$ values between GOT[8] and the present work, both of them empirically determined, the following comments could be made. In this work it has been our aim to reproduce as closely as possible the fundamental frequencies of the four D_{6h} benzene isotopomers: C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$. Hence the determined set of $F_{i,k}$ values is primarily designed to satisfy this particular requirement. GOT[8] have also based their empirical determination of the harmonic force constants on the experimentally measured fundamentals of some lower symmetry benzene species (such as 1,3,5-$C_6H_3D_3$, 1,4-$C_6H_4D_2$, and 1,2,4,5-$C_6H_2D_4$), as well as the most important available Coriolis constants. In forthcoming work we plan to perform calculations on these quantities, using our specific procedure described above, to further test the reliability of our set of $F_{i,k}$ values.

The full set of harmonic force constants $F_{i,k}$ empirically determined in the present work were used to calculate a set of local bond (valence) harmonic force constants, which are an important test for the physical feasibility of the $F_{i,k}$ values. The obtained set of local force constants was discussed and compared to the values, derived using other authors' data. Serious distinctions were observed in some of the values, which results in a changed physical picture of local coupling strengths, characterizing the potential energy hypersurface of benzene. The major conclusion from these calculations is that the set of $F_{i,k}$ values empirically derived in the present work are reasonable, because they lead to a physically consistent picture of local bond force constants.

The empirically determined set of $F_{i,k}$ values were used to calculate a set of harmonic NM frequencies ω_k for each of the four D_{6h} benzene isotopomers, using our own code for implementation of Wilson's **F**−**G** analysis. The presently determined ω_k set for benzene C_6H_6 was found quite close to the best empirically determined set of GOT,[8] however substantially different from and generally at values lower than the theoretically calculated set ω_{calc} of MTL,[13] as well as the estimated set ω_{est}, obtained using experimentally measured fundamentals, combined with theoretically calculated anharmonic constants.

Thus a major conclusion from the results obtained in this work could be that the set of harmonic force constant values obtained empirically are very good approximations to the true harmonic force constants for benzene. It is noteworthy that such good conformity with the experimentally measured fundamentals of benzene could be achieved with a very small number of anharmonic constants taken into account. Moreover, the only large one among them is the diagonal cubic force constant f_{sss}, characterizing the local bond C−H stretch anharmoniicity. This implies that anharmonicity in benzene is indeed exclusively concentrated on the C−H stretches, the remaining modes being very nearly harmonic (at the lower excitation energies). Another important conclusion could be derived from the fact that the determined harmonic NM frequencies for benzene C_6H_6 were consistently found to be very close to the fundamental frequencies, much closer than the estimated values ω_{est};[11,16] i.e., the NM anharmonic corrections $\nu_k - \omega_k$ were found to be much smaller than the theoretically calculated ones. This could be taken as an indication that theoretical calculations tend to strongly overestimate most of the harmonic as well as anharmonic force constants in benzene.[11,16]

Our work on the S_0 potential hypersurface of benzene will be continued by including the most important nondiagonal higher order (both potential and kinetic) interaction Hamiltonian terms in our vibrational calculation procedure. By exploring the experimentally measured overtone and combination levels, involved in the well-known cases of Fermi resonance interactions, we shall try to determine the most important (largest) anharmonic nondiagonal (cubic and quartic) force constants for benzene. This will most probably lead to a further refinement and improvement of the empirically determined harmonic force constant values, through a better fit achieved between the calculated and experimentally measured vibrational energy levels (both fundamentals as well as higher excited overtone and combinations).

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