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Empirical Determination of the Harmonic Force Constants in Benzene. 2. The C−H Stretch System

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The aim of this work is twofold. In the first part, a detailed description is given of a specific vibrational model, designed for calculations on the vibrational energy levels in benzene and benzene isotopic species of D_{6h} symmetry. For the description of the C−H stretch system in benzene, a local mode (LM) formalism was applied, while, for the remaining non-C−H stretch vibrations, a symmetrized mode (SM) treatment was applied: this was called the combined LM/SM model. The model is based on a set of complex symmetrized curvilinear vibrational coordinates, which can be expressed as simple linear combinations of Whiffen's coordinates. The description in terms of complex symmetrized coordinates and wave functions allows for the construction of a separable symmetrized infinite-dimensional vibrational basis set, which is of crucial importance for large-scale calculations. In the second part of this work, using the described complex symmetrized LM/SM vibrational model, calculations have been carried out on a large number of vibrational energy levels of four benzene D_{6h} isotopomers. The aim of the calculations was to redetermine a reliable set of harmonic force constants for benzene. Some of the force constant values obtained in the present work are substantially different from previous determinations by other authors. Using the presently determined set of harmonic force constant values in the calculations, a very good fit has been obtained to a large number of experimentally measured vibrational (both fundamental and overtone) energy levels of various symmetries, belonging to all four D_{6h} benzene isotopomers: C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$.

I. Introduction

The ground electronic state potential surface of benzene has been the object of numerous studies.[1−15] For a semirigid molecule such as benzene, the potential field can be expanded as a Taylor series in terms of displacement coordinates from the equilibrium position:

$$V = (1/2)\sum_{i,k} F_{i,k}S_iS_k + (1/6)\sum_{i,k,j} F_{i,j,k}S_iS_kS_j + ... \qquad (1)$$

Here S_k = symmetrized curvilinear (Whiffen's) coordinates,[4] $F_{i,k}$ = harmonic force constants, $F_{i,k,j}$ = anharmonic cubic force constants, etc. 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 $F_{i,k}$ is 34, there being only 237 unique cubic force constants $F_{i,k,j}$, etc. In general, the molecular potential energy surface can be expanded in a variety of coordinate types. Very often the expansion in terms of normal coordinates is used in preference to the symmetrized coordinates S_k. In that case the nondiagonal quadratic force constants $\Phi_{i,k}$ vanish; however, the relevant series expansion is more slowly convergent, because a considerable number of higher order force constants (cubic, quartic, etc.) attain significant values. Another advantage of symmetrized curvilinear coordinates over mass-weighted normal ones is that the force constants $F_{i,k}$, $F_{i,k,j}$, ... are identical for all isotopic species, which sustain the D_{6h} symmetry of benzene (e.g., C_6H_6, C_6D_6, $^{13}C_6H_6$, and $^{13}C_6D_6$).[23]

A great deal of work over the years has been concentrated on the accurate determination of the harmonic force constants $F_{i,k}$,[1−12,14] whose values are most essential for the expansion in eq 1. In general, two possible routes can lead to the determination of $F_{i,k}$.

Chronologically the one established earlier was the empirical determination of the force constants,[1−8] which proceeds in the following way. Regarding $F_{i,k}$ as variable parameters, calculations are being perfomed (e.g., making use of Wilson's FG analysis[1]) to establish a correspondence between a set of $F_{i,k}$ values and certain experimentally observable quantities (mainly fundamental vibrational frequencies for C_6H_6 and some of its isotopomers[6−8,16−27]). In general, the empirical determination of $F_{i,k}$ is carried out for each symmetry block of vibrations separately.[1,8] A full account of the work done in this direction can be found in the benchmark paper by Goodman, Ozkabak, and Thakur.[8] A serious problem with this approach comes from the fact that benzene is a strongly anharmonic molecule (mainly due to the anharmonicity of the C−H stretch bonds). As a result of this many anharmonic force constants $F_{i,k,j}$ and $F_{i,k,j,l}$ attain nonnegligible values and also have to be taken into account. This makes the number of variable parameters already too large for a reliable determination of the harmonic force constant values.

The second route, which is drawing enhanced interest lately, consists of the ab initio or density functional computations on $F_{i,k}$[8,10,12,14] or even higher order force constants $F_{i,k,j}$ and $F_{i,k,j,l}$.[11,15,28] So far, the most accurate ab initio harmonic force field for benzene has been obtained by Martin, Taylor, and Lee.[12] In general, the verification of the computationally obtained force field is carried out by using the harmonic force constants as input parameters for the calculation of fundamental frequencies or other quantities, which can be checked against

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the experimentally measured data. However, here the same problem arises again, which is due to the strong molecular anharmonicity: it is not clear to what extent the mismatch between the theoretically calculated and the experimentally measured values is due to inaccuracies in the calculated harmonic force constants $F_{i,k}$ or to the interference of the anharmonic force constants, such as $F_{i,k,j}$ and $F_{i,k,j,l}$.[8,11,14] In fact, the harmonic force constants $F_{i,k}$ are related rigorously to the harmonic normal mode (NM) frequencies ω_i but not to the fundamental frequencies ν_i, which are the experimentally observable quantities. However, in such a strongly anharmonic molecule as benzene, the anharmonic corrections $\Delta_i = \omega_i - \nu_i$ are quite large, especially for some of the modes. In second-order perturbation theory (disregarding resonance effects), the anharmonic corrections Δ_i are given by

$$\Delta_i = -x_{ii}(1 + d_i) - (1/2)\sum_{k\neq i} x_{ik}d_k - g_{ii} \qquad (2)$$

where x_{ii}, x_{ik}, and g_{ii} are the anharmonic constants and d_i is the degeneracy of the ith mode. The anharmonic constants x_{ii}, x_{ik}, and g_{ii} can be expressed analytically through the cubic and quartic force constants $F_{i,k,j}$ and $F_{i,i,k,k}$. Thus, the relation between harmonic, ω_i, and fundamental, ν_i, frequencies involves anharmonic force constants, whose values are still less reliably known than the harmonic ones. Without going into further detail, we just note that at present in the literature there exist several sets of harmonic force constants for benzene, derived using different methods, which have been discussed in refs 11−14 and elsewhere. They differ substantially from each other.

Our approach to an empirical determination of the harmonic force constants[29,30] is based on two main points. First is the well-known fact that anharmonicity in benzene, although extremely strong, is almost entirely concentrated on the (six) individual C−H bond stretches. The C−H stretch system in benzene is most adequately described in terms of the local mode (LM) formalism, where the anharmonicity is of entirely diagonal type.[31−34] The main advantage from using the LM approach consists of the fact that, for the vibrational characterization of the C−H stretch system in benzene, only a single (diagonal) anharmonic force constant, f_{sss}, is required (instead of seven cubic ones in terms of symmetrized coordinates, $F_{2,2,2}$, $F_{2,7,7}$, $F_{2,20,20}$, $F_{2,13,13}$, $F_{7,7,7}$, $F_{7,20,20}$, and $F_{7,13,20}$[29]), besides the four harmonic force constants f_{ss}, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$, replacing the symmetrized force constants $F_{2,2}$, $F_{20,20}$, $F_{7,7}$, and $F_{13,13}$. Second, we are making full use of the high molecular symmetry (D_{6h}) by employing a specific complex symmetrized vibrational treatment (basis set),[30,35,36] which is outlined further below. The main advantage from the completely symmetrized separable (infinite-dimensional) vibrational basis set employed is that large-scale vibrational calculations can readily be performed with reasonably small Hamiltonian matrix sizes. This is so because all selected basis states, required for a convergent calculation on the molecular vibrational levels of a certain symmetry type, can be chosen to belong to one and the same symmetry type.

Taking all this into account, in our work[29,30] as well as in the present work, a specific combined vibrational model was employed, designed to reduce the number of significant force constants, required for the adequate description of benzene vibrational levels, to the minimum. This is achieved by using local bond coordinates (and force constants) for the description of the C−H stretch system and symmetrized coordinates and force constants for the non-C−H stretch (“ring”) modes. This is called the combined LM/SM (SM = symmetrized mode) model. A model of this type was previously used by Zhang et al.[37,38] however in nonsymmetrized form. We have used a preliminary version of our model previously for studying higher C−H stretch overtone absorption spectra.[36,39]

In our recent work[29] we have investigated only the totally symmetrical vibrational block $A_{1g}(\nu_1,\nu_2)$ of benzene. From a very good fit achieved between the calculated[29] and experimentally measured[8,22,23] fundamental frequencies ν_1 and ν_2 for all four benzene isotopomers, C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6H_6$, and $^{13}C_6D_6$, a set of force constant values $F_{1,1}$ and $F_{1,1,1}$ (characterizing the ring mode ν_1), a set of force constants f_{ss}, $f_{1,2}$, $f_{1,3}$, $f_{1,4}$, and f_{sss} (pertaining to the C−H stretch system), and $F_{1,2}$ (describing the coupling between both vibrational systems) have been determined. In a subsequent work,[30] the $E_{1u}(\nu_{18},\nu_{19},\nu_{20})$ mode block was studied and the harmonic force constant values $F_{18,18}$, $F_{19,19}$, $F_{20,20}$, $F_{18,19}$, $F_{18,20}$, and $F_{19,20}$ were determined empirically from a fit to the experimentally measured fundamentals ν_{18}, ν_{19}, and ν_{20} (as well as some C−H stretch overtone energies) for benzene C_6H_6.[17,18,31,40] In both cases, limited scale calculations have been carried out, encompassing only the Hamiltonian terms, pertaining to a single symmetry mode block in benzene, $A_{1g}(\nu_1,\nu_2)$[29] and $E_{1u}(\nu_{18},\nu_{19},\nu_{20})$,[30] respectively. At present it has become clear that the calculations,[29,30] involving only a single symmetry vibrational block, can yield correct values for the force constants belonging to the ring modes, e.g., $F_{1,1}$, $F_{18,18}$, $F_{19,19}$, $F_{18,19}$, $F_{18,20}$, $F_{19,20}$, etc., but not for the harmonic force constants, describing the C−H stretch system: f_{ss}, $f_{1,2}$, $f_{1,3}$, $f_{1,4}$. Determination of correct values for these latter force constants requires the implementation of large-scale calculations, involving the Hamiltonian terms for all four symmetry mode blocks in benzene, containing a C−H stretch vibration: A_{1g}, E_{2g}, B_{1u}, E_{1u}. Such large-scale calculations will be carried out in the present work to obtain empirically an improved set of harmonic force constant values f_{ss}, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$. In addition the values previously obtained[29,30] for the ring mode harmonic force constants as well as some cubic diagonal force constants will be essentially confirmed (with small modifications), on the basis of a very good fit achieved between the theoretically calculated and the experimentally measured fundamentals as well as some overtone energies (of different symmetries) for all four benzene D_{6h} isotopomers, C_6H_6, C_6D_6, $^{13}C_6H_6$, and $^{13}C_6D_6$.

This work is organized as follows. In section II a brief outline of complex symmetrized formalism in symmetric top point groups as well as a more detailed treatment of D_{6h} (the benzene symmetry group) complex symmetry species (irreducible representations) is given. On this basis, expressions for the curvilinear complex symmetrized vibrational coordinates (simple linear combinations of Whiffen’s coordinates[4]) are listed and discussed. In section III the theoretical LM description of the C−H stretch Hamiltonian in benzene and its symmetry-adapted eigenfunctions is given in detail, in particular local and nonlocal basis states of all possible symmetry types. In section IV the zeroth-order and interaction Hamiltonians are defined, as well as the basis set functions in symmetrized and product form. Next, a search procedure for selection of an active space of basis vectors and derivation of the relevant Hamiltonian matrix is outlined, whose diagonalization is subsequently carried out using a Lanczos tridiagonalization routine. In section V are presented and discussed the results from the block-limited and large-scale numerical calculations, yielding the A_{1g}, E_{2g}, B_{1u}, and E_{1u} fundamentals as well as some vibrational overtone energies for the four D_{6h} benzene isotopomers C_6H_6, C_6D_6, $^{13}C_6H_6$, and $^{13}C_6D_6$. By adjustment of the calculated vibrational

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

D_{6h}	c_6	$c_2'(\psi\to\psi^*)$	$c_2''(\psi\to\psi^*)$	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 ($\psi\to\psi^*$) attached to the symmetry operations c_2' and 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' and c_2'' = rotations by π about two axes, perpendicular to the top axis of the molecule, and perpendicular to each other. $F = e^{i\pi/3}$, and $F^* = e^{-i\pi/3}$. $S \times A = S$, $E_{1a,b} \times B = E_{2b,a}$, $E_{2a,b} \times B = E_{1b,a}$, $E_{1b,a} \times E_{1b,a} = E_{2a,b}$, $E_{1a,b} \times E_{1b,a} = A$, $E_{2a,b} \times E_{2b,a} = A$, $E_{1a,b} \times E_{2a,b} = B$, $E_{1a,b} \times E_{2b,a} = E_{1b,a}$, $g \times u = u$, and $u \times u = g$.

TABLE 2: Character Table of the Symmetry Species of Point Group D_{6h}[a]

D_{6h}	c_6	c_2'	c_2''	i
A_{1g}	1	1	1	1
A_{2g}	1	−1	−1	1
A_{1u}	1	1	1	−1
A_{2u}	1	−1	−1	−1
B_{1g}	**−1**	1	−1	1
B_{2g}	**−1**	−1	1	1
B_{1u}	**−1**	1	−1	−1
B_{2u}	**−1**	−1	1	−1
E_{1g}	1	0	0	2
E_{2g}	**−1**	0	0	2
E_{1u}	1	0	0	−2
E_{2u}	**−1**	0	0	−2

[a] Reference 1. $S \times A = S$, $E_1 \times B = E_2$, $E_2 \times B = E_1$, $E_1 \times E_1 = E_2 \times E_2 = A_1 + A_2 + E_2$, $E_1 \times E_2 = B_1 + B_2 + E_1$, $g \times u = u$, and $u \times u = g$.

energies to the experimentally measured frequencies, values for the most important harmonic and anharmonic force constants, relevant to the C−H stretch vibrational system as well as to the relevant ring vibrations in benzene, have been determined. In section VI we conclude.

II. Complex Symmetry Species for D_{6h} and Symmetrized Curvilinear Vibrational Coordinates for Benzene

In D_{6h} symmetry (as well as in any symmetric top point group) it can be shown[30] that specific "complex symmetry species" (irreducible representations of the group) can be defined, replacing the conventional real representations (symmetry species).[1] For a quantum (molecular) system, belonging to a symmetric top point group, the Hamiltonian eigenfunctions (electronic, vibrational, etc.) can be defined in complex form, as eigenfunctions of the angular momentum z-component as well (z is the symmetric top axis). The main advantage from the introduction of complex symmetry species (CSSs) is that they behave effectively as 1-D (nondegenerate) symmetry species in the sense that (i) they are multiplicative, i.e., the product of any two CSS functions belongs to a well-defined CSS of the group again, and (ii) a Hamiltonian matrix element, $\langle i|H|k\rangle$, can be nonzero (and totally symmetric) only in the case when $|i\rangle$ and $|k\rangle$ belong to one and the same CSS. Otherwise it will necessarily be zero. Such an approach allows the symmetry properties of symmetric top point groups (where doubly degenerate irreducible representations E occur) to be reduced to the simple multiplicative form of abelian groups (with nondegenerate irreducible representations only). Using CSSs, it is possible to define readily infinite dimensional molecular Hamiltonian eigenfunction basis sets (electronic, vibrational, etc.) in separable (product) form.

In Table 1 the transformation properties of complex symmetry species of the symmetric top point group D_{6h} are summarized, under the basic symmetry operations (generators) of the group. In the same table also the multiplication rules for the CSSs are given. Table 1 can be compared to the well-known character table for this group (e.g., ref 1), displayed in Table 2. There are several important distinctions between real and complex symmetry species. Each real 2-D symmetry species (e.g., E_{1u}, E_{2g}, etc., Table 2) has been decomposed into two complex conjugated CSSs (described by complex conjugated functions), e.g., $E_{1u} \to (E_{1ua}, E_{1ub})$, $E_{2g} \to (E_{2ga}, E_{2gb})$, etc., which can effectively be regarded as 1-D symmetry species of D_{6h}, analogous to those occurring in the point group C_6.[1] There is important distinction in the definition of symmetry operations c_2' and c_2'' (rotations by $\pi/2$ around two in-plane axes, perpendicular to each other) between Tables 1 and 2. In the case of CSSs (Table 1) besides rotations, these operations also include complex conjugation of the function transformed (e.g., E_{1ua} and E_{1ub} are transformed into each other). The nondegenerate real symmetry species A_{1g}, A_{2g}, B_{1u}, B_{2u}, etc. (Table 2) are replaced by CSSs A_g, B_u, etc. (Table 1). These latter symmetry species are a new concept and should be explained in more detail. The real symmetry species A_{1g} (Table 2) is readily seen to transform according to the A_g symmetry species in Table 1. However, the symmetry species A_{2g} (Table 2) does not transform like any one of the complex symmetry species displayed in Table 1. But if we take the product iA_{2g}, the obtained complex function is readily seen to transform according to CSS A_g again (Table 1). What is more interesting, a complex function can be defined as $f = (A_{1g} + iA_{2g})/2^{1/2}$ (whose real and imaginary parts are ortho-normalized and transform according to the symmetry species A_{1g} and A_{2g}, respectively), which transforms according to the CSS A_g (Table 1). Functions of this type, with both real and imaginary parts nonzero, naturally arise in cc pairs, as the excited vibrational states (overtones) of a 2-D harmonic oscillator, being the eigenfunctions of both Hamiltonian and angular momentum z-component operators. In the general case, a product of two functions, f_1 and f_2, belonging to the complex symmetry species E_{1ua} and E_{1ub}, respectively (which do not belong to the same cc pair, i.e., $f_1^* \neq f_2$), is a function, f_3, belonging to the A_g CSS of the general form, i.e., with both components A_{1g} and A_{2g} nonzero, orthogonal, and normalized: $f_3(A_g) = f_1(E_{1ua})\, f_2(E_{1ub}) = (A_{1g} + iA_{2g})/2^{1/2}$. In a similar manner, the complex symmetry species $A_u = A_{2u} \pm iA_{1u}$, $B_g = B_{1g} \pm iB_{2g}$, and $B_u = B_{2u} \pm iB_{1u}$ have been defined in Table 1.

A brief discussion is due concerning the correspondence between multiplication rules for real symmetry species (Table 2) and CSSs (Table 1). E.g., consider the rule (Table 2)[1]

$$E_{1u} \times E_{2u} = E_{1g} + B_{1g} + B_{2g} \tag{3}$$

In the case of complex symmetry species, using (E_{1ua}, E_{1ub}) instead of E_{1u}, and (E_{2ua}, E_{2ub}) instead of E_{2u}, the following system of multiplication rules corresponds to the above rule (eq 3):

$$E_{1ua}\times E_{2ua} = B_g = B_{1g} + iB_{2g}, \quad E_{1ua}\times E_{2ub} = E_{1gb}$$
$$E_{1ub}\times E_{2ua} = E_{1ga}, \quad E_{1ub}\times E_{2ub} = B_g{}^* = B_{1g\,-}\, iB_{2g} \qquad (4)$$

As already discussed in our pervious work,[30,36] benzene vibrations can be described in terms of complex curvilinear symmetrized vibrational coordinates q_k (transforming according to the CSSs of D_{6h}, Table 1), which are obtained as simple linear combinations of Whiffen's symmetry coordinates.[4] Expressions for the q_k coordinates as linear combinations of local (bond stretch and angle distortion) coordinates[1,4] as well as vice versa, since the transformation matrixes are unitary, are given in Table 3. The coordinates q_k have already been introduced in ref 36, in slightly modified form. These complex coordinates have been used in our previous work on benzene and will be used in the present work as well.

III. LM Symmetrized Description of the C−H Stretch Vibrational System in Benzene

The zeroth-order Hamiltonian $H_0{}^{CH}$ for the C−H stretch vibrational system in benzene is written in the form

$$H_0{}^{CH} = \sum_{i=1}^{6}\left[-\frac{\hbar^2}{2}g_{ss}\frac{\partial^2}{\partial s_i{}^2} + D_s(1 - e^{-assi})^2\right] \qquad (5)$$

consisting of six uncoupled identical Morse oscillators. $g_{ss} = 1/m_H + 1/m_C$ (m_H, m_C = the masses of the H and C atoms, respectively), a_s = the anharmonic parameter, and D_s = the dissociation energy. The Morse potential can be expanded in powers of s:

$$D_s(1 - e^{-ass})^2 = (1/2)f_{ss}s^2 + (1/6)f_{sss}s^3 + (1/24)f_{ssss}s^4 + ... \qquad (6)$$

where $f_{ss} = 2D_s(a_s)^2$, $f_{sss} = -6D_s(a_s)^3 = -3a_sf_{ss}$, etc. are diagonal harmonic, cubic, etc. force constants. Hence, all force constants of a Morse oscillator, of arbitrary order, can be expressed through the two parameters D_s and a_s. A Morse oscillator Hamiltonian is exactly solvable, with eigenfunctions $|n\rangle$ and eigenvalues E_n:

$$E_n = \omega_{CH}\left(n + \frac{1}{2}\right) - x_{CH}\left(n + \frac{1}{2}\right)^2 \qquad (7)$$

where $\omega_{CH} = (1/2\pi)(f_{ss}g_{ss})^{1/2}$ = harmonic frequency, $x_{CH} = (1/2)\omega_{CH}(a_sk_s)^2$ = anharmonic constant, and $k_s = [\hbar(g_{ss}/f_{ss})^{1/2}]^{1/2}$. The eigenfunctions ψ of $H_0{}^{CH}$ are products of six Morse oscillator eigenfunctions, $\psi = \prod_{i=1}{}^6|n_i\rangle_i$, corresponding to n_i excitation quanta in the ith oscillator, the energy of such a configuration being given by $E_\psi = \sum_{i=1}{}^6E_{n_i}$. E.g., $|2\rangle_1|1\rangle_3 = 2_11_3$ is an eigenstate which has two excitation quanta in bond oscillator 1 and one quantum in oscillator 3, while oscillators 2 and 4−6 have zero excitation quanta. A configuration n_i is of purely local type, since only one bond oscillator (the ith) is excited with n quanta, while a state with more than one oscillator excited is of nonlocal character; the stronger, the more evenly are the excitations distributed among the six bond oscillators. A state (configuration) $\psi = \prod_{i=1}{}^6|n_i\rangle_i$ is said to belong to the $n = \prod_{i=1}{}^6n_i$ overtone system.

To obtain complex-symmetry-adapted orthogonal wave functions φ, appropriate linear combinations of the configurations ψ must be taken,[32−34] which can have one of the following complex symmetry species (Table 1): $A_g = A_{1g}$, $A_g = iA_{2g}$, $B_u = iB_{1u}$, $B_u = B_{2u}$, E_{2ga}, E_{2gb}, E_{1ua}, E_{1ub}. This is an entirely combinatoric problem, which can be solved in the way described below. To introduce the necessary notation

$$\varphi = |L;S(f);m_1n_2...k_6\rangle = \frac{1}{L^{1/2}}\sum_{k=0}^{L-1}C_km_{1+k}n_{2+k}...k_{6+k} \qquad (8)$$

where L = the normalization factor (it can take one of the following values, 1, 2, 3, 6, 12), S = the (complex) symmetry species of φ, f = the type specifier, which will be introduced a little later, the subscript $i+k$ should be read as $i+k-6$ whenever $i+k$ exceeds 6, and the symmetrized state is obtained by rotating the initial configuration $m_1n_2...k_6$ $L - 1$ times in clockwise direction around the benzene ring by an appropriate angle (fraction of 2π) and multiplying each time by an appropriate phase factor C_k. In ref 29 expressions have been given for the A_{1g} symmetry states only, which are required for investigation of the $A_{1g}(\nu_1,\nu_2)$ vibrational system in benzene. In the present work, the C−H stretch states of all possible symmetry types are described in detail and an algorithm is designed for generating these states.

Overtone manifold $n = 0$ consists of one A_{1g} (the ground) state, with all $n_k = 0$: $\varphi_0 = |1;A_{1g};0...0\rangle$.

TABLE 3: Complex Symmetrized Vibrational Coordinates $\boldsymbol{q_i}$ of Benzene[a]

	s_1	s_2	s_3	s_4	s_5	s_6
$\boldsymbol{q}_2(A_g{=}A_{1g})$	g	g	g	g	g	g
$q_{7a}(E_{2ga})$	g	gG*	$g(G^*)^2$	$g(G^*)^3$	$g(G^*)^4$	$g(G^*)^5$
$\boldsymbol{q}_{7b}(E_{2gb})$	g	gG	gG^2	gG^3	gG^4	gG^5
$\boldsymbol{q}_{20a}(E_{1ua})$	ig	igF*	$ig(F^*)^2$	$ig(F^*)^3$	$ig(F^*)^4$	$ig(F^*)^5$
$\boldsymbol{q}_{20b}(E_{1ub})$	$-ig$	$-igF$	$-igF^2$	$-\boldsymbol{igF}^3$	$-\boldsymbol{igF}^4$	$-\boldsymbol{igF}^5$
$\boldsymbol{q}_{13}(B_u{=}iB_{1u})$	ig	$-ig$	ig	$-ig$	ig	$-ig$
	t_1	t_2	t_3	t_4	t_5	t_6
$\boldsymbol{q}_1(A_g{=}A_{1g})$	g	g	g	g	g	g
$q_{8a}(E_{2ga})$	$g(G^*)^5$	g	gG*	$g(G^*)^2$	$g(G^*)^3$	$g(G^*)^4$
$\boldsymbol{q}_{8b}(E_{2gb})$	gG^5	g	gG	gG^2	gG^3	gG^4
$\boldsymbol{q}_{14}(B_u{=}B_{2u})$	$-g$	g	$-g$	g	$-g$	g
$q_{19a}(E_{1ua})$	$g(F^*)^5$	g	gF*	$g(F^*)^2$	$g(F^*)^3$	$g(F^*)^4$
$\boldsymbol{q}_{19b}(E_{1ub})$	gF^5	g	gF	gF^2	gF^3	gF^4
	$\boldsymbol{\alpha}_1t_0$	$\boldsymbol{\alpha}_2t_0$	$\boldsymbol{\alpha}_3t_0$	$\boldsymbol{\alpha}_4t_0$	$\boldsymbol{\alpha}_5t_0$	$\boldsymbol{\alpha}_6t_0$
$\boldsymbol{q}_{6a}(E_{2ga})$	g	gG*	$g(G^*)^2$	$g(G^*)^3$	$g(G^*)^4$	$g(G^*)^5$
$\boldsymbol{q}_{6b}(E_{2gb})$	g	gG	gG^2	gG^3	gG^4	gG^5
$\boldsymbol{q}_{12}(B_u{=}iB_{1u})$	ig	$-ig$	ig	$-ig$	ig	$-ig$
	β_1s_0	$\boldsymbol{\beta}_2s_0$	$\boldsymbol{\beta}_3s_0$	$\boldsymbol{\beta}_4s_0$	$\boldsymbol{\beta}_5s_0$	$\boldsymbol{\beta}_6s_0$
$\boldsymbol{q}_3(A_g{=}iA_{2g})$	ig	ig	ig	ig	ig	ig
$q_{9a}(E_{2ga})$	ig	igG*	$ig(G^*)^2$	$ig(G^*)^3$	$ig(G^*)^4$	$ig(G^*)^5$
$\boldsymbol{q}_{9b}(E_{2gb})$	$-ig$	$-igG$	$-igG^2$	$-\boldsymbol{igG}^3$	$-\boldsymbol{igG}^4$	$-\boldsymbol{igG}^5$
$\boldsymbol{q}_{15}(B_u{=}B_{2u})$	g	$-g$	g	$-g$	g	$-g$
$q_{18a}(E_{1ua})$	ig	igF*	$ig(F^*)^2$	$ig(F^*)^3$	$ig(F^*)^4$	$ig(F^*)^5$
$\boldsymbol{q}_{18b}(E_{1ub})$	$-ig$	$-igF$	$-igF^2$	$-\boldsymbol{igF}^3$	$-\boldsymbol{igF}^4$	$-\boldsymbol{igF}^5$
	$\boldsymbol{\delta}_1t_0$	$\boldsymbol{\delta}_2t_0$	$\boldsymbol{\delta}_3t_0$	$\boldsymbol{\delta}_4t_0$	$\boldsymbol{\delta}_5t_0$	$\boldsymbol{\delta}_6t_0$
$\boldsymbol{q}_{16a}(E_{2ua})$	igF*	igF*G*	$igF^*(G^*)^2$	$igF^*(G^*)^3$	$igF^*(G^*)^4$	$igF^*(G^*)^5$
$\boldsymbol{q}_{16b}(E_{2ub})$	$-igF$	$-igFG$	$-igFG^2$	$-\boldsymbol{igFG}^3$	$-\boldsymbol{igFG}^4$	$-\boldsymbol{igFG}^5$
$\boldsymbol{q}_4(B_g{=}iB_{2g})$	ig	$-ig$	ig	$-ig$	ig	$-ig$
	γ_1s_0	$\boldsymbol{\gamma}_2s_0$	$\boldsymbol{\gamma}_3s_0$	$\boldsymbol{\gamma}_4s_0$	$\boldsymbol{\gamma}_5s_0$	$\boldsymbol{\gamma}_6s_0$
$\boldsymbol{q}_5(B_g{=}iB_{2g})$	ig	$-ig$	ig	$-ig$	ig	$-ig$
$q_{10a}(E_{1ga})$	ig	igF*	$ig(F^*)^2$	$ig(F^*)^3$	$ig(F^*)^4$	$ig(F^*)^5$
$\boldsymbol{q}_{10b}(E_{1gb})$	$-ig$	$-igF$	$-igF^2$	$-\boldsymbol{igF}^3$	$-\boldsymbol{igF}^4$	$-\boldsymbol{igF}^5$
$\boldsymbol{q}_{11}(A_u{=}A_{2u})$	g	g	g	g	g	g
$q_{17a}(E_{2ua})$	ig	igG*	$ig(G^*)^2$	$ig(G^*)^3$	$ig(G^*)^4$	$ig(G^*)^5$
$\boldsymbol{q}_{17b}(E_{2ub})$	$-ig$	$-igG$	$-igG^2$	$-\boldsymbol{igG}^3$	$-\boldsymbol{igG}^4$	$-\boldsymbol{igG}^5$

[a] Conversion matrices 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: $q_i = \sum A_{ik}x_k$. Columns: $x_i = \sum A_{ik}{}^*q_k$. s_0 and t_0 are equilibrium C−H and C−C bond lengths, respectively, $g = 1/6^{1/2}$, $F = e^{i\pi/3}$, $F^* = e^{-i\pi/3}$, $G = e^{2i\pi/3}$, and $G^* = e^{-2i\pi/3}$.

Next, overtone manifold $n = 1$ contains six states, each of them obtained from the initial configuration $1_1 0_2$... by using the phase factors identical to those used to obtain the CST coordinates q_2, q_{13}, $q_{7a,b}$, and $q_{20a,b}$ from the six local bond stretches s_i (s-type, Table 3):

$$\begin{aligned}
\varphi_1 &= |6;\mathrm{A}_{1g};1_1\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5} 1_{1+k}0_{2+k}...0_{6+k} \\
\varphi_2 &= |6;\mathrm{B}_u{=}i\mathrm{B}_{1u};1_1\rangle = \frac{i}{6^{1/2}}\sum_{k=0}^{5}(-1)^k 1_{1+k}0_{2+k}...0_{6+k} \\
\varphi_3 &= |6;\mathrm{E}_{1ua};1_1\rangle = \frac{i}{6^{1/2}}\sum_{k=0}^{5}(F^*)^k 1_{1+k}0_{2+k}...0_{6+k} \\
\varphi_4 &= |6;\mathrm{E}_{1ub};1_1\rangle = \frac{-i}{6^{1/2}}\sum_{k=0}^{5}F^k 1_{1+k}0_{2+k}...0_{6+k} \\
\varphi_5 &= |6;\mathrm{E}_{2ga};1_1\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5}(G^*)^k 1_{1+k}0_{2+k}...0_{6+k} \\
\varphi_6 &= |6;\mathrm{E}_{2gb};1_1\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5}G^k 1_{1+k}0_{2+k}...0_{6+k}
\end{aligned} \tag{9}$$

where $F = e^{i\pi/3}$, $F^* = e^{-i\pi/3}$, $G = e^{2i\pi/3}$, and $G^* = e^{-2i\pi/3}$.

Next, overtone manifold $n = 2$ is considered, encompassing 21 symmetrized states. Here there are already both purely local configurations (giving rise to 6 symmetrized states) and nonlocal configurations (15 symmetrized states). The six purely local states $\varphi_7-\varphi_{12}$ are obtained in a manner identical to that of the $n = 1$ states (nine). As an example, the first one of them is shown here:

$$\varphi_7 = |6;\mathrm{A}_{1g};2_1\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5} 2_{1+k}0_{2+k}...0_{6+k}$$

Next, there are six nonlocal states, $\varphi_{13}-\varphi_{18}$, originating from the configuration $1_1 1_2 0_3$..., which are obtained analogously to the t-type (local bond C−C stretches t_i) coordinates q_1, q_{14}, $q_{8a,b}$, and $q_{19a,b}$ (Table 3):

$$\begin{aligned}
\varphi_{13} &= |6;\mathrm{A}_{1g};1_2 1_3\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5} 0_{1+k}1_{2+k}1_{3+k}0_{4+k}...0_{6+k} \\
\varphi_{14} &= |6;\mathrm{B}_u{=}\mathrm{B}_{2u};1_2 1_3\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5}(-1)^k 0_{1+k}1_{2+k}1_{3+k}...0_{6+k} \\
\varphi_{15} &= |6;\mathrm{E}_{1ua};1_2 1_3\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5}(F^*)^k 0_{1+k}1_{2+k}1_{3+k}...0_{6+k} \\
\varphi_{16} &= |6;\mathrm{E}_{1ub};1_2 1_3\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5}F^k 0_{1+k}1_{2+k}1_{3+k}...0_{6+k} \\
\varphi_{17} &= |6;\mathrm{E}_{2ga};1_2 1_3\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5}(G^*)^k 0_{1+k}1_{2+k}1_{3+k}...0_{6+k} \\
\varphi_{18} &= |6;\mathrm{E}_{2gb};1_2 1_3\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5}G^k 0_{1+k}1_{2+k}1_{3+k}...0_{6+k}
\end{aligned} \tag{10}$$

Next, there are six nonlocal states, $\varphi_{19}-\varphi_{24}$, originating from the configuration $1_6 1_2 0_3$... of the symmetry species $\mathrm{A}_g = \mathrm{A}_{1g}$, $\mathrm{B}_u = i\mathrm{B}_{1u}$, E_{2ga}, E_{2gb}, E_{1ua}, and E_{1ub} (s-type). Here we give only the A_{1g} state:

$$\varphi_{19} = |6;\mathrm{A}_{1g};1_2 1_4\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5} 0_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}1_{6+k}$$

And to finish with manifold $n = 2$, there is still the configuration $1_1 1_4$, which yields three more symmetrized states:

$$\begin{aligned}
\varphi_{25} &= |3;\mathrm{A}_{1g};1_1 1_4\rangle = \frac{1}{3^{1/2}}\sum_{k=0}^{2} 1_{1+k}0_{2+k}0_{3+k}1_{4+k}0_{5+k}0_{6+k} \\
\varphi_{26} &= |3;\mathrm{E}_{2ga};1_1 1_4\rangle = \frac{1}{3^{1/2}}\sum_{k=0}^{2}(G^*)^k 1_{1+k}0_{2+k}0_{3+k}1_{4+k}0_{5+k}0_{6+k} \\
\varphi_{27} &= |3;\mathrm{E}_{2gb};1_1 1_4\rangle = \frac{1}{3^{1/2}}\sum_{k=0}^{2}G^k 1_{1+k}0_{2+k}0_{3+k}1_{4+k}0_{5+k}0_{6+k}
\end{aligned} \tag{11}$$

Next, consider the $n = 3$ overtone manifold. This manifold contains 56 symmetrized states in total. In the first place, there are six purely local (s-type) states, φ_{28}–φ_{33}, arising from the configuration 3_1 (located at the lowest energy within the manifold, analogous to the $n = 1$ and $n = 2$ cases, considered above). Here, only the first one of them will be displayed:

$$\varphi_{28} = |6;\mathrm{A}_{1g};3_1\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5} 3_{1+k}0_{2+k}...0_{6+k}$$

The remaining 47 states belonging to the $n = 3$ manifold are of nonlocal character. There are six (s-type) states, $\varphi_{34}-\varphi_{39}$, originating from the configuration $1_6 1_1 1_2$, the first one of which is

$$\varphi_{34} = |6;\mathrm{A}_{1g};1_6 1_1 1_2\rangle = \frac{1}{6^{1/2}}\sum_{k=0}^{5} 1_{1+k}1_{2+k}0_{3+k}...1_{6+k}$$

Next, there are two $L = 2$ states, φ_{40} and φ_{41}, originating from the configuration $1_1 1_3 1_5$, which are given by the expressions:

$$\begin{aligned}
\varphi_{40} &= |2;\mathrm{A}_{1g};1_1 1_3 1_5\rangle = \frac{1}{2^{1/2}}(1_1 1_3 1_5 + 1_2 1_4 1_6) \\
\varphi_{41} &= |2;\mathrm{B}_g{=}\mathrm{B}_{1g};1_1 1_3 1_5\rangle = \frac{1}{2^{1/2}}(1_1 1_3 1_5 - 1_2 1_4 1_6)
\end{aligned} \tag{12}$$

The remaining configurations belonging to $n = 3$ are asymmetrical with respect to both c_2' and c_2'' rotations (Table 1) and therefore are symmetrized as $L = 12$ states. Consider first the configuration $2_1 1_2$, which gives rise to 12 symmetrized states, $\varphi_{42}-\varphi_{53}$:

$$
\begin{aligned}
\varphi_{42} &= |12;\mathrm{A_g{=}A_{1g}};2_1 1_2\rangle = \frac{1}{12^{1/2}}\sum_{k=0}^{5} \\
&\qquad (1_{6+k}2_{1+k}0_{2+k}0_{3+k}0_{4+k}0_{5+k} + 2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k}) \\
\varphi_{43} &= |12;\mathrm{A_g{=}}i\mathrm{A_{2g}};2_1 1_2\rangle = \frac{i}{12^{1/2}}\sum_{k=0}^{5} \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} - 0_{1+k}0_{2+k}1_{3+k}2_{4+k}0_{5+k}0_{6+k}) \\
\varphi_{44} &= |12;\mathrm{B_u{=}}i\mathrm{B_{1u}};2_1 1_2\rangle = \frac{i}{12^{1/2}}\sum_{k=0}^{5}(-1)^k \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} - 0_{1+k}0_{2+k}1_{3+k}2_{4+k}0_{5+k}0_{6+k}) \\
\varphi_{45} &= |12;\mathrm{B_u{=}B_{2u}};2_1 1_2\rangle = \frac{1}{12^{1/2}}\sum_{k=0}^{5} \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} + 0_{1+k}0_{2+k}1_{3+k}2_{4+k}0_{5+k}0_{6+k}) \\
\varphi_{46} &= |12;\mathrm{E_{1ua}}(s);2_1 1_2\rangle = \frac{i}{12^{1/2}}\sum_{k=0}^{5}(F^*)^k \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} + 2_{1+k}0_{2+k}0_{3+k}0_{4+k}0_{5+k}1_{6+k}) \\
\varphi_{47} &= |12;\mathrm{E_{1ub}}(s);2_1 1_2\rangle = \frac{-i}{12^{1/2}}\sum_{k=0}^{5}F^k \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} + 2_{1+k}0_{2+k}0_{3+k}0_{4+k}0_{5+k}1_{6+k}) \\
\varphi_{48} &= |12;\mathrm{E_{1ua}}(t);2_1 1_2\rangle = \frac{1}{12^{1/2}}\sum_{k=0}^{5}(F^*)^k \\
&(2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} + 0_{1+k}0_{2+k}1_{3+k}2_{4+k}0_{5+k}0_{6+k}) \\
\varphi_{49} &= |12;\mathrm{E_{1ub}}(t);2_1 1_2\rangle = \frac{1}{12^{1/2}}\sum_{k=0}^{5}F^k \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} + 0_{1+k}0_{2+k}1_{3+k}2_{4+k}0_{5+k}0_{6+k}) \\
\varphi_{50} &= |12;\mathrm{E_{2ga}}(s);2_1 1_2\rangle = \frac{1}{12^{1/2}}\sum_{k=0}^{5}(G^*)^k \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} + 0_{1+k}0_{2+k}1_{3+k}2_{4+k}0_{5+k}0_{6+k}) \\
\varphi_{51} &= |12;\mathrm{E_{2gb}}(s);2_1 1_2\rangle = \frac{1}{12^{1/2}}\sum_{k=0}^{5}G^k \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} + 0_{1+k}0_{2+k}1_{3+k}2_{4+k}0_{5+k}0_{6+k}) \\
\varphi_{52} &= |12;\mathrm{E_{2ga}}(\beta);2_1 1_2\rangle = \frac{i}{12^{1/2}}\sum_{k=0}^{5}(G^*)^k \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} - 2_{1+k}0_{2+k}0_{3+k}2_{4+k}0_{5+k}1_{6+k}) \\
\varphi_{53} &= |12;\mathrm{E_{2gb}}(\beta);2_1 1_2\rangle = \frac{-i}{12^{1/2}}\sum_{k=0}^{5}G^k \\
&\qquad (2_{1+k}1_{2+k}0_{3+k}0_{4+k}0_{5+k}0_{6+k} - 2_{1+k}0_{2+k}0_{3+k}2_{4+k}0_{5+k}1_{6+k})
\end{aligned}
\tag{13}
$$

As is seen, an asymmetrical configuration such as $2_1 1_2$ yields 12 states with the following symmetries: there are two (E_{1ua}, E_{1ub}) pairs of *s*-type and *t*-type, respectively (Table 3); there are two (E_{2ga}, E_{2gb}) pairs of *s*-type and *β*-type, respectively (Table 3); the remaining symmetry species are $A_g = A_{1g}$, $A_g = iA_{2g}$, $B_u = iB_{1u}$, and $B_u = B_{2u}$.

The remaining two asymmetrical configurations from the $n = 3$ manifold, each of them giving rise to $L = 12$ states (with the symmetries described above for the $2_1 1_2$ configuration) are $2_1 3$ and $1_1 1_2 1_4$.

So far, all possible schemes, required for the symmetrization of any configuration, belonging to arbitrary overtone nuber *n*, have already been explored. An algorithm has been designed and incorporated into the general code for calculation of benzene vibrational frequencies for automatic symmetrization of an arbitrary configuration, arising in the course of the search and active space selection procedure.

IV. Zeroth-Order and Interaction Hamiltonians, Basis Set Functions, AI Search Procedure, and Hamiltonian Matrix Manipulation

H_0^{CH} (eq 5) is the zeroth-order Hamiltonian pertaining to the C−H stretching system, whose symmetrized eigenstates are the functions φ_k, described in detail in the preceding section. The full zeroth-order Hamiltonian (for the present model treatment) is written as $H_0 = H_0^{\mathrm{CH}} + H_0^{\mathrm{ring}}$, where H_0^{ring} is the sum of (1-D and 2-D) harmonic (or Morse) oscillator Hamiltonians describing the ring symmetrized modes in benzene, in terms of complex symmetrized coordinates q_i (Table 3).

The model representation of the ring modes in benzene requires some additional clarification. These modes are described as symmetrized modes (in terms of complex symmetrized coordinates) in contrast to the C−H stretches, described as local modes. According to their symmetry species, the symmetrized modes are either 1-D (e.g., B_{1u} and A_{1g}) or 2-D (e.g., E_{1u}, E_{2g}, etc.). The easiest way to proceed is to regard them as (1-D or 2-D) harmonic oscillators, characterized by harmonic frequencies ω_k. The formalism employed for description of 1-D and 2-D harmonic oscillator Hamiltonian eigenfunctions (and their complex symmetry species), as expressed in terms of complex symmetrized coordinates q_k, has been detailed in our previous work.[35,36] In the present work, some of the symmetrized modes involved will be considered as anharmonic oscillators, in the following empirical sense. For a vibration *k*, described as an anharmonic 1-D oscillator with harmonic frequency ω_k and anharmonic constant x_k, the energy levels are given by a spectroscopic formula analogous to eq 7:

$$E_n = \omega_k(n + 1/2) + x_k(n + 1/2)^2$$

. In the framework of the Morse oscillator formalism, the anharmonic constant x_k can be related to an effective cubic force constant, $F'_{k,k,k}$, through the relation $F'_{k,k,k} = -3(2\omega_k x_k)^{1/2}$. This "effective force constant" does not have a distinct physical meaning in the case of a nontotally symmetric mode (i.e., any mode, other than ν_1) but is a parameter representative of the overall effect of several (unknown) cubic and quartic force constants. Even in the case of the totally symmetric mode ν_1, $F'_{1,1,1}$ does not usually coincide with the molecular specific force constant $F_{1,1,1}$, but it is an empirical parameter describing the overall effect of a multitude of anharmonic force constants contributing to the anharmonicity of the ν_1 mode.

Next, an empirical formula describing the energy levels of a 2-D anharmonic oscillator is $E(n,l) = \omega_k(n + 1) + x_k(n + 1)^2 + g_{kk}l^2$, where $l = n, n - 2, ..., -n$. By substituting $n = n_a + n_b$ and $l = n_{a\,-}\,n_b$ (n_a and n_b are the occupation numbers of the two separate oscillators) and taking for simplicity $x_k = g_{kk}$, this formula takes the form $E(n,l) = E(n_a,n_b) = \omega_k(n_a + 1/2) + 2x_k(n_a + 1/2)^2 + \omega_k(n_b + 1/2) + 2x_k(n_b + 1/2)^2$. Hence, the energy levels of a 2-D oscillator can be obtained as the superposition of two identical anharmonic oscillators, whose harmonic frequency is ω_k and anharmonic constant is $2x_k$. In that case, the effective cubic force constant characterizing the anharmonicity of this oscillator can be given by a formula analogous to that in the 1-D oscillator case: $F'_{k,k,k} = -6(\omega_k x_k)^{1/2}$. In the following, the "effective cubic force constants" $F'_{k,k,k}$ for some of the considered 1-D or 2-D symmetrized modes (in addition to the harmonic force constants $F_{i,k}$ determining the harmonic frequencies ω_k) will be regarded as adjustable parameters, whose values will be varied to reproduce the experimentally observed fundamental frequencies ν_k, as well as some overtone levels.

In the calculations presented below, only the following ring modes belonging to the four symmetry blocks in benzene containing a C−H stretch vibration (A_{1g}, E_{2g}, B_{1u}, E_{1u}) have been included:

(A_{1g} block) ν_1 mode, described by symmetrized coordinate $q_1 = S_1$ (Whiffen's coordinate[4]); the harmonic force constant involved is $F_{1,1}$, and the effective cubic force constant is $F'_{1,1,1}$; (

E_{1u} block) ν_{18}, ν_{19} modes; each of them is described as a 2-D oscillator in terms of symmetrized coordinates q_{18a} and q_{18b} (of complex symmetry species E_{1ua} and E_{1ub}, respectively), q_{19a} (E_{1ua}), and q_{19b} (E_{1ub}) (Table 3); the harmonic force constants involved are $F_{18,18}$ and $F_{19,19}$, and the effective cubic force constant is $F'_{18,18,18}$; (

B_{1u} block) ν_{12} mode, described as a 1-D oscillator in terms of the coordinate q_{12} (complex symmetry species $B_u = iB_{1u}$); the harmonic force constant involved is $F_{12,12}$; (

E_{2g} block) ν_6, ν_8, ν_9 modes; each of them is described as a 2-D harmonic oscillator in terms of symmetrized coordinates q_{6a} (E_{2ga}), q_{6b} (E_{2gb}), q_{8a} (E_{2ga}), q_{8b} (E_{2gb}), q_{9a} (E_{2ga}), and q_{9b} (E_{2gb}) (Table 3); the harmonic force constants involved are $F_{6,6}$, $F_{8,8}$, and $F_{9,9}$, and the effective cubic force constants are $F'_{8,8,8}$ and $F'_{9,9,9}$.

The eigenfunctions χ of the ring zeroth-order Hamiltonian H_0^{ring} are obtained as products of harmonic oscillator eigenfunctions $\chi_k(q_k)$ for each one of the ring modes summarized above:

$$\chi = \prod_k \chi_{nk}(q_k) = |n_1,n_{12},n_{6a},n_{6b},...\rangle \tag{14}$$

The eigenfunctions $|i\rangle$ of the full zeroth-order Hamiltonian $H_0 = H_0^{\text{CH}} + H_0^{\text{ring}}$ are obtained as the product of φ_k (the symmetrized eigenfunction of the C−H stretch Hamiltonian H_0^{CH}) and of χ (the symmetrized eigenfunction of the ring Hamiltonian H_0^{CH}): $|i\rangle = \varphi\chi$. All of the harmonic oscillator eigenfunctions $\chi_k(q_k)$ have well-defined CSSs (which has been detailed in our previous work[35]), and therefore, their product has well-defined CSSs as well. And since φ_k is also symmetrized, the basis vectors of the present description $|i\rangle$ also have a well-defined CSS.

Since the modes have been described in terms of symmetrized curvilinear (not normal) coordinates, two basis states, $|i\rangle$ and $|k\rangle$ (belonging to one and the same CSS), can be coupled to each other by quadratic interaction Hamiltonian terms:

$$H^{i,k} = -\hbar^2 G_{i,k} \frac{\partial^2}{\partial q_i \partial q_k{}^*} + F_{i,k} q_i q_k{}^* \tag{15}$$

for the case of two nondegenerate coordinates, e.g., q_{12} and q_{13}, and

$$H_{(d)}{}^{i,k} = -\hbar^2 G_{i,k}\left(\frac{\partial^2}{\partial q_{ia}\partial q_{kb}} + \frac{\partial^2}{\partial q_{ib}\partial q_{ka}}\right) + F_{i,k}(q_{ia}q_{kb} + q_{ib}q_{ka}) \tag{16}$$

for the case of two degenerate coordinates, e.g., (q_{6a}, q_{6b}) and (q_{7a}, q_{7b}) (Table 3). $G_{i,k}$ are Wilson's nondiagonal **G**-matrix elements[1] and $F_{i,k}$ are the relevant nondiagonal harmonic force constants. One of the coordinates i or k can be a C−H stretch coordinate (q_2, $q_{7a,b}$, q_{13}, $q_{20a,b}$). In such a case, for the calculation of the relevant interaction Hamiltonian matrix elements, this coordinate has to be expanded in terms of the local bond C−H stretches s_i (Table 3). Besides the terms of types $H^{i,k}$ and $H_{(d)}{}^{i,k}$, the quadratic interaction Hamiltonian also contains three small terms, corresponding to the (potential) coupling between different C−H bond stretches s_i:

$$H_1{}^{\text{CH}} = V_1{}^{\text{CH}} = f_{1,2}(s_1s_2 + s_2s_3 + ... + s_6s_1) + f_{1,3}(s_1s_3 + s_2s_4 + ... + s_6s_2) + f_{1,4}(s_1s_4 + s_2s_5 + s_3s_6) \tag{17}$$

where $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$ are small nondiagonal quadratic force constants.[1,8] The complete form of the quadratic interaction Hamiltonian is given by

$$H^{\{\text{int}\}} = H^{1,2} + H^{12,13} + H_{(d)}{}^{6,7} + H_{(d)}{}^{6,8} + H_{(d)}{}^{6,9} + H_{(d)}{}^{7,8} + H_{(d)}{}^{7,9} + H_{(d)}{}^{8,9} + H_{(d)}{}^{18,19} + H_{(d)}{}^{18,20} + H_{(d)}{}^{19,20} + H_1{}^{\text{CH}} \tag{18}$$

The quadratic nondiagonal force constants involved in the interaction Hamiltonian H^{int} are $F_{1,2}$, $F_{18,19}$, $F_{18,20}$, $F_{19,20}$, $F_{12,13}$, $F_{6,7}$, $F_{6,8}$, $F_{6,9}$, $F_{7,8}$, $F_{7,9}$, $F_{8,9}$, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$. In this work we are not taking into account any cubic or higher order Hamiltonian interaction terms.

In our preceding work,[30] the calculation of matrix elements of the type $\langle i|H^{1,2}|k\rangle$, with both basis functions $|i\rangle$ and $|k\rangle$ belonging to the totally symmetric species A_{1g}, has been discussed in considerable detail. For the general case, when $|i\rangle$ and $|k\rangle$ belong to an arbitrary CSS, and when other terms of the interaction Hamiltonian besides $H^{1,2}$ are involved, the calculation of coupling matrix elements $\langle i|\text{H}^{\text{int}}|k\rangle$ is a nontrivial task. The main difficulties arise in the calculation of that part of the matrix element involving a symmetrized C−H stretch coordinate. A specific algorithm has been designed for calculation of the C−H stretch containing part, and incorporated into the general algorithm, employed for computing the matrix elements $\langle i|H^{\text{int}}|k\rangle$.[29]

The AI search procedure, employed for selecting an active space (AS) from the infinite manifold of available symmetrized basis states $|k\rangle$, and setting up of the Hamiltonian matrix, has been delineated before.[30,35] Starting with an appropriately chosen initial basis state, $|0\rangle$, the algorithm proceeds to select all basis states $|k\rangle$ (of the same CSS as $|0\rangle$), coupled to this state through matrix elements of the interaction Hamiltonian H^{int}. In practice this is implemented by applying successively on $|0\rangle$ all terms from H^{int} (18), expressed in operator form. Simultaneously, the energies E_k of the selected states $|k\rangle$, as well as the relevant coupling matrix elements $\langle 0|H^{\text{int}}|k\rangle$, are calculated and stored into computer memory, as the diagonal and nondiagonal elements of the Hamiltonian matrix $H_{k,k}$ and $H_{0,k}$, respectively. The search algorithm has several adjustable parameters. One of them is C, which determines the minimum matrix element to energy difference ratio, for which a new state is selected. In the next stage of the search, each one of the initially selected states $|k\rangle$ is explored, applying H^{int} in operator form as above, and as a result more basis states $|j\rangle$ are selected. Their energies E_j and coupling matrix elements $\langle k|H^{\text{int}}|j\rangle$ are calculated and built into the Hamiltonian matrix $H_{i,k}$. This procedure is carried on until a sufficiently large and representative AS of dimensionality N (which is another one of the adjustable parameters) has been selected. For the purpose of the calculations in this work, the initial state $|0\rangle$ was usually chosen as one of the C−H stretch fundamentals $|0\rangle = |6;S;1_1\rangle$ (where S is one of the CSSs $A_g = A_{1g}$, $B_u = iB_{1u}$, E_{2ga}, and E_{1ua}), with no ring modes excited.

To obtain the eigenvalues of the selected Hamiltonian matrix $H_{i,k}$, it had to be diagonalized numerically. For this purpose, because of the large dimensionality N, a Lanczos tridiagonalization procedure has been used.[41,42] For each isotopomer of C_6H_6 explored, an additional calculation had to be carried out to obtain the energy of the ground vibrational state. For this calculation, the initial state was chosen as $|0\rangle = |1;A_{1g};0\rangle$. To obtain the molecular vibrational levels, which can then be compared to experimentally observed fundamental, overtone, or combination frequencies, the ground vibrational state energy must be subtracted from the computed eigenvalues of $H_{i,k}$. In each calculation, the dimensionality N of the selected AS has been increased, and some other parameter values varied, until convergent and realistic results have been obtained.

V. Results and Discussion

As already mentioned above, in benzene there are four vibrational symmetry blocks involving a C−H stretch vibration: $A_{1g}(\nu_1,\nu_2)$, $E_{2g}(\nu_6,\nu_7,\nu_8,\nu_9)$, $B_{1u}(\nu_{12},\nu_{13})$, $E_{1u}(\nu_{18},\nu_{19},\nu_{20})$. In general, using the model described above, two types of calculations are possible and have been performed in the present work, according to the specific case considered. The first one is block-limited calculation, i.e., taking into account only the Hamiltonian terms pertaining to the vibrations of a single vibrational mode block with a given symmetry type. This procedure is analogous to the well-known Wilson FG analysis.[1] Such block-limited calculations have already been performed in our previous work[29,30] for the vibrational blocks of symmetries A_{1g} and E_{1u}. The second type of (large-scale) calculation incorporates all the Hamiltonian terms pertaining to all the vibrations belonging to the four symmetry blocks in benzene containing a C−H stretch. In the block-limited calculations, the available vibrational level density is small. As a result of this, the Hamiltonian matrixes required for convergent results to be obtained are comparatively small dimensional, N not exceeding 2000 as a rule. Hence, the block-limited calculations are conveniently fast, because they do not involve manipulation of large dimensional Hamiltonian matrixes. Block-limited calculations can easily be performed for each one of the four vibrational symmetry blocks involving a C−H stretch by selecting basis states (of the relevant symmetry type) whose composition includes only excitations of the vibrations belonging to this block. On the other hand, in the large-scale calculation, the level density involved is already quite high and very large dimensional Hamiltonian matrixes are required (on the order of $N = 70000$) to obtain convergent results. Of course the large-scale calculations are expected to yield results which are closer to reality, as compared to the block-limited calculations, because they encompass more fully the levels of the C−H stretch vibrational system of benzene. Therefore, the feasibility of the results obtained from block-limited calculations should be checked against the results from the large-scale calculations performed at a sufficiently large N value (after convergence has been achieved). In the present work, both types of calculations, block-limited as well as large-scale, have been performed. The choice between one or the other type of calculation has been made for each concrete case, taking into account a number of considerations of convenience and feasibility of the results obtained. Our experience with both types of calculations has led to the following observations and conclusions, which were helpful to make the right choice. In the large-scale calculations, upon increasing the dimensionality N, the calculated C−H stretch fundamental frequencies (at ∼3000 cm^{-1}) were found to converge at a much smaller value of N (as a rule around ∼40000), as compared to the non-C−H stretch (ring) frequencies, which required values of 70000 and higher to converge. It was also found that, for a given set of input force constant values, the converged values of the ring fundamentals obtained from the (rather difficult) large-scale calculations practically coincided with those obtained from the (quite fast) block-limited calculations. However, this was not true for the C−H stretch fundamentals, whose values obtained from the block-limited calculations could differ by as much as 20−30 cm^{-1} from the results of large-scale calculations. Of course, the C−H stretch frequencies obtained from the large-scale calculations should be considered as the correct ones. Both block-limited and large-scale calculations have shown that the ring mode fundamentals calculated were sensitive to the input values of the harmonic force constants related to these modes, e.g., $F_{1,1}$, $F_{1,2}$, $F_{6,6}$, $F_{6,7}$, etc., but depended negligibly upon the values of the force constants f_{ss}, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$ characterizing the C−H stretch system. These latter force constant values were however determined for the four C−H stretch frequencies ν_2, ν_7, ν_{13}, and ν_{20} only, not affecting the ring fundamentals.

From these observations the following practical rules could be derived, which were used for adjustment (variation) of the input force constant values to obtain a good fit of the theoretically calculated fundamentals to the experimentally measured fundamentals. As a first step, the harmonic force constants pertaining to the ring modes can be determined, using fast block-limited calculations, by adjustment of their values (regarded as variable parameters), until a good fit was achieved of the calculated to the experimentally measured ring fundamentals. Having determined the values of the ring mode harmonic force constants ($F_{1,1}$, $F_{1,2}$, etc.), as a second step, large-scale calculations can be performed to obtain the best values for the force constants f_{ss}, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$ characterizing the C−H stretch system. Fortunately, these large-scale calculations do not require very high N values, since, as pointed out above, the C−H stretch fundamentals converged already at about $N = 40000$.

Table 4 presents the results from the calculations on the ring fundamental frequencies belonging to the four C−H stretch containing symmetry blocks in benzene for each one of the four D_{6h} isotopomers C_6H_6, C_6D_6, $^{13}C_6H_6$, and $^{13}C_6D_6$. These are the values corresponding to the best possible fit with the experimentally measured fundamentals. The latter are also displayed in the table for comparison. A survey of the data presented in Table 4 shows that there is a particularly good fit achieved of the calculated to the experimentally measured fundamentals, practically for all four D_{6h} isotopomers. The first and second overtone energy levels of the totally symmetric mode ν_1 are also shown in Table 4 and are seen to be in satisfactory agreement with the corresponding experimentally measured values.[25,43]

The values of the relevant harmonic force constants corresponding to this set of ring fundamentals (Table 4) are summarized in Table 5a. The active space dimension, required for convergence of these block-limited calculations, did not exceed 2000 as a rule. The values for the C−H stretch force constants employed in these calculations, whose effect upon the ring fundamentals was negligible, were used as determined in our previous work.[29] Part of the results contained in Table 5a were published previously.[29,30] The present calculations have confirmed the previously obtained results concerning the

TABLE 4: Calculated Fundamental Frequencies of Non-C−H Stretch Vibrations (cm^{-1}) for D_{6h} Symmetry Benzenes, Corresponding to the Best Fit Values for the Force Constant Parameters (mdyn and A), Given in Table 5

		C_6H_6		C_6D_6		$^{13}C_6H_6$		$^{13}C_6D_6$	
		calc	exptl	calcd	exptl	calcd	exptl	calcd	exptl
A_{1g}	ν_1	993.0	993.071 [23]	945.7	945.583 [23]	957.4	957.4 [40]	915.6	916.6 [8]
	$2\nu_1$	1984.6	1984.9 [25,43]	1889.9	1889.8 [25]				
	$3\nu_1$	2974.6	2975.4 [25,43]	2832.8	2832.6 [25]				
E_{1u}	ν_{18}	1038.4	1038.2670 [17]	814.1	814.2969 [17]	1018.6	1018.379 8 [17]	808.1	808.5479 [47]
	ν_{19}	1484.0	1483.9854 [17]	1336.8	1335.2212 [17]	1453.3	1454.257 6 [17]	1295.3	1295.756 4 [47]
B_{1u}	ν_{12}	1013.7	1013.7 [27]	964.6	970[a] [16]	977.3		934.0	
E_{2g}	ν_6	609.0	608.13 [23]	576.2	580.2 [48]	587.1	584.2 [49]	558.5	561.3 [8]
	ν_9	1177.2	1177.776 [23]	866.3	867.0 [23]	1169.9		862.4	
	ν_8	1602.5	1600.9764 [50]	1554.3	1558.3 [23]	1548.9		1499.0	

[a] Estimated from combinations in ref 16.

TABLE 5: Calculated Harmonic as Well as Some Important Cubic Diagonal Force Constants Pertaining to the Four C−H Stretch Containing Vibrational Blocks in Benzene, A_{1g}, E_{2g}, B_{1u}, E_{1u}, Compared to the Previously Empirically Determined Values by Goodman et al. [Ref 8] (for the Harmonic Constants) or Obtained from ab Initio Computations by Maslen et al. [Ref 11] (mdyn and A)

(a) Harmonic Force Constants Pertaining to the Non-C−H Stretch (Ring) Vibrations

	$F_{1,1}$	$F_{1,2}$	$F_{18,18}$	$F_{19,19}$	$F_{18,19}$	$F_{18,20}$	$F_{19,20}$	$F_{12,12}$	$F_{12,13}$
calculated	7.630	0.030	0.931	7.403	0.221	0.214	0.590	7.661	−0.010
Goodman et al.[8]	7.616	0.157	0.926	7.380	0.209	0.151	0.572	7.658	−0.237

	$F_{6,6}$	$F_{8,8}$	$F_{9,9}$	$F_{6,7}$	$F_{6,8}$	$F_{6,9}$	$F_{7,8}$	$F_{7,9}$	$F_{8,9}$
calculated	0.667	6.690	0.910	0.020	0.388	−0.235	0.054	−0.066	−0.030
Goodman et al.[8]	0.644	6.690	0.895	−0.136	0.308	−0.140	0.054	−0.066	−0.398

(b) Harmonic Force Constants Pertaining to the C−H Stretch System

	f_{ss}	$f_{1,2}$	$f_{1,3}$	$f_{1,4}$	$F_{2,2}$	$F_{7,7}$	$F_{13,13}$	$F_{20,20}$
calculated	5.515	0.007	0.008	−0.005	5.540	5.495	5.522	5.519
Goodman et al.[8]	5.547	0.007	0.008	−0.022	5.554	5.510	5.571	5.568

(c) Cubic Diagonal Force Constant f_{sss} and Effective Anharmonic Force Constants $F'_{k,k,k}$ for Some of the More Strongly Anharmonic Symmetrized Modes

	f_{sss}	$F'_{1,1,1}$	$F'_{8,8,8}$	$F'_{9,9,9}$	$F'_{18,18,1\,8}$
calculated	−29.72	−16.73	−10.71	−1.08	−1.50
Maslen et al.[11]	**−34.289**	−18.289	−11.633		

TABLE 6: Calculated Fundamental Frequencies of C−H Stretch Vibrations (cm^{-1}) for D_{6h} Symmetry Benzenes, Corresponding to the Best Fit Values for the Force Constant Parameters (mdyn and A), Given in Table 5b

		C_6H_6		C_6D_6		$^{13}C_6H_6$		$^{13}C_6D_6$	
		calc	exptl	calcd	exptl	calcd	exptl	calcd	exptl
A_{1g}	ν_2	3076.1	3073.942 [23]	2300.3	2303.44 [23]	3064.9	3049.8 [40]	2283.6	2283.9 [8]
E_{1u}	ν_{20}	3064.8	3064.3674 [17]	2285.7	2289.3 [40]	3055.3	3065.4540 [17]	2268.8	2266.0796 [47]
	CH ($n = 2$)	6004.5	6005 [44]	4489.3	4497 [31]				
	CH ($n = 3$)	8836.4	8827 [44]	6660	6634 [31]				
B_{1u}	ν_{13}	3027.2	3028[b] [39] 3057[a] [16]	2249.4	2285[a] [16]	3019.6		2234.1	
E_{2g}	ν_7	3059.1	3056.7 [23]	2285.6	2272.5 [23]	3049.2		2267.3	

[a] Estimated from combinations in ref 16. [b] Estimated from combinations in ref 14.

harmonic force constants $F_{1,1}$, $F_{1,2}$, $F_{18,18}$, $F_{19,19}$, $F_{18,19}$, $F_{18,20}$, and $F_{19,20}$ (with slight modifications).[29,30]

As already pointed out, the block-limited calculations were found not suitable for determination of the C−H stretch fundamentals. This is probably due to the fact that each one of them involved only partially the excited (overtone) levels belonging to the C−H stretch system (as described in detail in the previous section). Hence, the values for the force constants f_{ss}, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$, obtained in our previous work[29,30] by block-limited calculations, were not correct and will have to be modified in the present work. For the correct determination of C−H stretch fundamental and overtone frequencies, large-scale calculations had to be carried out, encompassing all Hamiltonian terms and vibrational modes belonging to the four symmetry blocks A_{1g}, E_{2g}, B_{1u}, and E_{1u}. Before the fitting procedure employed in this case is described, some additional considerations should be mentioned. It is well-known that the C−H stretch fundamentals, due to their high frequencies (∼3000 cm^{-1}), are inevitably more or less strongly perturbed by nearby combination or overtone levels of the ring modes through higher order (mainly cubic) interactions. Since in the present work we are not taking into account any cubic or higher order nondiagonal Hamiltonian coupling terms, it is not reasonable to expect that a particularly good fit could be achieved of the calculated to the experimentally measured C−H stretch frequencies. Nevertheless, as will be seen below, we have been able to determine a set of harmonic force constant values f_{ss}, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$ for the C−H stretch system, allowing for a satisfactory reproduction of the majority of C−H (C−D) stretch fundamentals (as well as some of the lower overtone energies), which have been experimentally measured. There are several prominent exceptions of strong mismatch between calculated and experimentally observed values. Some of them can be presumably explained as strong Fermi resonances, which have not been deperturbed, or as wrongly indirectly estimated frequencies from experimentally observed combinations in the literature. To carry out the adjustment procedure, we have proceeded in the following way. First of all, we are taking into account the observation[29] that the calculated values for the $\nu_2(A_{1g})$ C−H (C−D) stretch fundamentals of all four benzene isotopomers solely depend on the value of the force constant $F_{2,2} = f_{ss} + 2(f_{1,2} + f_{1,3}) + f_{1,4}$, but not on the values of f_{ss}, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$ separately. To make use of this observation, we have set initially $f_{1,2} = f_{1,3} = f_{1,4} = 0$, $F_{2,2} = f_{ss}$, and performed large-scale calculations on the $\nu_2(A_{1g})$ fundamentals of the four benzene D_{6h} isotopomers, varying the value of $F_{2,2} = f_{ss}$, and aiming to achieve a satisfactory fit with as many as possible of the four ν_2 fundamentals experimentally measured.[8,23,40] It was found that the best fit was achieved at $F_{2,2} = 5.540$. The calculated ν_2 frequencies are displayed in Table 6, together with the relevant experimentally measured values. The fit is quite acceptable for the isotopomers C_6H_6 ($\Delta = 2.15$ cm^{-1}), C_6D_6 ($\Delta = 3.14$ cm^{-1}), and $^{13}C_6D_6$ ($\Delta = 0.3$ cm^{-1}), but very poor for $^{13}C_6H_6$ ($\Delta = 15.1$ cm^{-1}), where Δ is the difference between theoretically calculated and experimentally measured frequencies. This latter case can be attributed to strong Fermi interaction. On the basis of this fit, $F_{2,2} = 5.540$ was accepted as the correct value.

C−H (C−D) stretch vibrations in benzene are an example of well-expressed local mode behavior due to the weak interactions among different C−H bonds. For such a system it follows from LM theory that the C−H (C−D) stretch overtone energies are determined almost entirely by the values of the bond diagonal force constants f_{ss} and f_{sss}, being practically independent of the values of the small nondiagonal force constants $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$. Those latter force constants are determined only for the four fundamental C−H (C−D) stretch frequencies. Consequently, purely local C−H stretch overtone states of different symmetries (e.g., $|6;A_{1g};n_1\rangle$, $|6;E_{1u};n_1\rangle$, etc., for $n > 1$) are practically isoenergetic, while the fundamentals at $n = 1$ are not. On the other hand, the energies of E_{1u} overtone states $|6;E_{1u};n_1\rangle$ for C_6H_6 and C_6D_6 isotopomers have been measured experimentally.[31,44] Taking this into account, large-scale calculations were performed on several lower C−H (C−D) stretch overtone energies of the states $|6;E_{1u};n_1\rangle$ for both C_6H_6 and C_6D_6 isotopomers, varying the values of force constants f_{ss} and f_{sss}, and trying to obtain a reasonable fit of the calculated to the experimentally measured overtone energy levels. These large-scale calculations were carried out at $N = 50000$, which ensured good convergence of the results. The best possible fit was achieved at $f_{ss} = 5.515$ and $f_{sss} = -29.72$. The calculated first and second C−H (C−D) stretch E_{1u} overtone energies for the isotopomers C_6H_6 and C_6D_6 are displayed in Table 6 (lower rows), together with the available experimentally measured data. It is seen that the fit for the C_6H_6 overtones is particularly good, while that for C_6D_6 can hardly be called satisfactory. However, it should be taken into account that the absorption peaks for C_6D_6 overtones measured by Reddy et al.[31] are very broad, and therefore, the transition energy was determined only approximately. In fact, the estimates of Reddy et al.[31] for the lower C_6H_6 overtone transitions were also found to be rather poor approximations when the high-precision data became available.[44−46] So, the values $f_{ss} = 5.515$ and $f_{sss} = -29.72$ were accepted as the correct ones. Having so far determined the values of $F_{2,2}$ and f_{ss}, a linear relation could be derived for the three nondiagonal small force constants $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$: $F_{2,2} - f_{ss} = 0.025 = 2(f_{1,2} + f_{1,3}) + f_{1,4}$.

Next, large-scale calculations on the C−H stretch fundamentals ν_7, ν_{13}, and ν_{20} for all four benzene isotopomers were carried out, with the force constants $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$ being varied independently, however satisfying the above constraint. The aim was to achieve the best possible fit for the calculated to the experimentally measured (where available) C−H stretch fundamentals ν_7, ν_{13}, and ν_{20}. As a result of the calculations, the following values have been determined for the small nondiagonal force constants: $f_{1,2} = 0.007$, $f_{1,3} = 0.008$, $f_{1,4} = -0.005$. All obtained harmonic force constant values pertaining to the C−H stretch system are summarized in Table 5b. The C−H stretch fundamentals ν_7, ν_{13}, and ν_{20} for the four benzene isotopomers considered, calculated with this set of input force constant values (Table 5b), are displayed in Table 6. The values of experimentally measured frequencies are also displayed for comparison, where the data are available.

For the ν_{20} fundamentals (strongly IR active) the most accurate experimentally measured data exist. It is seen that the results from the calculations for the ν_{20} fundamentals are satisfactory fits for all isotopomers with the exception of $^{13}C_6H_6$ (similarly to the case of ν_2), where the calculated value deviates by as much as 10 cm^{-1} from the experimentally measured one. In the case of the ν_7 (Raman active) frequency, experimental data are available for benzene and deuteriobenzene only. The calculated value of ν_7 for C_6H_6 fits satisfactorily to the experimentally measured value, while for C_6D_6 the fit is rather poor ($\Delta = 13.1$ cm^{-1}). In the case of ν_{13}, the fundamentals have not been measured directly, but estimated for benzene and deuteriobenzene from combinations with other modes. For this fundamental, the mismatch between calculated and estimated values (for the condensed phase)[16] is seen to be particularly strong (Table 6). However, this mode is known for its extremely strong Fermi interactions with other mode combinations. Furthermore, recently Cane et al.[14] have estimated ν_7 in gas-phase C_6H_6 from another combination and have obtained the value of 3028 cm^{-1}, which practically coincides with the theoretically calculated one (Table 6).

In Table 5 all harmonic and diagonal anharmonic force constants determined in the present work have been summarized, together with a set of values obtained by other authors[8,11] for comparison. As pointed out above, the values for harmonic force constants pertaining to the C−H stretch system (f_{ss} in particular) deviate considerably from that determined in our previous work.[29] The calculated force constant values pertaining to the essentially harmonic ring modes should be regarded as very reliable, judging by the very good fit achieved between the calculated and experimentally measured fundamentals for all four benzene isotopomers. Some of these force constants however diverge considerably from the best available empirically determined set of Goodman et al.[8] In particular, some nondiagonal quadratic force constants were obtained much smaller than the previous determinations ($F_{1,2}$, $F_{6,7}$, $F_{8,9}$, $F_{12,13}$, Table 5). The presently determined set of C−H stretch quadratic force constants f_{ss}, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$ should probably be regarded as less reliable, because of the uncertainties connected with the multitude of Fermi interactions, affecting more or less strongly most of the C−H stretch fundamentals.

VI. Conclusion

In the first part of this work, it has been our aim to introduce a specific vibrational model designated for calculations on the vibrational energy levels in benzene. The first key feature of the model is its combined LM/SM character. For the description of the C−H stretch system in benzene, an LM formalism was applied (using the six local bond C−H stretch coordinates s_k), while, for the remaining non-C−H stretch vibrations, a symmetrized mode treatment based on symmetrized vibrational coordinates was applied. The model is entirely based on the Morse oscillator formalism: the local C−H stretches are regarded as six identical Morse oscillators, and some of the symmetrized ring vibrations are also considered as Morse oscillators, the remaining modes being described as harmonic oscillators. Our main reason for using such a combined model was to achieve the fastest possible convergence of the benzene potential energy expansion, i.e., the smallest possible number of higher order force constants, attaining nonnegligible values. When expanded in terms of the combined LM/SM set of coordinates, the potential function takes the following form:

$$V = \sum_{i=1}^{6}\left(\frac{1}{2}f_{ss}{s_i}^2 + \frac{1}{6}f_{sss}{s_i}^3 + ...\right) + f_{1,2}(s_1s_2 + s_2s_3 + ... + s_6s_1) + f_{1,3}(s_1s_3 + s_2s_4 + ... + s_6s_2) + f_{1,4}(s_1s_4 + s_2s_5 + s_3s_6) + \frac{1}{2}F_{1,1}{S_1}^2 + \frac{1}{6}F_{1,1,1}{S_1}^3 + F_{1.2}S_1S_2 + ... \quad (19)$$

In this representation, the only higher order force constants retained are cubic diagonal: the local one, f_{sss}, and several symmetrized ones, $F_{k,k,k}$.

The second key feature of the model is the set of complex symmetrized curvilinear vibrational coordinates used, which can be expressed as simple linear combinations of Whiffen's coordinates. The complex vibrational coordinates and wave functions (Hamiltonian eigenfunctions) for the description of vibrational motion in benzene were shown to possess interesting transformation behavior under the symmetry operations of the molecular (symmetric top) point group D_{6h}. This behavior was analyzed and classified as a CSS. CSSs can be defined for all symmetric top point groups. The description in terms of complex symmetrized coordinates and wave functions allows for the construction of a separable symmetrized infinite-dimensional vibrational basis set. Employment of such a highly symmetrized formalism (basis set and Hamiltonian representation) strongly (by more than an order of magnitude) reduces the size of the Hamiltonian matrix required for convergence of large-scale computations, as compared to the case of a nonsymmetrized treatment.

In the second part of this work, the complex symmetrized LM/SM vibrational model was applied to carry out calculations on a large number of vibrational energy levels (mainly fundamentals) of four benzene D_{6h} isotopomers: C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$. The principal aim of the calculations was to determine a reliable set of harmonic force constants for benzene. Using the determined force constant values, it has been possible to reproduce very well a large number of experimentally measured vibrational (both fundamental and overtone) energy levels of various symmetries for all four benzene D_{6h} species. It is noteworthy that this fit was obtained with a very small number of "effective" higher order force constants taken into account (Table 5c).

Thus, a major conclusion from the results obtained in this work could be that the set of harmonic force constant values obtained are very good approximations to the true harmonic force constants for benzene. It is noteworthy that a considerable number of these values are substantially different from the best available set of empirically determined values, given by Goodman et al.[8] (Table 5). Another important conclusion from the results of the present calculations is that the LM/SM model based on the combined LM/SM expansion of the potential energy (eq 19) is a very good representation.

Our work in this direction will be continued. In the first place, a complete set of symmetrized harmonic force constants for benzene will be obtained (by considering the non-C−H stretch containing blocks of vibrations, $A_{2\,g}(\nu_3)$, $B_{2\,g}(\nu_4, \nu_5)$, $E_{1\,g}(\nu_{10})$, $A_{2u}(\nu_{11})$, $B_{2u}(\nu_{14}, \nu_{15})$, $E_{2u}(\nu_{16}, \nu_{17})$, in addition to the already studied four C−H stretch containing blocks). Using them, a set of internal (valence) harmonic force constants will be calculated to check the physical feasibility of the obtained harmonic force field. Having determined a reliable set of benzene ground electronic state harmonic force constants, we shall introduce a number of nondiagonal cubic (as well as some quartic) force constants in the large-scale calculations, together with the relevant higher order kinetic Hamiltonian terms. In this way we hope to be able to achieve a better fit to the experimentally known C−H stretch fundamental frequencies as well as a realistic description of the vibrational structure and IVR in the range of the first C−H stretching overtone (at 6000 cm^{-1}), where very detailed experimental data have become available lately.[34−36]

References and Notes

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