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On the Empirical Determination of Some Harmonic and Anharmonic Force Constants in Benzene

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In this work, the problem for the quality of empirically determined harmonic force constants in ground electronic state benzene has been carefully reexamined, for the case when strongly anharmonic vibrations are involved and in particular for the A_{1g} (ν_1 and ν_2) vibrational system. A numerical procedure, based on a local bond Hamiltonian representation for the C−H stretch system and a symmetrized coordinate treatment for the ν_1(C−C) mode, has been described and applied to the determination of the harmonic $F_{1,1}$, $F_{2,2}$, and $F_{1,2}$, and some important (diagonal) anharmonic force constants, instead of the traditional *FG* analysis. As a reference data for the determination of the required force constants, the set of experimentally observed ν_1 and ν_2 fundamentals for four D_{6h} benzene species C_6H_6, C_6D_6, $^{13}C_6H_6$, and $^{13}C_6D_6$ have been employed. The harmonic force constants as well as harmonic frequencies obtained in this work have substantial deviations from previous determinations. Using the presently determined force constant values, a very good fit of the calculated to the experimentally observed frequencies has been achieved.

I. Introduction

The ground electronic state potential surface of benzene has long been established as a benchmark for empirical potential surface methods.[1−8] A great body of spectroscopic data is available for benzene as well as for the isotopically labeled species,[9−18] which has allowed us to derive a highly accurate empirical harmonic force field.[6−8] Although the empirically generated complete harmonic force field by Goodman and coworkers[6−8] is capable of reproducing very well practically all spectroscopic observables for benzene C_6H_6, still some discrepancies remain, concerning in particular the C−H stretch fundamentals and some frequencies of the same symmetry as the C−H stretches [e.g., modes no. 6, 7, 8, and 9 (of E_{2g} symmetry) and modes no. 12 and 13 (of B_{1u} symmetry), in Wilson's numbering, cf. Table 5 from ref 8]. Furthermore, still larger discrepancies occur in the vibrational frequencies of the isotopically labeled D_{6h} benzenes (C_6D_6, $^{13}C_6H_6$, and $^{13}C_6D_6$).

Ab initio methods have been widely applied to the determination of the harmonic and higher order force constants in benzene.[19−22] At the present state of the art, these methods are not suitable for determination of the harmonic force constants with spectroscopic accuracy; however, it was argued by Maslen et al.[22] that ab initio methods should be much more efficient for anharmonic force constants.

The benzene potential field can be described as a series expansion in a variety of coordinate types. Using symmetrized curvilinear (Whiffen's) coordinates S_k,[4] it takes the form

$$V = \frac{1}{2}\sum_{i,k} F_{i,k} S_i S_k + \frac{1}{6}\sum_{i,k,j} F_{i,j,k} S_i S_k S_j + ... \qquad (1)$$

Here, $F_{i,k}$ are harmonic force constants, $F_{i,k,j}$ are anharmonic cubic force constants, etc. The advantage of working in terms of symmetrized curvilinear coordinates is that the force constants $F_{i,k}$, $F_{i,k,j}$, ... are identical for all isotopic species, which sustain the symmetry of benzene (e.g., C_6H_6, C_6D_6, $^{13}C_6H_6$, and $^{13}C_6H_6$).

The harmonic force constants $F_{i,k}$ are the most important ones in expansion 1, because (i) they are the largest and determining ones and (ii) their values stay unchanged, when rectilinear symmetrized coordinates are used instead of curvilinear ones.[23] In general, the empirical determination of harmonic force constants $F_{i,k}$ is carried out for each symmetry block of vibrations separately, using as a reference data the relevant harmonic normal mode (NM) frequencies (of one or more isotopic species) ω_i, by means of the standard Wilson's *FG* analysis.[1] For example, for the A_{1g} block in benzene, consisting of the symmetrized vibrations S_1 (a C−C stretch) and S_2 (a C−H stretch), the three relevant harmonic force constants $F_{1,1}$, $F_{2,2}$, and $F_{1,2}$ can be determined, if known are the harmonic NM frequencies ω_1 and ω_2 for C_6H_6 plus one of ω_1 and ω_2 for C_6H_6.[8] The most serious problem with this approach is that the harmonic frequencies ω_1 and ω_2 are not experimentally observable, but the corresponding fundamental frequencies ν_1 and ν_2 are. Therefore, for the determination of harmonic force constants $F_{i,k}$, fundamental frequencies ν_i have usually been employed, instead of harmonic NM frequencies ω_i, assuming ν_i and ω_i are reasonably close. There are however certain strongly anharmonic vibrations (e.g., the C−H stretches) for which the anharmonic corrections $\Delta_i = \omega_i - \nu_i$ are quite large. In such cases, the *FG* analysis could yield incorrect values for $F_{i,k}$, if determined using ν_i instead of ω_i. In second-order perturbation theory (disregarding resonance effects), the anharmonic corrections Δ_i are given by the expression

$$\nu_i = \omega_i + x_{ii}(1 + d_i) + \frac{1}{2}\sum_{k \neq i} x_{ik} d_k + g_{ii} \qquad (2)$$

where x_{ii}, x_{ik}, and g_{ii} are anharmonic constants and d_i is the degeneracy. In principle, the anharmonic constants can be expressed through the cubic and quartic force constants $F_{i,k,j}$ and $F_{i,k,j,l}$, as well as terms containing G-matrix derivatives.

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Goodman et al.[8] have taken into account only the diagonal anharmonic constant x_{ii} (derived from higher C−H stretch overtone absorption spectra[24]) in calculating the anharmonic corrections Δ_i to C−H stretch fundamentals in benzene; thus, they took $\Delta_2 = 2x_{22} = 117$ cm^{-1}, and hence $\omega_2 = \nu_2 + \Delta_2 = 3191$ cm^{-1}. However, there are indications, that Δ_2 might be obtained significantly larger when nondiagonal anharmonic constants are also taken into account. Thus, Maslen et al.[22] have obtained from ab initio calculations $\Delta_2 = 138$ cm^{-1}, which leads to a very different value for ω_2.

On the other hand, it is a generally accepted idea, that the system of C−H stretch vibrations in benzene is much more conveniently and reliably described as a set of six identical, one-dimensional, strongly anharmonic, very weakly coupled to each other, local bond Morse oscillator Hamiltonians (in local coordinates s_i, $i = 1, ..., 6$), instead of symmetrized (S_2, S_{13}, S_7, and S_{20}) and NM oscillators.[24−29] In this local mode (LM) description, the basis C−H stretch vibrational functions are obtained as appropriately symmetrized linear combinations of products of six Morse oscillator eigenfunctions, belonging to one of the following symmetry types: A_{1g}, A_{2g}, B_{1u}, B_{2u}, E_{2g}, or E_{1u}. The C−H stretch basis functions of a given symmetry type will be coupled to the block of symmetrized non-C−H-stretch vibrations of the same symmetry type, to yield the experimentally observable vibrational frequencies. In particular, the C−H stretch basis functions of A_{1g} symmetry will be strongly coupled (through nondiagonal harmonic interaction terms) to the eigenstates of the totally symmetric C−C stretch oscillator S_1. The investigation of this coupling between a local mode and a symmetrized mode cannot be done analytically (as is the familiar *FG* analysis in the case of only symmetrized modes), but it must be done by numerical diagonalization of an appropriately selected Hamiltonian matrix. In general, the described approach can be classified as combined LM + SM (symmetrized mode) treatment.[28−31] Such an approach is particularly suitable for exploration of higher excited C−H stretch overtone states, their absorption spectra, and dynamics.[28−31]

It is our aim to demonstrate that this approach is very useful for the lower excited vibrational states as well. In the present work, we are studying the A_{1g} (ν_1 and ν_2) vibrational system in benzene. This work is organized as follows. In section II is outlined the theoretical LM description of the C−H stretch Hamiltonian in benzene and its symmetry adapted eigenfunctions, in particular local and nonlocal basis states of A_{1g} symmetry type. The transformation of the C−H stretch Hamiltonian from LM (s_i) to SM (S_i) coordinates is considered, and the correspondence of harmonic and anharmonic force constants in both types of representations is discussed. In section III the harmonic interaction Hamiltonian, coupling A_{1g} C−H stretch basis states to eigenstates of the S_1 mode, is considered. Next, a search procedure is outlined, for selection of an active space and derivation of the relevant Hamiltonian matrix, whose diagonalization is subsequently carried out using a Lanczos tridiagonalization routine. In section IV are presented and discussed the results from the numerical calculations, yielding the A_{1g} (ν_1 and ν_2) fundamentals of 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 ν_1 and ν_2 fundamentals to the experimentally measured frequencies (summarized in Table 1), values for the most important harmonic and anharmonic force constants, relevant to the C−H stretch vibrational system as well as to the $S_1(A_{1g})$ vibration in benzene, have been determined. It is shown, that for the correct description of the ν_2 fundamentals (at ∼3000 cm^{-1}), resonant anharmonic interactions with other benzene vibrations must also be taken into account. In section V we conclude.

TABLE 1: Experimentally Observed Fundamental Frequencies A_{1g} (ν_1 and ν_2) for D_{6h} Symmetry Benzenes (in cm^{-1}),[8,15,16] Employed as a Reference Data for Empirical Determination of the Force Constants

	C_6H_6	C_6D_6	$^{13}C_6H_6$	$^{13}C_6D_6$
ν_1	993.071	945.583	957.4	916.6
ν_2	3073.942	2303.44	3049.8	2283.9

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

The Hamiltonian of the C−H stretch vibrational system in benzene is written in the form

$$H^{CH} = H_0^{CH} + H_1^{CH},$$

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

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

where H_0^{CH} is the zeroth order Hamiltonian, consisting of six uncoupled Morse oscillators, $g_{ss} = \mathbf{1}/m_H + \mathbf{1}/m_C$ (m_H and m_C are the mass of H and C atoms, respectively), a_s is the anharmonic parameter, D_s is the dissociation energy, H_1^{CH} is the interaction Hamiltonian, and $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$ are small force constants, describing the coupling between different C−H bond oscillators. The Morse potential is expanded in powers of s:

$$D_s(1 - e^{-a_s s})^2 = D_s\left[(a_ss)^2 - (a_ss)^3 + \frac{7}{12}(a_ss)^4 - ...\right] = \frac{1}{2}f_{ss}s^2 + \frac{1}{6}f_{sss}s^3 + \frac{1}{24}f_{ssss}s^4 + ... \quad (4)$$

where f_{ss}, f_{sss}, etc. are diagonal harmonic, cubic, etc. force constants. The energy levels of a Morse oscillator are given by the formula

$$E_n = \omega_{CH}\left(n + \frac{1}{2}\right) - x_{CH}\left(n + \frac{1}{2}\right)^2 \quad (5)$$

where ω_{CH} is the harmonic frequency and x_{CH} is the anharmonic constant:

$$\omega_{CH} = \frac{1}{2\pi}\sqrt{f_{ss}g_{ss}}, \quad x_{CH} = \frac{1}{2}\omega_{CH}(a_sk_s)^2, \quad k_s = \sqrt{\hbar\sqrt{g_{ss}/f_{ss}}} \quad (6)$$

$$f_{ss} = \frac{\omega_{CH}}{k_s^{\,2}}, \quad f_{sss} = -\frac{3f_{ss}}{k_s}\sqrt{\frac{2x_{CH}}{\omega_{CH}}} = -\frac{3}{k_s^{\,3}}\sqrt{2\omega_{CH}x_{CH}} \quad (7)$$

The C−H stretch Hamiltonian H^{CH} can also be presented in terms of symmetrized coordinates instead of the local bond stretches s_i. We shall be using the complex symmetrized coordinates q_i[30] instead of Whiffen's coordinates S_i,[4] because in terms of q_i the potential field expansion to arbitrary powers of the coordinates contains only totally symmetric terms and the minimum number of independent force constants (for the C−H stretch coordinates, the relations are $q_2 = S_2$, $q_{13} = iS_{13}$, $q_{7a,b} = 1/\sqrt{2}(S_{7a} \pm iS_{7b})$, and $q_{20a,b} = 1/\sqrt{2}(S_{20a} \pm iS_{20b})$. Only those terms in the expansion of the C−H stretch potential field to fourth order are given, which contain the A_{1g} coordinate q_2:

$$\mathrm{V} = q_2^{\,2}\left(\frac{1}{2}f_{ss} + f_{1,2} + f_{1,3} + \frac{1}{2}f_{1,4}\right) + q_2^{\,3}\frac{f_{sss}}{6\sqrt{6}} + q_2 q_{20a} q_{20b}\frac{f_{sss}}{\sqrt{6}} + q_2 q_{13}^{\,2}\frac{f_{sss}}{2\sqrt{6}} + q_2 q_{7a} q_{7b}\frac{f_{sss}}{\sqrt{6}} + q_2^{\,4}\frac{f_{ssss}}{144} - q_2(q_{7a}q_{20a}^{\,2} + q_{7b}q_{20b}^{\,2})\frac{f_{ssss}}{12} + q_2^{\,2}q_{20a}q_{20b}\frac{f_{ssss}}{12} + q_2^{\,2}q_{7a}q_{7b}\frac{f_{ssss}}{12} - q_2 q_{13}(q_{7a}q_{20b} + q_{7b}q_{20a})\frac{f_{ssss}}{6} - q_2(q_{7a}^{\,3} + q_{7b}^{\,3})\frac{f_{ssss}}{36} + q_2^{\,2}q_{13}^{\,2}\frac{f_{ssss}}{24} + \ldots \quad (8)$$

Hence, the relevant symmetrized force constants are: $F_{2,2} = f_{ss} + 2f_{1,2} + 2f_{1,3} + f_{1,4}$, $F_{2,2,2} = f_{sss}/\sqrt{6}$, $F_{2,7,7} = F_{2,20,20} = f_{sss}/\sqrt{6}$, $F_{2,2,2,2} = f_{ssss}/\sqrt{6}$, $F_{2,13,7,20} = -f_{ssss}/\sqrt{6}$, etc. From this expansion in symmetrized coordinates, it is obvious that, although the small quadratic nondiagonal coupling terms have disappeared, nondiagonal cubic, quartic, etc. force constants arise, which are as large as the relevant diagonal anharmonic constants $F_{2,2,2}$, $F_{2,2,2,2}$, ... These latter constants are however much smaller than the diagonal force constants for a local bond oscillator, f_{sss}, f_{ssss}, etc. (This observation holds for the other symmetrized C−H stretches q_{13}, $q_{7a,b}$, and $q_{20a,b}$ as well). Hence, the symmetrized C−H stretch modes are more weakly diagonally anharmonic but strongly anharmonically coupled to each other, whereas the local bond oscillators are more strongly diagonally anharmonic, however, practically uncoupled to each other. This is why the C−H stretch vibrations in benzene are more satisfactorily described as local bond oscillators than as symmetrized (and normal) modes.

The eigenfunctions of H_0^{CH} are products of six Morse oscillator eigenfunctions $|n_i\rangle$: $\prod_{i=1}^{6}|n_i\rangle_i$, with their energy being given by

$$E = \sum_{i=1}^{6}\left[\omega_{\mathrm{CH}}\left(n_i + \frac{1}{2}\right) - x_{\mathrm{CH}}\left(n_i + \frac{1}{2}\right)^2\right] \quad (9)$$

For example, $|2\rangle_1|1\rangle_3$ is an eigenstate which has two excitation quanta in bond oscillator number 1 and one quantum in oscillator number 3, whereas oscillators 2, 4, 5, and 6 have zero excitation quanta and have (for compactness) been excluded from the notation. A state $|n\rangle_i$ is of purely local type, because only one bond oscillator is excited, whereas 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 is said to belong to the $n = \sum_{i=1}^{6} n_i$ overtone system. To obtain the symmetry adapted eigenstates of H_0^{CH}, appropriate linear combinations of the product states $\varphi = \sum_{k=0}^{5} C_k \prod_{i=1}^{6}|n_{\mathrm{i}}\rangle_{i+k}$ must be taken,[25−27] which can have one of the following symmetry types: A_{1g}, A_{2g}, B_{1u}, B_{2u}, E_{2g}, or E_{1u}. It is not an easy task to generate the symmetrized eigenstates of all symmetry types for arbitrary overtone manifolds n. So far, we have been able to design an algorithm generating the states of A_{1g} symmetry only, which are required for investigation of the A_{1g} (ν_1 and ν_2) vibrational system in benzene. Some of the lower excited A_{1g} eigenstates of local and nonlocal character are as follows. Overtone manifold $n = 0$ consists of one A_{1g} state $\varphi^{(0)} = \sum_{i=0}^{6}|0\rangle_i$, at energy $E_0 = 3(\omega_{\mathrm{CH}} - x_{\mathrm{CH}}/2)$. Overtone manifold $n = 1$ contains six states, one of them is of A_{1g} symmetry, $\varphi^{(1)} = 1/\sqrt{6}(|1\rangle_1 + |1\rangle_2 + ... + |1\rangle_6)$, at energy $E_1 = 4(\omega_{\mathrm{CH}} - 7x_{\mathrm{CH}})/2$. Overtone manifold $n = 2$ contains 21 states, four of them are of A_{1g} symmetry: one purely local state, $\varphi_0^{(2)} = 1/\sqrt{6}(|2\rangle_1 + |2\rangle_2 + ... + |2\rangle_6)$ at energy $E_2 = 5(\omega_{\mathrm{CH}} - 3x_{\mathrm{CH}}/2)$ and three nonlocal states at energy $E_{1+1} = 5\omega_{\mathrm{CH}} - 13x_{\mathrm{CH}}/2$: $\varphi_1^{(2)} = 1/\sqrt{6}(|1\rangle_1|1\rangle_2 + |1\rangle_2|1\rangle_3 + ... + |1\rangle_6|1\rangle_1)$, $\varphi_2^{(2)} = 1/\sqrt{6}(|1\rangle_1|1\rangle_3 + |1\rangle_2|1\rangle_4 + ... + |1\rangle_6|1\rangle_2)$, and $\varphi_3^{(2)} = 1/\sqrt{3}(|1\rangle_1|1\rangle_4 + |1\rangle_2|1\rangle_5 + |1\rangle_3|1\rangle_6)$, etc.

Both the local and nonlocal A_{1g} eigenstates of the C−H stretch system, described above, are coupled strongly (harmonically) to the eigenstates of the A_{1g} C−C stretch vibration S_1 in benzene. This vibration is described by a Morse oscillator Hamiltonian in terms of the symmetry coordinate S_1:

$$H^{\mathrm{CC}} = \frac{\hbar^2}{2}g_{\mathrm{CC}}\frac{\partial^2}{\partial S_1^{\,2}} + D_{\mathrm{C}}(1 - \mathrm{e}^{-a_{\mathrm{c}}s_1})^2,$$

$$D_C(1 - \mathrm{e}^{-a_{\mathrm{c}}s_1})^2 = \frac{1}{2}F_{1,1}S_1^{\,2} + \frac{1}{6}F_{1,1,1}S_1^{\,3} + \ldots \quad (10)$$

where

$$g_{\mathrm{CC}} = 1/m_{\mathrm{c}}; \quad E_m = \omega_1^s\left(m + \frac{1}{2}\right) - x_1\left(m + \frac{1}{2}\right)^2 \quad (11)$$

energy of overtone levels in the S_1 vibration, whose harmonic frequency ω_1^s and anharmonic constant x_1 are expressed through the force constants $F_{1,1}$ and $F_{1,1,1}$ (using formulas analogous to 6 and 7). S_1 is however much more weakly anharmonic ($x_1/\omega_1^s \approx 0.001$) than the local bond C−H oscillator ($x_{\mathrm{CH}}/\omega_{\mathrm{CH}} \approx 0.015$).

The basis states for the description of the considered vibrational system A_{1g} (ν_1 and ν_2), consisting of the A_{1g} C−H stretch eigenstates $\varphi_i^{(n)}$ and the eigenstates $|m\rangle$ of the S_1 Hamiltonian (eq 10), are obtained as products: $\psi = \varphi_i^{(n)}|m\rangle = |\varphi_i^{(n)},m\rangle$. The energy of such a basis state is given by

$$E_\psi = \sum_{i=1}^{6}\left[\omega_{\mathrm{CH}}\left(n_i + \frac{1}{2}\right) - x_{\mathrm{CH}}\left(n_i + \frac{1}{2}\right)^2\right] + \omega_1^s\left(m + \frac{1}{2}\right) - x_1\left(m + \frac{1}{2}\right)^2 \quad (12)$$

III. Interaction Hamiltonian and Hamiltonian Matrix Manipulation

The eigenstates $|\varphi_i^{(n)},m\rangle$ are coupled to each other through a quadratic interaction Hamiltonian:

$$H^{1,2} = -\hbar^2 G_{1,2}\frac{\partial^2}{\partial S_1\,\partial S_2} + F_{1,2}S_1S_2 = -\hbar^2 G_{1,2}\frac{1}{\sqrt{6}}\frac{\partial}{\partial S_1}\sum_{k=1}^{6}\frac{\partial}{\partial s_k} + F_{1,2}S_1\frac{1}{\sqrt{6}}\sum_{k=1}^{6}s_k \quad (13)$$

where $F_{1,2}$ is a nondiagonal harmonic force constant and $G_{1,2} = -1/m_c$ is a kinetic coupling constant. In calculating the matrix elements $\langle\varphi_k^{(l)}, r|H^{1,2}|\varphi_i^{(n)},m\rangle$, the integrals in s_k are calculated using Morse oscillator formalism:

$${}_k\left\langle n+1\middle|\frac{\partial}{\partial s_k'}\middle|n\right\rangle_k = \sqrt{\frac{n+1}{2}}\sqrt{\frac{(R-2n-2)^2-1}{R(R-n-1)}} = -{}_k\left\langle n\middle|\frac{\partial}{\partial s_k'}\middle|n+1\right\rangle_k \quad (14)$$

$${}_k\langle n+1|s_k'|n\rangle_k = \frac{R}{R+2n-2}\,{}_k\left\langle n+1\middle|\frac{\partial}{\partial s_k'}\middle|n\right\rangle_k = {}_k\langle n|s_k'|n+1\rangle_k$$

where $s'_k = k_s s_k$ is a dimensionless coordinate and $R = \omega_{CH}/x_{CH}$, whereas the integrals in S_1 are the simpler harmonic oscillator expressions (obtained from (14) at $R \rightarrow \infty$).

Besides $H^{1,2}$, there is also a second (weak) interaction Hamiltonian H_1^{CH} (eq 3), which is responsible for couplings only among the eigenstates of the C−H stretch system. The magnitude of these coupling terms is determined by the small force constants $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$.

Thus, the C−H stretch system is characterized by force constants f_{ss}, f_{sss}, $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$, the S_1 vibration is characterized by $F_{1,1}$ and $F_{1,1,1}$, and the coupling between both is characterized by $F_{1,2}$. For a calculation on the eigenstates of the resulting A_{1g} (ν_1 and ν_2) vibrational system to be performed, values must be ascribed to each of these eight force constant parameters. The following G-matrix elements are also required for the calculation, whose values vary according to the isotopomer considered: $g_{ss} = 1/m_H + 1/m_C$, $g_{CC} = 1/m_C$, and $g_{1,2} = -1/m_C$.

Having defined the basis states and coupling matrix elements, a search procedure has been designed for selecting an active space (AS) from the infinite manifold of available basis states and setting up of the Hamiltonian matrix. Starting with an appropriately chosen initial basis state $|\varphi_i^{(n)},m\rangle$, the algorithm proceeds to select all basis states coupled to this state through matrix elements of the interaction Hamiltonian ($H^{int} = H^{1,2} + H_1^{CH}$); next, each of these initially selected states is explored, and more basis states are selected, which are coupled to it by H^{int}; this procedure is carried on until a sufficiently large and representative AS of dimensionality N has been selected. Simultaneously, the Hamiltonian matrix $H_{n,k}$ is obtained, which consists of the basis state energies E_ψ (eq 12) as diagonal elements and the relevant coupling matrix elements $\langle\varphi_k^{(l)},r|H^{int}|\varphi_i^{(n)},m\rangle$ as nondiagonal elements. The dimensionality N of the selected AS can be varied, by varying the values of several parameters of the search, as described previously.[30,31] (A typical value sufficient for obtaining convergence in our calculations was $N \approx 300$.) To obtain the eigenvalues of the studied vibrational system, the selected Hamiltonian matrix was diagonalized numerically, using a Lanczos tridiagonalization procedure.[32,33] These eigenvalues can then be compared to experimentally observable fundamental frequencies and overtone and combination level energies.

IV. Results and Discussion

The set of experimentally measured ν_1 and ν_2 fundamentals for all four D_{6h} benzene species C_6H_6, C_6D_6, $^{13}C_6H_6$, and $^{13}C_6D_6$,[8,15,16] which have been employed as a reference data in the calculations, are summarized in Table 1. A correspondence can easily be established between the eigenstates obtained as a result of the diagonalization and the basis states, described above. In the first place, it was found that the energy E'_n of eigenstates, corresponding to purely local C−H stretch states $|n\rangle_i$, could be fairly well described by the energy E'_n, calculated according to the formula

$$E''_n = (\omega'_{CH} - x'_{CH})n - x'_{CH}n^2 \tag{15}$$

for suitable values of the parameters ω'_{CH} and x'_{CH}. It is noteworthy that the derived value of ω'_{CH} was very different from the input harmonic frequency ω_{CH} (eqs 5 and 6; to be discussed later) but the anharmonic constant x'_{CH} was practically identical to the input anharmonic constant, i.e., $x'_{CH} \approx x_{CH}$. Because it is expected that the same anharmonic constant value x'_{CH} should hold for the C−H stretch overtones of E_{1u} symmetry (IR active) which have been measured experimentally,[24] we have fixed the input anharmonic constant at $x_{CH} = x'_{CH} = 58.6$ (in accord with Goodman et al.[8]). From this value for x_{CH} and the input value for the harmonic force constant f_{ss}, the value of f_{sss} was determined, using formulas 6 and 7.

TABLE 2: Calculated A_{1g} Fundamental Frequencies ν_1 and ν_2 (in cm^{-1}) for D_{6h} Symmetry Benzenes[a]

	C_6H_6	C_6D_6	$^{13}C_6H_6$	$^{13}C_6D_6$
ν_1	993.087	945.476	957.55	915.48
ν_2	3050.346	2304.79	3039.41	2286.69

[a] Fermi resonance interactions of the 2^1 state with 19^2 and 3^2 are not taken into account.

The progression in the ν_1 mode, corresponding to purely S_1 vibrational overtone states $|m\rangle$, is very clearly discernible in the calculated eigenvalue spectrum, with anharmonic constant $x'_1 \approx x_1$. This anharmonic constant is however very well-known from experimentally observed long progressions in the ν_1 mode in benzene, as $x'_1 = 0.65$.[18] Thus, analogously to the above, the value for $F_{1,1,1}$ could be determined from $x_1 = x'_1 = 0.65$ and the input $F_{1,1}$ value. In this way, the number of independently variable input force constant parameters could be reduced by two: f_{sss} and $F_{1,1,1}$.

The ν_1 fundamentals (at about 1000 cm^{-1}) are sufficiently low in energy and therefore not likely to be perturbed by resonances with other vibrational levels, whereas in the case of the ν_2 fundamentals (at ~3000 cm^{-1}), Fermi resonance interactions with combinations or overtones of vibrations, external to the considered A_{1g} (ν_1 and ν_2) system, might incur a considerable shift in their original position. Therefore, it was our first aim in the calculations to reproduce correctly the experimentally measured fundamental frequencies ν_1 for all four isotopomers (summarized in Table 1) by adjusting the values for the remaining freely variable six force constants: f_{ss}, $f_{1,2}$, $f_{1,3}$, $f_{1,4}$, $F_{1,1}$, and $F_{1,2}$. For this reason, the effect of small variations in the input values of each one of the parameters f_{ss}, $f_{1,2}$, $f_{1,3}$, $f_{1,4}$, $F_{1,1}$, and $F_{1,2}$ on the four pairs of calculated (ν_1 and ν_2) values had to be examined. As a rule, each parameter was found to have a specific effect on each one of the eight ν_1 and ν_2 values, different from that of the other parameters; furthermore, the ν_1 and ν_2 frequencies for the pair of species C_6H_6 and $^{13}C_6H_6$ were affected in an almost identical manner, different from that for the other pair C_6D_6 and $^{13}C_6D_6$. For example, an increase of $F_{1,2}$ by 0.01 produced an increase of ν_1 by 0.14 and a decrease of ν_2 by 0.46, for C_6H_6 and $^{13}C_6H_6$, and an increase of ν_1 by 0.28 and a decrease of ν_2 by 0.67, for C_6D_6 and $^{13}C_6D_6$, etc. Variations in the three small force constants $f_{1,2}$, $f_{1,3}$, and $f_{1,4}$, however, did not have independent significance; they could be varied with respect to each other, without changing the resultant ν_1 and ν_2 values, as long as the magnitude of the linear combination $2(f_{1,2} + f_{1,3}) + f_{1,4}$ was preserved. In this way, the number of independently variable parameters could be reduced by two more. By suitable adjustment of the parameters f_{ss}, $F_{1,1}$, $F_{1,2}$, and $2(f_{1,2} + f_{1,3}) + f_{1,4}$, it has been possible to achieve an almost perfect fit of the calculated to the experimentally measured ν_1 fundamentals for all four D_{6h} benzene species C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$. The set of calculated ν_1 and ν_2 values are displayed in Table 2. This fit was obtained with following values of the force constant parameters (in mdyn and A): $f_{ss} = 5.580$, $F_{1,1} = 7.645$, $F_{1,2} = 0.030$, $f_{sss} = -30.070$, $F_{1,1,1} = -16.758$, $f_{1,2} = 0.012$, $f_{1,3} = 0.004$, $f_{1,4} = -0.002$, $[2(f_{1,2} + f_{1,2}) + f_{1,4} = 0.030]$. We note that this set of force constant values is unique, i.e., neither of them can be varied substantially without deteriorating the obtained best fit to the four ν_1 frequencies. The discussion of the obtained force constant values will be deferred until a little later.

TABLE 3: Calculated A_{1g} Fundamental Frequencies ν_1 and ν_2 (in cm^{-1}) for D_{6h} Symmetry Benzenes, Taking into Account Fermi Resonance Interactions of the ν_2 Fundamental and Corresponding to the Best Fit Values for the Force Constant Parameters (in mdyn and A): $f_{ss} = 5.580$, $F_{1,1} = 7.645$, $F_{1,2} = 0.030$, $f_{sss} = -30.070$, $F_{1,1,1} = -16.758$, $f_{1,2} = 0.012$, $f_{1,3} = 0.004$, $f_{1,4} = -0.002$, $[2(f_{1,2} + f_{1,3}) + f_{1,4} = 0.030]$

	C_6H_6	C_6D_6	$^{13}C_6H_6$	$^{13}C_6D_6$
ν_1	993.078	945.47	957.55	915.47
ν_2	3073.96	2305.13	3052.08	2286.91

From Table 2, it is seen that, although all four ν_1 fundamentals are satisfactorily reproduced, the ν_2 values are quite far from their experimentally measured positions, in particular for the two H-isotopomers C_6H_6 and $^{13}C_6H_6$. Hence, it is expected that the ν_2 fundamentals for the H isotopomers are affected by strong Fermi resonance with overtone states of other benzene vibrations, outside the A_{1g} (ν_1 and ν_2) system. Obviously, these vibrations will also have to be taken into account in order to obtain realistic results for the four ν_2 fundamentals.

In this connection, we note that, in terms of curvilinear (symmetrized) coordinates, cubic kinetic interactions (first derivatives of G-matrix elements) are expected to prevail over cubic potential terms. On the other hand, G-matrix derivatives can be calculated exactly, whereas anharmonic force constants are practically unknown. Therefore, in the following estimations, only kinetic interaction terms have been taken into account, completely disregarding potential couplings. Calculations on G-matrix derivatives in benzene (which have been described in considerable detail previously[30]) show that the C−H stretch fundamental ν_2 is coupled most strongly kinetically (by terms $\sim 1/m_H$) to the overtone states k^2 (at energy $2\omega_k^s$) of the symmetrized vibrations S_3, S_9, S_{15}, and S_{18} (of C−H in-plane wagging type). (The frequency ω_k^s of a symmetrized vibration S_K, can be calculated by means of f-la 6, using the values of $G_{k,k}$[1] and $F_{k,k}$.[8]*) Of them. only* $S_3(A_{2g})$ and $S_{18}(E_{1u})$ have frequencies ($\omega_3^s = 1347$ cm^{-1} and $\omega_{18}^s = 1388$ cm^{-1}) whose first overtones are reasonably close to ν_2. Considering first the S_{18} case, the leading cubic kinetic interaction term, coupling 2^1 (ν_2) to 18^2 ($2\omega_{18}^s$), is obtained as

$$T_{2/18,18} = -\frac{4\hbar^2}{s_0}\left(\frac{1}{m_H} + \frac{1}{m_C}\right) S_2 \left(\frac{\partial^2}{\partial {S_{18a}}^2} + \frac{\partial^2}{\partial {S_{18b}}^2}\right)$$

where s_0 is the equilibrium C−H bond length. However, S_{18} is coupled strongly (through harmonic kinetic and potential terms) to two other E_{1u} modes: the S_{19} vibration ($\omega_{19}^s = 1244$ cm^{-1}) and S_{20} ($\omega_{20}^s \sim 3000$ cm^{-1}), the latter one belonging to the C−H stretch system.[1] In fact, S_{18} and S_{19} are coupled more strongly to each other and less strongly to S_{20}, because the frequencies ω_{18}^s and ω_{19}^s are rather close to each other but much smaller than ω_{20}^s. To take into account the coupling between S_{18} and S_{19}, which leads to substantial frequency shifts, partial normalization of the vibrations S_{18} and S_{19} has been carried out, using conventional *FG* analysis (and the relevant values of $G_{18,19}$[1] and $f_{18,19} = 0.209$ [8]). In this way, the NM frequencies $\omega_{18} = 1052$ cm^{-1} and $\omega_{19} = 1500$ cm^{-1} (for benzene C_6H_6) were obtained, as well as the relevant (curvilinear) NM coordinates: $Q_{18} = a_{18,18}S_{18} + a_{18,19}S_{19}$ and $Q_{19} = a_{19,18}S_{18} + a_{19,19}S_{19}$. It is seen that these partially normalized frequencies are reasonably close to the experimentally measured NM frequencies.[8,10,11] However, an inconsistency in the choice of the S_{18} and S_{19} symmetrized coordinates by Whiffen[4] seems to have occurred. Indeed, the S_{18} vibration (of C−H wagging character) has higher frequency ω_{18}^s than the frequency ω_{19}^s of the S_{19} (C−C stretching) vibration. Upon normalization, the S_{18} vibration is transformed into the NM Q_{19} (of prevailing C−H wagging character), whose frequency ω_{19} is higher than ω_{18} (NM Q_{18}, predominantly C−C stretching). Therefore, it would be more suitable to interchange Whiffen's notation of the symmetrized coordinates S_{18} and S_{19}. Now, the first overtone 19^2 of the NM Q_{19} ($2\omega_{19} = 3000$ cm^{-1}) is seen to be quite close to ν_2. The kinetic term coupling the states 2^1 and 19^2, attains the form

$$T_{2/19,19} = -\frac{4\hbar^2}{s_0}\left(\frac{1}{m_H} + \frac{1}{m_C}\right) (a_{19,18})^2 S_2 \left(\frac{\partial^2}{\partial {Q_{19a}}^2} + \frac{\partial^2}{\partial {Q_{19b}}^2}\right)$$

Analysis of the relative positions of the 2^1 and 19^2 states and the magnitude of the matrix element $\langle 2^1|T_{2/19,19}|\mathbf{19}^2\rangle$ in all four isotopic species shows that, in both C_6H_6 and $^{13}C_6H_6$, the 19^2 state is located energetically very close below 2^1 and strongly coupled to it as $\sim 1/m_H$, whereas in C_6D_6 and $^{13}C_6D_6$, it was located far above 2^1 and coupled less strongly, as $\sim 1/m_D$ (m_D is mass of the deuterium atom). Hence, the state 19^2 is expected to shift the ν_2 fundamental in C_6H_6 and $^{13}C_6H_6$ to higher frequencies and practically leave unchanged the C_6D_6 and $^{13}C_6D_6$ isotopomers, which is the required behavior (cf. the data for ν_2 in Tables 1 and 2). The (kinetic) coupling of the 3^2 state (at energy $2\omega_3^s$) to ν_2 was also taken into account by means of a procedure, analogous to the above-described; this case is even simpler because S_3 is the only vibration of A_{2g} symmetry in benzene.

Calculations were performed on all four benzene isotopomers with the states 3^2 and 19^2 and their coupling matrix elements to ν_2, included in the Hamiltonian matrix. The results from the calculation of the entire set of fundamentals ν_1 and ν_2 for the four D_{6h} benzene species C_6H_6, C_6D_6, $^{13}C_6H_6$, $^{13}C_6D_6$ are displayed in Table 3. From a comparison of the values of Tables 3 and 1, it is seen that the agreement between calculated ν_1 and ν_2 values with experimentally measured fundamentals for all four D_{6h} benzene isotopomers is particularly good, in fact much better than previously achieved.[8] The fit is obtained at the following values of the harmonic and anharmonic force constants (in mdyn and A): $f_{ss} = 5.580$, $F_{1,1} = 7.645$, $F_{1,2} = 0.030$, $f_{sss} = -30.070$, $F_{1,1,1} = -16.758$, $f_{1,2} = 0.012$, $f_{1,3} = 0.004$, $f_{1,4} = -0.002$, $F_{2,2} = f_{ss} + 2(f_{1,2} + f_{1,3}) + f_{1,4} = 5.610$. It is noteworthy, that the determined harmonic force constant values show considerable deviations from the previous highest precision empirical determinations.[8] Indeed, the diagonal force constants f_{ss}, $F_{1,1}$, and $F_{2,2}$ determined in this work are substantially larger than the best estimates, obtained using *FG* analysis ($f_{ss} = 5.547$, $F_{1,1} = 7.616$, and $F_{2,2} = 5.554$; ref 8). Most interesting is, however, the behavior of the nondiagonal force constant ($F_{1,2} = 0.157$; ref 8), which is reduced to a very small value $F_{1,2} = 0.030$, according to the present determination. It is noteworthy that this small value for $F_{1,2}$ is in line with Whiffen's constraint of all C−H stretching and other-vibration potential interactions to zero.[4] Hence, the interaction of the A_{1g} C−H stretching vibrational system with the S_1(C−C) mode seems to be almost entirely kinetic, through the $G_{1,2}$ term (eq 13). The values of diagonal anharmonic cubic force constants $f_{sss} = -30.070$ and $F_{1,1,1} = -16.758$ obtained here are about 10% smaller than the ab initio determined values by Maslen et al.[22] of -34.289 and -18.289, respectively.

From the determined harmonic force constant values, harmonic frequencies can readily be calculated for all four isotopomers: the local bond Morse oscillator frequency ω_{CH} is

TABLE 4: Calculated Harmonic Frequencies ω_{CH}, ω_1, and ω_2 (See Text) for D_{6h} Symmetry Benzenes (in cm^{-1})

	C_6H_6	C_6D_6	$^{13}C_6H_6$	$^{13}C_6D_6$
ω_1	994.23	947.22	958.87	917.02
ω_2	3213.19	2386.72	3201.73	2368.29
ω_{CH}	3191.76	2343.46	3181.21	2330.43

TABLE 5: Energy E'_n of Eigenstates, Corresponding to Purely Local C−H Stretch States $|n\rangle_i$ (of A_{1g} Symmetry Type) vs *n*, Obtained from Diagonalization of the Hamiltonian Matrix and Energy E''_n vs *n*, Calculated Using the Approximate Formula 15, at the Following Values of the Parameters: $\omega'_{CH} = 3137.5$ and $x'_{CH} = 58.5$ (E'_n, E''_n, ω'_{CH}, and x'_{CH} in cm^{-1})

n	E'_n	E''_n
1	3050.0	3020.5
2	5920.4	5924.0
3	8708.0	8710.5
4	11378.7	11380.0
5	13931.3	13932.5
6	16367.8	16368.0
7	18686.8	18686.5
8	20889.6	20888.0
9	22975.2	22972.5

obtained using the f_{ss} and g_{ss} values and f-la 6 and the NM frequencies ω_1 and ω_2 are obtained by means of *FG* analysis, using the quantities $F_{1,1}$, $F_{2,2}$, $F_{1,2}$, $G_{1,1}$, $G_{2,2}$ and $G_{1,2}$. The values obtained for the harmonic frequencies of all four molecules are displayed in Table 4.

From Table 4, it is seen that the ω_2 values determined in this work considerably exceed those derived by Goodman et al.[8] This is easily understood, because Goodman et al.[8] used only diagonal anharmonic constant contributions to the anharmonic corrections. The ω_1 values in both works are however in better accord. On the other hand, the presently determined values of ω_2 (C_6H_6) = 3213 cm^{-1} and ω_2 (C_6D_6) = 2387 cm^{-1} for benzene and deuteriobenzene are rather close to the values ω_{est} (C_6D_6) = 3208 cm^{-1} and ω_{est} (C_6D_6) = 2381 cm^{-1}, respectively, estimated in ref 22 in the following manner: the anharmonic correction Δ_2 calculated using ab initio anharmonic force constants was summed with the experimentally observed fundamental ν_2.

Results on the energy E'_n of eigenstates, corresponding to purely local C−H stretch states $|n\rangle_i$ in benzene, calculated using the set of force constants determined above, are summarized in Table 5 (second column). As pointed out above, the energy levels E'_n are satisfactorily described by the values E''_n calculated using formula 15. It has been found that the best overlap is obtained at following values of the parameters involved in f-la 15: $\omega'_{CH} = 3137.5$ and $x'_{CH} = 58.5$ (in cm^{-1}). The results from the calculations using f-la 15 (E''_n) are displayed in the third column of Table 5. As already discussed, the anharmonic correction x'_{CH} for the observed energy levels, practically coincides with the value x_{CH}, characterizing the input local bond Morse oscillator. It is interesting to note, however, that the obtained value of $\omega'_{CH} = 3137.5$ cm^{-1} is very far from both the local bond Morse oscillator harmonic frequency, $\omega_{CH} = 3191.8$ cm^{-1}, as well as the NM Q_2 harmonic frequency, $\omega_2 = 3213$ cm^{-1}, and cannot therefore be used, if experimentally observed, to make any conclusions about their magnitude.

V. Conclusion

The present work deals with the accurate determination of some harmonic and anharmonic force constants in benzene from the experimentally observed fundamental vibrational frequencies. The method of determination is not based on the traditional (analytical) *FG* analysis in terms of symmetrized vibrational coordinates S_K[1] (which is unreliable when strongly anharmonic modes are involved) but on a LM Hamiltonian and symmetrized eigenfunction representation (in terms of local bond coordinates s_K) of the C−H vibrational subsystem in benzene. This approach is most suitable for treatment of the strong diagonal anharmonizm of the C−H stretches, but requires numerical procedures for its implementation. In the present work, the A_{1g} (ν_1 and ν_2) vibrational system in benzene has been the object of investigation. The harmonic and some anharmonic force constants, associated with this system, have been determined from a fit of the calculated to the experimentally measured fundamentals ν_1 and ν_2 of four D_{6h} benzene isotopomers: C_6H_6, C_6D_6, $^{13}C_6H_6$, and $^{13}C_6D_6$. Some additional experimentally obtained data on the anharmonic characteristics of the ν_1 and ν_2 modes have also been taken into account. In particular, a good fit for the ν_2 fundamentals in C_6H_6 and $^{13}C_6H_6$ could not be achieved before a Fermi resonance interaction with the overtone states of another vibration was also included in the calculation. The result is a very good fit of the calculated to the experimentally measured ν_1, ν_2 fundamentals for all 4 D_{6h} benzene isotopic species. The harmonic force constant values, determined from this fit, show significant deviation from the previously obtained highly accurate force field of Goodman et al.:[8] the diagonal force constants are increased by about 0.04 ($F_{1,1} = 7.645$ and $F_{2,2} = 5.610$), whereas the nondiagonal force constant is dramatically reduced by 0.127 ($F_{1,2} = 0.030$). Such large corrections to the harmonic force constants should be expected to be of crucial importance for the reliable knowledge of the force field in a molecule like benzene, taking into account an overall conclusion by Goodman et al.[8] that “for prediction of frequencies to the 1−2 cm^{-1} vibrational resolution level required by spectroscopists to secure band assignments, it is necessary to have a force field in which the force constants are known, in general, to 0.01 mdyn/A”.

In forthcoming work, the studies on the precise determination of ground electronic state benzene harmonic force constants for vibrational modes of the other symmetries besides A_{1g} will be carried on. For this purpose, the algorithm for description of symmetrized local bond (of both local and nonlocal type) C−H stretch eigenfunctions of all possible symmetry types (A_{1g}, A_{2g}, B_{1u}, B_{2u}, E_{2g}, and E_{1u}) will be developed in due detail, complementing the previously employed formalism,[30,31] which was restricted only to the purely local C−H stertching states. The non-C−H stretching vibrations (which are less strongly anharmonic) will be treated as nonlocal symmetrized modes S_K. Using this combined LM + SM approach, it will be our aim to obtain high precision values for all of the harmonic and the key anharmonic benzene force constants. We hope that using these values for the force constants and employing our nonperturbative algorithm could allow the detailed investigation of the benzene vibrational structure and IVR in the range of the first C−H stretching overtone (at 6000 cm^{-1}), where the conventional spectral analysis, based on perturbation theory does not yield satisfactory results,[22] because of the plethora of resonances, but where very detailed experimental data have been obtained lately.[34−36]

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