

## Empirical Determination of the Harmonic Force Constants in Benzene. 4. The Fermi Resonances

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In this article, we present a continuation of our work on the refinement of the harmonic force constants  $F_{i,k}$  in benzene (in symmetrized Whiffen's coordinates) and on a growing number of higher order (anharmonic) force constants,  $F_{i,j,k}$  and  $F_{i,j,k,l}$ , that are of importance for the benzene isotopomer invariant potential energy surface. The refined set of harmonic and anharmonic force constants improves the agreement between the experimental levels and those calculated theoretically. The emphasis of the present work is on the analysis of the two notable Fermi resonances in benzene ( $\nu_8 + n\nu_1 \leftrightarrow (n+1)\nu_1 + \nu_6$ , where  $n = 0, 1, \dots, m$ , and  $\nu_{20} \leftrightarrow \nu_8 + \nu_{19} \leftrightarrow \nu_1 + \nu_6 + \nu_{19}$ ). For this purpose, we have further extended our fully dimensional, fully symmetrized, and nonperturbative vibrational procedure to the vibrational structure of the benzene isotopic species with  $D_{6h}$  symmetry.

### I. Introduction

The ground electronic state potential energy surface (PES) of benzene has been established as a benchmark potential surface for the evaluation of molecular vibrational models.<sup>1–37</sup> For the fundamental frequencies of benzene and some of its isotopomers, a sizable body of experimental spectroscopic data is now available in the literature.<sup>16–37</sup> For a semirigid molecule such as benzene, the PES can be safely presented in the form of a Taylor series expansion in terms of a chosen set of vibrational coordinates.<sup>1</sup> This expansion is particularly useful when geometrical (symmetrized, Whiffen's<sup>1,4</sup>) coordinates  $S_k$  are employed instead of mass-weighted normal coordinates, as the PES expression (expansion coefficients, i.e., force constants  $F_{i,k}$ ,  $F_{i,j,k}$ , etc.) is independent of isotopic substitution:

$$U = 1/2 \sum_{i,k} F_{i,k} S_i S_k + 1/6 \sum_{i,k,j} F_{i,j,k} S_i S_k S_j + \dots \quad (1)$$

The exact shape of the benzene ground state PES, in isotopically invariant form, is required, for example, for assessment of the radiationless  $T_1 \rightarrow S_0$  (ISC) rate constant in  $C_6H_6$  and  $C_6D_6$ .<sup>38–41</sup> This surface has been the target of extensive analytical research, from the standpoint of various empirical, semiempirical, as well as ab initio calculations.<sup>1–16</sup> Of central importance is the reliable determination of the harmonic force constants  $F_{i,k}$ ,<sup>1–13,15</sup> whose values are needed for the correct overall description of the energy hypersurface.

Ab initio<sup>13</sup> as well as semiempirical (density functional)<sup>12,15,16</sup> theoretical methods are as yet inferior for empirical determina-

tions<sup>8</sup> for the assessment of the harmonic force constants in a molecule the size of benzene. In fact, all sets of theoretically determined  $F_{i,k}$  values differ considerably from the empirically determined values that reproduce the (experimentally measured) fundamental vibrational frequencies  $\nu_k$  of four benzene isotopomers ( $C_6H_6$ ,  $C_6D_6$ ,  $^{13}C_6H_6$ ,  $^{13}C_6D_6$ ).<sup>8</sup>

In a series of articles culminating in a benchmark review article,<sup>8</sup> Goodman and collaborators, through the use of conventional Wilson's F-G analysis,<sup>1,8</sup> empirically determined the best set of (34) harmonic force constants for benzene after taking into account the strongest anharmonicities.

In a recent series of articles,<sup>42–45</sup> we attempted to further refine the values of the harmonic force constants for benzene by making use of a full scale vibrational model and algorithms that were designed for calculating the fundamental frequencies from a set of input values for the harmonic as well as the most important anharmonic force constants  $F_{i,k}$ ,  $F_{i,j,k}$ , ... Meanwhile, the available rich database of experimental spectroscopic evidence for benzene and for some of its isotopomers<sup>17–37,46–52</sup> was further extended. The fundamentals have recently been reconsidered and summarized by Trombetti and coauthors.<sup>16,28</sup> Despite the numerous experimental studies, however, the values of several fundamental frequencies, especially those of the C–H stretch modes, remain unclear.<sup>8,15,53</sup> One of the most mysterious fundamentals,  $\nu_{13}$ , has recently been measured for  $C_6H_6$ .<sup>53</sup> The new value ( $\sim 3015 \text{ cm}^{-1}$ ) undoubtedly will be very useful for the further refinement of the harmonic force constant values.

Another difficulty that encumbers the straightforward determination of harmonic force constants in benzene comes from strong Fermi resonances, because they arise from essentially anharmonic interactions and prevent the direct experimental

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observation of some of the fundamental frequencies.<sup>8,18,30,34,54,55</sup> At a fundamental level, there are two notable Fermi resonances in benzene. The first one,  $\nu_8 \leftrightarrow \nu_1 + \nu_6$ ,<sup>34</sup> persists up to considerable excitation energies through the addition of  $\nu_1$  quanta to each manifold ( $\nu_8 + n\nu_1 \leftrightarrow (n+1)\nu_1 + \nu_6$ , where  $n = 0, 1, \dots$ ).<sup>54</sup> The second perturbation is a triple<sup>30</sup> (or even quadruple<sup>18,55</sup>) resonance:  $\nu_{20} \leftrightarrow \nu_8 + \nu_{19} \leftrightarrow \nu_1 + \nu_6 + \nu_{19}$  (or  $\nu_{20} \leftrightarrow \nu_8 + \nu_{19} \leftrightarrow \nu_1 + \nu_6 + \nu_{19} \leftrightarrow \nu_3 + \nu_6 + \nu_{15}$ ).

This work is the fourth in a series<sup>42,44,45</sup> aimed at the development and elaboration of a specific, fully symmetrized, nonperturbative algorithm designed for the investigation of the benzene vibrational structure. In the present work, we shall concentrate on the energy levels that are involved in Fermi resonance interactions. For this purpose, we introduce a number of anharmonic (cubic and quartic) Hamiltonian interaction terms in our formalism.<sup>42,44,45</sup> The calculation explicitly includes all 30 molecular vibrational degrees of freedom. The values of some important anharmonic force constants will be determined by fitting the calculated to the experimentally observed levels. This article is organized as follows. Our vibrational approach will be schematically outlined in section II. In section III, using this approach we will study the vibrational structure of the  $8_1 1_n \leftrightarrow 1_{n+1} 6_1$  Fermi resonances, for  $n = 0, 1, \dots$  In section IV, the vibrational structure of the  $20_1 \leftrightarrow 8_1 19_1 \leftrightarrow 1_6 19_1$  Fermi resonance will be investigated and the calculated vibrational structure will be compared to experimental data. In section V, we summarize the main results and conclusions.

## II. Vibrational Model and Large-Scale Computational Approach

Our vibrational model approach and large-scale calculation procedure<sup>38–40,63</sup> is based on the following main principles. Taking into account that anharmonicity in benzene is almost entirely concentrated in the (six equivalent) C–H bonds,<sup>56–59</sup> we describe the C–H stretch system in benzene in terms of six local bond stretch coordinates local mode (LM) formalism,<sup>56–60</sup> while all of the remaining 24 (non C–H stretch) vibrations in benzene are considered to be collective, symmetrized modes (SM), in terms of appropriately symmetrized vibrational coordinates  $S_k$ .<sup>1,4</sup> This is the so-called combined LM/SM representation. A specific feature of our approach is the definition and employment of complex symmetrized curvilinear coordinates  $q_k$  (defined in Table 2 from ref 44), rather similar to those of Whiffen's.<sup>4</sup> The basis harmonic oscillator eigenfunctions of the SM are directly and explicitly obtained in completely symmetrized form, while the C–H stretch (LM) Morse oscillator eigenfunctions have to be additionally symmetrized (in a simple and straightforward manner), as shown in our previous work.<sup>42–44</sup> By multiplying the (complex) symmetrized C–H stretch (LM) eigenfunction with the eigenfunctions of all SM oscillators, we obtained a simple, fully symmetrized, and separable vibrational basis set  $|k\rangle$  for benzene that allows for the full use of the high molecular symmetry ( $D_{6h}$ ).<sup>42,44</sup>

According to this model, the molecular vibrational (quantum mechanical) Hamiltonian  $H$  is given as the sum of two major parts. (i) The zeroth-order Hamiltonian  $H_0$ , whose eigenfunctions are the basis functions  $|k\rangle$ , specified above. Thus,  $H_0$  includes in general all diagonal harmonic force constants  $F_{i,i}$  and G-matrix elements  $G_{i,i}$ , for the SM part, as well as the collection of six identical (noninteracting) Morse oscillator Hamiltonians, for the LM part. (ii) The interaction Hamiltonian  $H_1$  contains a great variety of terms responsible for the various couplings among the basis states and hence among the molecular vibrational (LM and SM) modes. It includes nondiagonal

harmonic force constants  $F_{i,k}$  and G-matrix elements  $G_{i,k}$  essentially connecting pairs of SM  $i, k$  of equal symmetry. These bilinear coupling terms are a connection between the symmetrized modes and the normal-mode frequencies and are a crude approximation of the experimentally observable fundamentals. In addition,  $H_1$  contains a variety of higher-order anharmonic interaction terms that are responsible for the finer details of the molecular vibrational structure (at both the fundamental and higher vibrational excitation energies) and in particular for the correct description of the prominent Fermi resonance structure. A characteristic feature of our approach is that all the Hamiltonian interaction terms belonging to  $H_1$  are expressed in explicit (harmonic oscillator) raising and lowering operator forms.

For the calculation of the molecular vibrational energy levels, we apply a specific nonperturbative procedure, designed for working in the higher energy domain, where the vibrational level density grows very steeply, especially in a molecule the size of benzene. In contrast to the conventional variational method that yields all vibrational levels up to a given limit, our method is based on an artificial intelligence (AI) procedure (algorithm)<sup>61</sup> that is capable of calculating a selection of energy levels that are significantly involved in the coupling to an initially (suitably) chosen basis state  $|0\rangle$  and are energetically located in the vicinity of that state. The AI procedure applied by us has already been described in considerable detail before,<sup>62,63</sup> and therefore only a brief account will be given here. The two most important prerequisites for our method are first, the availability of a symmetrized separable vibrational basis set and second, the availability of all Hamiltonian interaction terms from  $H_1$ , in explicit operator form. The AI selection algorithm starts by applying consecutively all operator terms from  $H_1$  on the initially selected basis state,  $|0\rangle$ , thus generating new basis states  $|1\rangle, |2\rangle, \dots$  Each one of these states necessarily belongs to the same symmetry species as  $|0\rangle$  and is coupled to  $|0\rangle$  by a matrix element  $\langle 0|H_1|k\rangle$ . Each time a new state  $|k\rangle$  is generated, several criteria are applied to establish whether it should be selected or not. Two of the criteria have been described and applied previously.<sup>63</sup> The first one requires that the relative coupling strength  $K_{i,k}$  (the ratio of calculated matrix element to the energy gap) exceeds a small variable parameter C, whose value is fixed at the outset. The second criteria is that the cumulative (product) relative coupling strength  $f(|k\rangle)$  for a probed state  $|k\rangle$  should exceed a second variable small parameter W.<sup>63</sup> The third criterion, introduced here for the first time, is based on a third parameter R, an energy range around the initial state of the search  $|0\rangle$ . Each newly generated state  $|k\rangle$  outside that range receives an additional reduction (proportional to its energy gap from  $|0\rangle$ ) in its cumulative coupling strength. This third criterion ensures that the selected states are not energetically scattered too far from  $|0\rangle$ . After all operators from  $H_1$  have been applied on  $|0\rangle$  and a number of new basis states  $|k\rangle$  selected and the relevant coupling matrix elements calculated, the application of the  $H_1$  operators is next started on the first of the newly selected states,  $|1\rangle$ . This leads to the generation of states that have already been selected or new basis states. In the second case, the new state is tested and eventually selected if it satisfies the criteria. In both cases, the matrix element coupling the newly generated state with the parent state is calculated and stored as matrix element of the Hamiltonian matrix. Next, the algorithm proceeds to apply the  $H_1$  operators in sequence on each one of the selected basis states  $|2\rangle, |3\rangle, \dots$  This leads to the selection of more new basis states and the simultaneous formation of the Hamiltonian matrix. In the course of this procedure, some of

the states are selected as a result of a chain (path) of intermediately selected states, starting from  $|0\rangle$ . The purpose of the second criterion (cumulative coupling strength) is to limit the length of these coupling paths. Each one of the selected basis states is stored and kept in computer memory, together with the resulting Hamiltonian matrix elements. The selection process is terminated at that point, when the application of all operators from  $H_1$  on the last selected state,  $|N\rangle$ , does not lead to the selection of new basis states. The application of this AI procedure for the selection of an active space A of basis states has the advantage of being the smallest possible number  $N$  of basis states that are essentially involved in the coupling with the initially chosen state  $|0\rangle$  and thus is representative for the resulting vibrational level structure around that state. As a result, the Hamiltonian matrix is the smallest possible size for the problem under consideration and this fact is particularly useful for the subsequent diagonalization. The optimization of the selected space is due first to the explicit selection of only basis states of the same symmetry as  $|0\rangle$  and second to the effect of the selection criteria (appropriate choice of values for the selection parameters C, W, and R). The selection of an economic active space and Hamiltonian matrix of minimal possible size,  $N$ , creates an opportunity to explore the higher excited vibrational states in a molecule such as benzene where all of the vibrational degrees of freedom have been included.

For the molecular vibrational levels, the symmetric Hamiltonian matrix  $H_{i,k}$  generated as a result of the AI selection procedure has to be diagonalized. Because of the very large dimensions that  $N$  may assume, the diagonalization is carried out using preliminary Lanczos tri-diagonalization.

### III. Analysis of the $\nu_8 \leftrightarrow \nu_1 + \nu_6$ Fermi Resonance in Benzene

This is the most prominent Fermi resonance in  $C_6H_6$  benzene and persists up to quite high vibrational excitation energies through the consecutive addition of  $\nu_1$  quanta to both energy manifolds. This resonance can be very effectively analyzed in terms of symmetrized coordinates  $q_k$ <sup>44</sup> and symmetrized modes, thus revealing the intrinsic nature of the interactions involved in the isotopically invariant form.

It was important to initially establish the relative position of the  $8_1$  and  $6_11_1$  levels to zeroth order (i.e., without the cubic interactions that give rise to the Fermi interaction). These were found at the energies  $8_1 = 1598.4 \text{ cm}^{-1}$  and  $6_11_1 = 1601.2 \text{ cm}^{-1}$ . These two deperturbed energy levels practically coincide with those determined by Pliva et al.,<sup>64</sup> however, the assignment is contrary to theirs in that they assigned the upper level at  $1600 \text{ cm}^{-1}$  to  $\nu_8$ , while we have assigned the lower level of this pair at  $1598 \text{ cm}^{-1}$  to  $\nu_8$ . The difference of  $3 \text{ cm}^{-1}$  may not seem very significant, taking into account that in reality the two states are strongly mixed and pushed far away from each other by the interaction matrix elements. It is not difficult, by minor changes in the relevant harmonic force constant values, to adjust the two deperturbed states in reverse order:  $8_1$  to be the upper member at  $1601$  and  $6_11_1$  as the lower level at  $1598 \text{ cm}^{-1}$ . Indeed, for the description of this resonance and all the higher excited resonances containing equal number of  $\nu_1$  quanta, this would not make any difference. However, as we shall show in the following section, this is important for the correct analysis of the triple Fermi resonance around  $\nu_{20}$ . We note that, in their analysis, Knight et al.<sup>65</sup> and Fischer et al.<sup>66</sup> also assigned  $\nu_8$  as the lower of two nearby levels.

Essentially two cubic force constants (in terms of symmetrized coordinates) can contribute to the coupling of  $\nu_8$  and

$\nu_1 + \nu_6$ :  $F_{1,6,8}$  and  $F_{1,6,9}$ . The relevant Hamiltonian interaction terms contain both kinetic<sup>63</sup> and potential cubic parts and can be given as:

$$H_{1,6,8} = -\frac{1}{m_C\sqrt{2}}\left(q_{6a}\frac{\partial^2}{\partial q_1\partial q_{8a}} + q_{6b}\frac{\partial^2}{\partial q_1\partial q_{8b}}\right) - \frac{3}{m_C2\sqrt{2}}\left(q_1\frac{\partial^2}{\partial q_{6b}\partial q_{8a}} + q_1\frac{\partial^2}{\partial q_{6a}\partial q_{8b}}\right) + F_{1,6,8}q_1(q_{6a}q_{8b} + q_{6b}q_{8a}) \quad (2)$$

$$H_{1,6,9} = \frac{\sqrt{2}s_0}{8m_Ct_0}\left(q_{6a}\frac{\partial^2}{\partial q_1\partial q_{9a}} + q_{6b}\frac{\partial^2}{\partial q_1\partial q_{9b}}\right) - \frac{\sqrt{2}}{4m_C}\left(q_1\frac{\partial^2}{\partial q_{6b}\partial q_{9a}} + q_1\frac{\partial^2}{\partial q_{6a}\partial q_{9b}}\right) + F_{1,6,9}q_1(q_{6a}q_{9b} + q_{6b}q_{9a}) \quad (3)$$

where  $s_0$  and  $t_0$  are the equilibrium C–H and C–C bond lengths, respectively, and  $m_C$  is the mass of the C atom. We have included the relevant cubic terms, expressed in explicit operator form, into the Hamiltonian interaction operator  $H_1$  and performed large-scale calculations on these vibrational levels by choosing the initial state as either  $8_1$  or  $6_11_1$ . By varying the input values of the cubic force constant  $F_{1,6,8}$  as well as some of the harmonic force constants and comparing the results from the calculations with the experimentally measured energy levels,<sup>18,34,64,66</sup> we have been able to determine set force constant values that ensure a satisfactory agreement between the calculated and experimentally measured frequencies. It was found that the  $F_{1,6,9}$  Hamiltonian terms were not significant, while the  $H_{1,6,8}$  term (including the force constant  $F_{1,6,8}$ ) played the major role in producing the famous  $8_1 \leftrightarrow 6_11_1$  doublet in  $C_6H_6$  benzene. Therefore, we have set the cubic force constant  $F_{1,6,9}$  equal to zero (however, preserving the relevant kinetic part in the calculation) and varied the input value of the force constant  $F_{1,6,8}$  to match the calculated frequencies with the experimentally observed energy levels. The initial state was chosen as either  $8_1$  or  $6_11_1$ . It was found that, for  $F_{1,6,8} = -0.3$ , the two levels were at  $1591.6$  and  $1609.7 \text{ cm}^{-1}$ , in very good accord with the experimentally measured frequencies:<sup>34</sup>  $1591.327$  and  $1609.518 \text{ cm}^{-1}$ . As already pointed out, to achieve this agreement, we also had to introduce minor changes in the values of some of the harmonic force constants that were established in our previous work.<sup>45</sup> Thus,  $F_{6,6}$  was changed from  $0.671$  to  $0.660$  and  $F_{8,8}$  was changed from  $6.670$  to  $6.660$  (aJ and Angstrom).

It is noteworthy that, with these force constant values excited higher, experimentally observed<sup>66</sup> Fermi resonances  $8_11_n \leftrightarrow 1_{n+1}6_1$ , for  $n = 1, 2, \dots$  were satisfactorily reproduced. In ref 66, the energies of a great number of ground electronic state overtone and combination levels were established by measuring the dispersed fluorescence spectra that originated from a number of  $S_1$  benzene single vibronic levels (SVL):  $0^0$ ,  $1^1$ ,  $6^1$ ,  $6^11^1$ ,  $6^11^2$ , and  $6^11^3$ . To find the absolute frequencies of an SVL in a given spectrum and in particular those of  $6_11_n$  and  $8_11_{n-1}$  ( $n = 1, 2, \dots$ ) level pairs, we have calibrated all energy levels in a given spectrum<sup>66</sup> in such a way that assures that the two basic Fermi levels  $8_1$  and  $6_11_1$  reproduce the precisely measured values in ref 34. In this way, we obtain  $2581$  and  $2606 \text{ cm}^{-1}$ , respectively, for the  $8_11_1$  and  $6_11_2$  levels from the  $0^0$  dispersed fluorescence spectrum. Our calculation yields for these levels,  $8_11_1 = 2581.0$  and  $2606.4 \text{ cm}^{-1}$ , are in almost perfect accord with the experimental measurement.<sup>66</sup> Values of  $3571$  and  $3602 \text{ cm}^{-1}$ , respectively, can be estimated for the higher excited  $8_11_2$

and  $6_{13}$  levels from the  $0^0$  dispersed fluorescence spectrum.<sup>66</sup> Our present calculation for these levels yields 3569.7 and 3600.1  $\text{cm}^{-1}$ , again in very good accord with the spectral data. For the  $8_{13}$  and  $6_{14}$  pair, the appropriately calibrated experimentally measured  $0^0$  spectrum values are 4552 and 4591  $\text{cm}^{-1}$ , respectively. The results from our calculations for these levels are 4556.7 and 4591.9  $\text{cm}^{-1}$ . As seen, the agreement is spectacularly good for all the Fermi levels explored. This could be considered as strong evidence in favor of the vibrational model employed for benzene and for the selected values of the relevant harmonic and anharmonic force constants.

We have also carried out large-scale calculations to check the effect of the  $\nu_8 \leftrightarrow \nu_1 + \nu_6$  resonance on the vibrational level structure of the remaining  $D_{6h}$  symmetric isotopomers of benzene:  $\text{C}_6\text{D}_6$ ,  $^{13}\text{C}_6\text{H}_6$ , and  $^{13}\text{C}_6\text{D}_6$ . The following computational results have been obtained. In  $\text{C}_6\text{D}_6$ , the combination level  $\nu_1 + \nu_6$  lies at 1527  $\text{cm}^{-1}$ , that is, definitely below  $\nu_8$  whose deperturbed value (in the absence of the cubic interaction terms  $H_{1,6,8}$  and  $H_{1,6,9}$ ) was calculated to be 1552.8  $\text{cm}^{-1}$ . Taking  $H_{1,6,8}$  and  $H_{1,6,9}$  into account shifted the calculated value of  $\nu_8$  from 1552.8 to 1555.7  $\text{cm}^{-1}$  (the  $\nu_1 + \nu_6$  level is shifted down to 1525  $\text{cm}^{-1}$ ). Thus, even in  $\text{C}_6\text{D}_6$ , the Fermi resonance has a non-negligible effect and the resulting  $\nu_8$  frequency shifts closer to the experimentally measured value of 1558.3  $\text{cm}^{-1}$ .<sup>24</sup> Next, in  $^{13}\text{C}_6\text{H}_6$ , a Fermi resonance  $8_1 \leftrightarrow 6_{11}$  of strength similar to that in benzene  $\text{C}_6\text{H}_6$  is observed. Indeed, the deperturbed ( $H_{1,6,8}$  and  $H_{1,6,9}$  excluded) levels  $8_1$  and  $6_{11}$  are calculated at 1549.4 and 1542.1  $\text{cm}^{-1}$ , respectively. Including the  $H_{1,6,8}$  and  $H_{1,6,9}$  terms in the calculation yields for these levels the vibrational energies of 1554.8 and 1537.0  $\text{cm}^{-1}$ , respectively. Finally, for  $^{13}\text{C}_6\text{D}_6$ , the deperturbed frequencies of  $8_1$  and  $6_{11}$  were calculated as 1495.8 and 1477.1  $\text{cm}^{-1}$ , respectively. The Fermi resonance corrected frequencies are 1499.3 and 1474.9  $\text{cm}^{-1}$ .

Thus, it is obvious that in all three isotopomers,  $\text{C}_6\text{D}_6$ ,  $^{13}\text{C}_6\text{H}_6$ , and  $^{13}\text{C}_6\text{D}_6$ , the  $8_1$  frequency is definitely below  $6_{11}$ , while in benzene  $\text{C}_6\text{H}_6$  the two are almost coincident. According to our results,  $6_{11}$  is located slightly above  $8_1$ . Our calculations show that the Fermi resonance is also active in the remaining three benzene  $D_{6h}$  isotopomers, although weaker than that in benzene  $\text{C}_6\text{H}_6$ . Nevertheless, its effect should be taken into account when comparing the calculated to the experimentally measured frequencies (where available), especially for  $^{13}\text{C}_6\text{H}_6$  where the Fermi shift is comparatively large. Table 1 summarizes the calculated vibrational frequencies in benzene  $\text{C}_6\text{H}_6$  and some of its  $D_{6h}$  isotopomers that are affected by the Fermi resonances, and Table 2 contains the values of the harmonic and anharmonic force constants involved in the Fermi interactions.

#### IV. Analysis of the Triple $\nu_{20} \leftrightarrow \nu_8 + \nu_{19} \leftrightarrow \nu_1 + \nu_6 + \nu_{19}$ Fermi Resonance

This resonance encompasses the  $\nu_8 \leftrightarrow \nu_1 + \nu_6$  resonance previously analyzed. The conventional notation for the normal mode (NM) whose frequency is 1484  $\text{cm}^{-1}$  in  $\text{C}_6\text{H}_6$  is  $\nu_{19}$ . However, this notation is obviously not consistent and leads to some confusion when trying to relate the SM to NM.<sup>45</sup> In fact, in terms of the SM treatment, mode no. 18 is a C–H in-plane angle distortion<sup>1,4</sup> whose force constant is  $F_{18,18} = 0.931^{45}$  and SM frequency  $\omega_{18}^s$ , calculated using  $F_{18,18}$  and  $G_{18,18}$ ,<sup>1</sup> is 1388  $\text{cm}^{-1}$ . On the other hand, SM no. 19 is a C–C stretch<sup>1,4</sup> whose force constant is  $F_{19,19} = 7.403^{45}$  (typical for this type of mode) and the SM frequency, calculated using  $F_{19,19}$  and  $G_{19,19}$ ,<sup>1</sup> is  $\omega_{19}^s = 1244 \text{ cm}^{-1}$ . Upon normalization, the NM with the fundamental frequency of 1484  $\text{cm}^{-1}$  is much closer (by both frequency and relative weight) to the higher frequency SM no.

**TABLE 1: Summary of Some Calculated Fundamental Vibrational Frequencies and Combinations (in  $\text{cm}^{-1}$ ), Affected by Fermi Interactions, for Benzene  $\text{C}_6\text{H}_6$  and Some of Its  $D_{6h}$  Isotopomers**

molecule	frequency	calculated	experimentally measured
$\text{C}_6\text{H}_6$	$\nu_8$	1591.6	1591.327 <sup>34</sup>
	$\nu_6 + \nu_1$	1609.7	1609.518 <sup>34</sup>
$\text{C}_6\text{H}_6$	$\nu_8 + \nu_1$	2581.0	2581 <sup>54 a</sup>
$\text{C}_6\text{H}_6$	$\nu_6 + 2\nu_1$	2606.4	2606 <sup>54 a</sup>
$\text{C}_6\text{H}_6$	$\nu_8 + 2\nu_1$	3569.7	3571 <sup>54 a</sup>
$\text{C}_6\text{H}_6$	$\nu_6 + 3\nu_1$	3600.1	3602 <sup>54 a</sup>
$\text{C}_6\text{H}_6$	$\nu_8 + 3\nu_1$	4556.7	4552 <sup>54 a</sup>
$\text{C}_6\text{H}_6$	$\nu_6 + 4\nu_1$	4591.9	4591 <sup>54 a</sup>
$\text{C}_6\text{H}_6$	$\nu_8 + 4\nu_1$	5544.1	5534 <sup>54 b</sup>
	$\nu_6 + 5\nu_1$	5583.5	5585 <sup>54 b</sup>
$\text{C}_6\text{H}_6$	$\nu_{20}$	3050.1	3048 <sup>30</sup>
$\text{C}_6\text{H}_6$	$\nu_8 + \nu_{18}$	3081.2	3079 <sup>30</sup>
$\text{C}_6\text{H}_6$	$\nu_6 + \nu_1 + \nu_{18}$	3102.0	3101 <sup>30</sup>
$\text{C}_6\text{D}_6$	$\nu_8$	1555.7	1558.3 <sup>24</sup>
	$\nu_6 + \nu_1$	1525.3	
$^{13}\text{C}_6\text{H}_6$	$\nu_8$	1554.8	
	$\nu_6 + \nu_1$	1537.0	
$^{13}\text{C}_6\text{D}_6$	$\nu_8$	1495.8	
	$\nu_6 + \nu_1$	1477.1	

<sup>a</sup> Estimated from the  $0^0$  dispersed fluorescence spectrum in ref 61, by calibrating all levels so as to fit the  $8_1$  and  $6_{11}$  frequencies to the exact values from ref 34. <sup>b</sup> Estimated from the  $1^1$  dispersed fluorescence spectrum in ref 61, by calibrating all levels so as to fit the  $8_1$  and  $6_{11}$  frequencies to the exact values from ref 34.

**TABLE 2: Some Harmonic and Anharmonic Force Constants for Benzene (in  $\text{mdyn}$  and  $\text{\AA}$ ), Empirically Determined or Refined in This Work**

force constant <sup>a</sup>	present value	previous value
$F_{20,20}$	5.514	5.519 <sup>45</sup>
$F_{6,6}$	0.666	0.671 <sup>45</sup>
$F_{8,8}$	6.660	6.670 <sup>45</sup>
$F_{1,6,8}$	-0.300	-0.423 <sup>11 b</sup>
$F_{20,1,6,18}$	12.0	

<sup>a</sup> The harmonic force constants  $F_{20,20}$ ,  $F_{6,6}$ , and  $F_{8,8}$  are given in units  $\text{mdyn}/\text{\AA}$  ( $= \text{aJ}/\text{\AA}^2$ );  $F_{1,6,8}$  is in  $\text{mdyn}/\text{\AA}^2$  ( $= \text{aJ}/\text{\AA}^3$ ); and  $F_{20,1,6,18}$  is in  $\text{mdyn}/\text{\AA}^3$  ( $= \text{aJ}/\text{\AA}^4$ ). <sup>b</sup> Obtained from ab initio calculations on the quartic PES of benzene.

18 and should therefore be denoted as  $\nu_{18}$ , while the lower NM frequency 1038  $\text{cm}^{-1}$  is closer and corresponds to the lower frequency SM no. 19 and should naturally be assigned as  $\nu_{19}$ , thus reversing the conventional notation for these two modes.<sup>8</sup> In the following analysis, we shall use this changed notation for NM  $\nu_{18}$  and  $\nu_{19}$ .

The complex Fermi resonance  $\nu_{20} \leftrightarrow \nu_8 + \nu_{18} \leftrightarrow \nu_1 + \nu_6 + \nu_{18}$  is essentially governed by two coupling matrix elements. The first is a coupling between the  $8_1 18_1$  and  $6_{11} 18_1$  levels. These are in fact the two levels  $8_1$  and  $6_{11}$ , considered earlier with a quantum of  $\nu_{18}$  added to each one. The interaction Hamiltonian term coupling those two levels has already been identified above as  $H_{1,6,8}$  and contains the cubic force constant  $F_{1,6,8} = -0.3$ . The energies of the resulting pair of states, excluding and disregarding their coupling with the  $\nu_{20}$  mode, have been calculated here as 3074.1 and 3091.1  $\text{cm}^{-1}$ , respectively. As discussed in the preceding section, the upper level can be (predominantly)  $6_{11} 18_1$  and the lower  $8_1 18_1$ , or vice versa, according to the ordering of  $6_{11}$  and  $8_1$  (determined by a small change in the values of  $F_{6,6}$  and  $F_{8,8}$ ). This small change, however, reverses the order of the deperturbed  $8_1$  and  $6_{11}$  levels and thus interchanges the predominant character of the upper and lower levels in the Fermi diad. It is found to be of crucial

importance when the coupling to the third state  $20_1$  that is located at the lower energy of  $3065\text{ cm}^{-1}$  is taken into account.

The experimentally observed frequencies of the Fermi triad obtained from coupling of the three closely located states  $20_1$ ,  $8_118_1$ , and  $6_11_118_1$  are  $3048$ ,  $3079$ , and  $3101\text{ cm}^{-1}$ , respectively.<sup>30</sup> Furthermore, the intensities of both outer levels ( $3048$  and  $3101$ ) exceed that of the intermediate frequency  $3079\text{ cm}^{-1}$ .<sup>30</sup> As seen, the upper level at  $3101\text{ cm}^{-1}$  is strongly shifted from its deperturbed position of  $3091\text{ cm}^{-1}$  (see above) and more strongly coupled to the lower  $20_1$  level (which is the only source of spectral intensity in the triad), compared to the intermediate state (at  $3074.1\text{ cm}^{-1}$ ). The major cubic Hamiltonian interaction terms capable of coupling the SM  $20_1$  to the Fermi pair  $8_118_1$  and  $6_11_118_1$  are  $H_{20,8,18}$  and  $H_{20,8,19}$ . These two Hamiltonian terms also contain a kinetic and a potential part, the latter being determined by the cubic force constants  $F_{20,8,18}$  and  $F_{20,8,19}$ , respectively. The expressions for the potential parts are:

$$H_{20,8,18} = F_{20,8,18}(q_{20a}q_{8b}q_{18a} + q_{20b}q_{8a}q_{18b}) \quad (4)$$

$$H_{20,8,19} = F_{20,8,19}(q_{20a}q_{8b}q_{19a} + q_{20b}q_{8a}q_{19b}) \quad (5)$$

We have varied the values of the force constants  $F_{20,8,18}$  and  $F_{20,8,19}$  in an attempt to reproduce the three experimentally measured frequencies given above. This, however, turned out to be impossible. In all of the cases that were considered, the intermediate level was found to be more strongly perturbed than the higher energy one by interaction with the lower lying  $20_1$  state and to possess the higher intensity. This was invariably the case for each one of the relative locations of the two higher levels, as discussed above:  $8_118_1$  higher than  $6_11_118_1$  or vice versa.

Hence, it was necessary to look for another Hamiltonian interaction term that could induce the coupling between  $20_1$  and the Fermi pair  $8_118_1$  and  $6_11_118_1$ . For this purpose, we probed the quartic interaction Hamiltonian term  $H_{20,1,6,18}$  containing the quartic force constant  $F_{20,1,6,18}$ . The corresponding potential part is written as:

$$H_{20,1,6,18} = F_{20,1,6,18}q_1(q_{20a}q_{6b}q_{18a} + q_{20b}q_{6a}q_{18b}) \quad (6)$$

Including this term in the calculations produced the required effect, but only for the configuration when  $6_11_118_1$  was placed above  $8_118_1$ . The three frequencies, calculated at the value  $F_{20,1,6,18} = 12.0$ , were  $3050.1$ ,  $3081.2$ , and  $3102.3\text{ cm}^{-1}$ , in satisfactory agreement with the experimentally measured values:  $3048$ ,  $3079$ , and  $3101\text{ cm}^{-1}$ . Furthermore, the intensity distribution was correct, namely, the two states at  $3050.1$  and  $3102.3\text{ cm}^{-1}$  had higher intensity than the intermediate state when the entire initial excitation was localized on the zeroth order  $\nu_{20}$  (symmetrized) mode.

We consider all this an indication that the uppermost level in the triplet should originate from the  $6_11_118_1$  state while the intermediate level should be predominantly  $8_118_1$ . This implies that the two levels in the previously considered Fermi diad should have predominantly  $8_1$  and  $6_11_1$  character, in ascending order, respectively.

Using the same values for the harmonic and anharmonic force constants, we also performed calculations on the vibrational level structure around  $20_1$  in  $^{13}\text{C}_6\text{H}_6$ . In fact, calculations in our earlier work<sup>45</sup> yielded the value of  $\nu_{20} = 3055\text{ cm}^{-1}$ , which was  $10\text{ cm}$  below the experimentally measured value of  $3065\text{ cm}^{-1}$ .<sup>18</sup> In the present work, including in the calculations all cubic and quartic Hamiltonian interaction terms discussed above, we have

obtained  $\nu_{20} = 3062.1\text{ cm}^{-1}$ . This value of  $\nu_{20}$ , which has been pushed higher by the remaining two levels of the Fermi triad, is now much closer to the experimentally observed value of  $3065\text{ cm}^{-1}$ .<sup>18</sup>

## V. Conclusion

This work is the fourth in a series<sup>42,44,45</sup> aimed at an empirical determination of an improved and reliable set of harmonic force constants  $F_{i,k}$  for benzene, in the isotopically invariant form of symmetrized (Whiffen's) coordinates. Here it has been shown that the refinement of the harmonic force constants requires a detailed analysis of the well-known Fermi resonances taking into account the anharmonic (cubic and quartic) force constants. This is because the Fermi resonances in benzene distort the observed fundamental frequencies away from their related harmonic frequencies that define the harmonic force constants.

We have extended our vibrational model and large-scale calculations approach for  $D_{6h}$  benzenes by introducing a number of cubic and even quartic Hamiltonian interaction terms that are relevant to the Fermi interactions in question. Our aim has been to obtain an agreement of the calculated vibrational levels around the  $\nu_8$  and the  $\nu_{20}$  fundamentals with the experimentally observed Fermi doublet and triplet frequencies, respectively. In this way, we have been able to determine some important anharmonic force constants and additionally refine some of the harmonic force constants obtained previously<sup>45</sup> and also derive certain additional information about the vibrational level structure in benzene.

The findings in the present work could be summarized as follows. From a consideration of the Fermi resonance  $\nu_8 \leftrightarrow \nu_1 + \nu_6$ , we have come to the conclusion that the deperturbed (excluding Fermi interactions) vibrational level  $6_11_1$  is located slightly above the  $8_1$  level. The Fermi interaction between these two states is produced by the  $H_{1,6,8}$  Hamiltonian interaction term, with a cubic force constant of  $F_{1,6,8} = -0.3$ . To obtain the calculated energies of the Fermi doublet in good agreement with the experimentally measured frequencies, it was necessary to slightly change the previously determined values of the  $F_{6,6}$  and  $F_{8,8}$  harmonic force constants. The upper and lower levels in this doublet predominately are of  $6_11_1$  and  $8_1$  character. We have also carried out calculations on the Fermi resonance affected levels in the remaining three  $D_{6h}$  benzene isotopomers:  $\text{C}_6\text{D}_6$ ,  $^{13}\text{C}_6\text{H}_6$ , and  $^{13}\text{C}_6\text{D}_6$ . We have found that, in all three molecules, the two levels  $8_1$  and  $6_11_1$  are perceptibly affected by the cubic Hamiltonian interaction term  $H_{1,6,8}$ , and the effect is strongest in  $^{13}\text{C}_6\text{H}_6$ . Calculations on higher excited Fermi pairs in  $\text{C}_6\text{H}_6$  benzene  $8_11_k$  and  $6_11_{k+1}$  ( $k = 1, 2, \dots$ ) have yielded results in very good conformity with the experimentally measured data, and this should be regarded as a corroboration of the values determined for the harmonic and anharmonic force constants.

The theoretical study of the  $\nu_{20} \leftrightarrow \nu_8 + \nu_{18} \leftrightarrow \nu_1 + \nu_6 + \nu_{18}$  resonance in  $\text{C}_6\text{H}_6$  follows from the analyses of the  $\nu_8 \leftrightarrow \nu_1 + \nu_6$  resonance. Our calculations have shown that the coupling of the  $20_1$  level with the pair of levels  $8_118_1$  and  $6_11_118_1$  is mainly due to the quartic Hamiltonian interaction term  $H_{20,1,6,18}$  and a quartic force constant of  $F_{20,1,6,18} = 12.0$ .

Our theoretical work on the  $S_0$  potential hypersurface of benzene will be continued. The values of some harmonic and anharmonic force constants will be further refined by taking into account some of the recently measured fundamental frequencies<sup>53</sup> that differ substantially from previously adopted values. The calculations will be extended to the higher excited vibrational level structure of benzene, in the range of the first C–H stretch overtone.

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