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# Correlation of the Vibrational Spectra of Isotopomers: Theory and Application

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Using the concept of a mass reaction path, we developed an algorithm that leads to the correct correlation of the vibrational modes of two isotopomers. The mass reaction path is defined by weighted incremental changes of the masses in a molecule that, successively applied, convert the “mass reactant” into the “mass product”. Overlap criteria are used to correlate the vibrational modes in the correct way between two path points considering changes in symmetry, avoided crossings, and rotations among degenerate modes. The new algorithm is formulated in a way that it can be extended to the correlation of the vibrational spectra of structurally related molecules.

## 1. Introduction

The vibrational spectra of molecules embody a large amount of information on its electronic structure, charge distribution, geometry, conformation, etc.<sup>1–8</sup> However, it is difficult to unravel this information just using the measured vibrational frequencies. Quantum chemical theory can provide reasonable vibrational frequencies using the harmonic approximation and in this way relate to each measured frequency the associated vibrational mode, which in turn provides a basis for a systematic analysis of the vibrational spectrum. For example, using the adiabatic mode concept<sup>9–11</sup> each vibrational mode can be decomposed into internal coordinate modes so that the electronic features of bonds, functional groups, rings, etc. can be described in detail.

There are four different quantities of a molecule, which have a direct influence on its vibrational spectra, namely the number  $N$  of the atoms constituting the molecule, the molecular symmetry  $X$ , the masses  $m_i$  of the atoms (collected in the mass matrix  $\mathbf{M}$ ), and the electronic structure of the molecule as reflected by its force constant matrix  $\mathbf{K}$ . Changes in one or more of these quantities leads to changes in the vibrational spectra. If experimentalists are able to measure the changes in the vibrational spectra, one can draw conclusions with regard to the changes in the molecular quantities influencing the vibrational spectra. This may sound trivial; however, already a change in  $N$  represents a serious problem of correlating a smaller with a larger number of vibrational modes in such a way that changes in the electronic structure accompanying a change in the number of atoms are clearly identified.<sup>2</sup>

If one would be able to exactly identify changes in the vibrational spectra, which accompany a change in either  $N$ ,  $\mathbf{M}$ ,  $X$ , or  $\mathbf{K}$ , one would be able to extract valuable information from infrared or Raman spectra. Hence the automated correlation of the vibrational spectra of related species is an important goal of vibrational spectroscopy.<sup>1–8</sup> This goal can be split into partial problems by varying one of the four quantities influencing a vibrational spectrum and keeping all others fixed:

(1) changes in  $\mathbf{K}$  while  $N$ ,  $X$ , and  $\mathbf{M}$  are fixed: correlation of the vibrational spectra along a reaction path

(2) changes in  $\mathbf{K}$  and  $X$  while  $N$  and  $\mathbf{M}$  are fixed: correlation of the vibrational spectra of isomers and conformers

(3) changes in  $\mathbf{M}$  and  $X$  while  $N$  and  $\mathbf{K}$  are fixed: correlation of isotopomer spectra

(4) changes in  $\mathbf{K}$ ,  $\mathbf{M}$ , and  $X$  while  $N$  is fixed: correlation of the vibrational spectra of valence isomers

(5) Changes in  $N$ ,  $\mathbf{K}$ ,  $\mathbf{M}$ , and  $X$ : correlation of the vibrational spectra of different compounds

In the latter case, there must be at least some structural or chemical relationship between the compounds considered to make a correlation of the vibrational spectra meaningful (typical example: parent and substituted compound such as benzene and toluene).

We have recently worked on problem 1 because it is related to the description of a chemical reaction with the help of the reaction path Hamiltonian<sup>12</sup> and the unified reaction valley approach.<sup>13,14</sup> The reaction complex of a chemical reaction keeps its symmetry along the reaction path and can only change it at a stationary point (McIver-Stanton rules<sup>15</sup>). The problem of correlating the generalized normal modes along the reaction path were solved with a diabatic ordering of the vibrational modes (DMOD),<sup>16</sup> which was used already in a number of reaction mechanism studies.<sup>13,14,17,18</sup>

Problem 2 is closely related to problem 1: For each pair of conformers, one can identify a reaction path in conformational space and consider the correlation problem as the problem of monitoring the vibrational modes between reactant (conformer 1) and product (conformer 2). Special consideration has to be taken concerning the change in symmetry at the stationary points. A similar approach could be taken in the case of configurational isomers although this might lead to unusual reaction paths with high barriers. Clearly, this way is feasible; however, it leads to a large number of costly calculations whereas the additional gain in information is not needed in the normal case. Hence, problem 2 might be considered to be solved in a new way including a change in mass. For example a *cis*- and a *trans*-isomer, e.g., *cis*- and *trans*-difluoroethene, can be related by growing at a position of a H atom the mass of a F atom and shrinking at the position of a F atom the mass to a H atom. If these changes are accompanied by appropriate changes in the force constant matrix  $\mathbf{K}$ , it is possible to correlate the vibrational spectra of configurational isomers. However, to solve this task in an appropriate way we consider first the problem of correlating the vibrational spectra of isotopomers (task 3).

In the literature there have been simple recipes to estimate the isotope shifts of vibrational frequencies and correlate the vibrational spectra of isotopomers on the basis of these estimates.<sup>1–5,19–25</sup> Best known are the Teller–Redlich product rules<sup>19</sup> or the various sum rules for the vibrational frequencies of isotopomers.<sup>20–22</sup> Teller and later Wilson<sup>23</sup> described perturbational approaches, which use the fact that, apart from the substitution of hydrogen by deuterium, the mass change in a molecule caused by isotope substitution is normally rather small and can be considered as a mass perturbation to the unperturbed vibrational problem. Zivkovic has suggested a more general perturbation method to predict isotope shifts for vibrational frequencies.<sup>24,25</sup> This method no longer requires that the mass changes are small, and therefore, it is no longer limited to just a few favorable cases as the Teller–Wilson methods were.

Because we want to approach this problem in a general way leading also to simple solutions for problems 2 and 4 and, then, to an automated correlation of the vibrational spectra of any pair of compounds with a common chemical basis (all compounds with the same number of atoms and the same symmetry, parent compound and its derivatives, configurational and conformational isomers, etc.), we will disregard the known ways of predicting isotope shifts. Instead, we will solve problem 3 independent of the change in mass or symmetry just by assuming that the change in the force field (potential energy function) is negligible, which is certainly true for the harmonic approximation<sup>1–5</sup> generally used to calculate vibrational spectra with quantum chemical methods. For this purpose, we partition the problem into two subproblems:

(3a) changes in **M** while *N*, *X*, and **K** are fixed: correlation of the vibrational spectra of isotopomers of the same symmetry

(3b) changes in **M** and *X* while *N* and **K** are fixed: general correlation of the vibrational spectra of isotopomers.

For the purpose of solving these problems, we define a *mass reaction path* and a *mass reaction path Hamiltonian*. With the help of these definitions, we are able to apply the DMOD approach<sup>16</sup> to correlate the vibrational spectra of isotopomers. In chapter 2, we will describe the theory of correlating the vibrational spectra of isotopomers. In chapter 3, this theory will be applied both for the case that the symmetry *X* of the isotopomers is the same (problem 3a) and for the case that it is different (problem 3b).

## 2. Correlation of the Normal Modes of Isotopomers

If an atom of a molecule is replaced by an isotope of different mass, the measured vibrational frequencies of the molecule will reflect the change in mass by an isotope shift. This will be large if (a) the isotopic atom in question strongly participates in a normal mode movement (i.e., it contributes to the normal mode with a large amplitude) and (b) the mass change is large. It will be small if either condition (a) or (b) is not fulfilled. One might argue that the isotope shifts can be estimated with the help of perturbation theory;<sup>23–25</sup> however, there are two arguments speaking against such a solution. First, the most interesting isotope shifts in organic chemistry are those caused by a replacement of hydrogen by deuterium. In the case of a CH stretching frequency, the relevant mass changes by 7%, which can no longer be considered as a small change in mass. Second, the objective of this work is to develop a general purpose method, which is also able to handle the task of correlating the vibrational spectra of configurational isomers (task 2), valence isomers (task 4), or closely related molecules in general (task 5). Therefore, we disregard solutions offered by perturbation theory and follow a different approach.

Because the problem of correlating the vibrational spectra of a reaction complex changing from reactants to products along a reaction path has been solved,<sup>16</sup> it is desirable to use this technology also to solve the isotopomer problem. *This can be done by defining a mass reaction coordinate, which describes, e.g., the transformation of a hydrogen mass into a deuterium mass.* The corresponding mass reaction path is linear; i.e., it does not possess any curvature as in the case of the normal reaction path. It can be described by increasing the hydrogen mass by small mass increments from 1 to 2 and calculating for these changes at each point the corresponding vibrational modes and mode frequencies. The mass reaction path Hamiltonian has a trivial form without any coupling terms (e.g., between the vibrational modes), and the mass reaction complex (changing in a way that H is replaced by D) keeps its relative orientation along the path; i.e., rotations are excluded.

However, the isotopomer problem should be considered as just a special case of a more general problem in which both the masses and the electronic structure (force constant matrix **K**) are different, as in the case of valence isomers. In this case a mass reaction coordinate is coupled with a reaction coordinate describing the change in geometry and yet another coordinate describing the change in the atomic number and in the number of electrons. In this situation the mass reaction complex can rotate around the reaction path, which has to be considered when setting up the correlation algorithm.

The  $N_{\text{vib}} = 3K - L$  ( $L = 5$  or  $6$ ) vibrational modes of a mass reaction complex leading from one isotopomer to the next, span the vibrational space, which can be divided in vibrational subspaces of dimension  $g_i$  ( $g_i = 1, 2, 3$ , etc.) depending on the degree of degeneracy of the vibrational eigenstates. If the symmetry *X* of the mass reaction complex does not change from one isotopomer to the next, it is straightforward to correlate one vibrational subspace at one mass reaction coordinate point  $t_a$  to the appropriate vibrational subspace at mass reaction coordinate  $t_b$  and to order in this way the vibrational subspaces  $V_i^B$  so that they all correlate in the correct way with the vibrational subspaces  $V_j^A$ . The problem will become more difficult if the symmetry *X* changes from one isotopomer to the other so that also the number of subspaces and their dimension will be different. Hence, in the second step the more general case of a change in both **M** and *X* is considered and the algorithm generalized to handle this case as well.

It is straightforward to define a mass reaction path in the space based on mass-weighted coordinates. The direction of the mass reaction path is determined by the sign of a suitable mass increment  $\Delta m$ . At a given point  $t_a$  of the mass reaction path, defined by the path coordinate *t*, the generalized normal modes  $I_\mu^g(t_a)$  and the associated normal-mode frequencies,  $\omega_\mu(t_a)$ , are calculated by solving

$$\mathbf{K}(t_a)I_\mu^g(t_a) = \omega_\mu^2(t)I_\mu^g(t_a) \quad (1)$$

(**K** is the projected force constant matrix<sup>16</sup>), which yield  $N_{\text{vib}}$  eigenvectors of length  $N = 3K$  that span the  $N_{\text{vib}}$ -dimensional space. At points  $t_a$  and  $t_b$  separated by the mass increments

$$\Delta m_k = \frac{m_k^{\text{iso2}} - m_k^{\text{iso1}}}{f} \quad (2)$$

( $m^{\text{iso1}}$ ,  $m^{\text{iso2}}$  are the atomic masses of the isotope at start and at end; *f* is the appropriate scale factor between 10 and 10 000 constant for all *k*; index *k* runs over all atoms of the molecule; all  $\Delta m_k$  are collected in the vector  $\Delta \mathbf{m}$ , which defines the mass

reaction coordinate) eq 1 is solved:

$$\mathbf{K}_a \mathbf{a}_\mu = (\omega_\mu^a)^2 \mathbf{a}_\mu \quad (3a)$$

$$\mathbf{K}_b \mathbf{b}_\mu = (\omega_\mu^b)^2 \mathbf{b}_\mu \quad (3b)$$

where  $\mathbf{a}_\mu$  and  $\mathbf{b}_\mu$  denote generalized mass-weighted normal modes calculated at  $t_a$  and  $t_b$ , respectively, and  $\mathbf{K}_a = \mathbf{K}(t_a)$ ,  $\mathbf{K}_b = \mathbf{K}(t_b)$ . In the case of isotopomers, the force constant matrices are identical ( $\mathbf{F}_a = \mathbf{F}_b$ ) whereas as a result of mass-weighting  $\mathbf{K}_a \neq \mathbf{K}_b$  holds.

For the purpose of correlating the vibrational modes at  $t_a$  and  $t_b$ , the eigenvectors are rotated to maximize the overlap between them as given by their scalar products. If the eigenvectors  $\mathbf{a}_\mu$  and  $\mathbf{b}_\mu$  are collected in the ( $N * N_{\text{vib}}$ ) matrices  $\mathbf{A}$  and  $\mathbf{B}$ :

$$\mathbf{A} = (\mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_\mu, \dots, \mathbf{a}_{N_{\text{vib}}}) \quad (4a)$$

$$\mathbf{B} = (\mathbf{b}_1, \mathbf{b}_2, \dots, \mathbf{b}_\mu, \dots, \mathbf{b}_{N_{\text{vib}}}) \quad (4b)$$

then the overlap matrix between  $\mathbf{A}$  and  $\mathbf{B}$  will be defined as

$$\mathbf{S}_{BA} = \mathbf{B}^+ \mathbf{A} \quad (5a)$$

with elements

$$S_{ab} = \mathbf{b}_\mu^+ \mathbf{a}_\nu \quad (5b)$$

With the overlap matrix  $\mathbf{S}_{AB}$ , a transformation matrix  $\mathbf{T}$  is defined<sup>16</sup>

$$\mathbf{T} = (\mathbf{S}_{BA}^+ \mathbf{S}_{BA})^{-1/2} \mathbf{S}_{BA}^+ \quad (6)$$

which fulfills the condition

$$\text{Tr}(\mathbf{B}^+ \mathbf{B}') = \max \quad (7)$$

with

$$\mathbf{B} \approx \mathbf{B}' = \mathbf{A} \mathbf{T} \quad (8)$$

and

$$\mathbf{T} \mathbf{T}^+ = \mathbf{I} \quad (9)$$

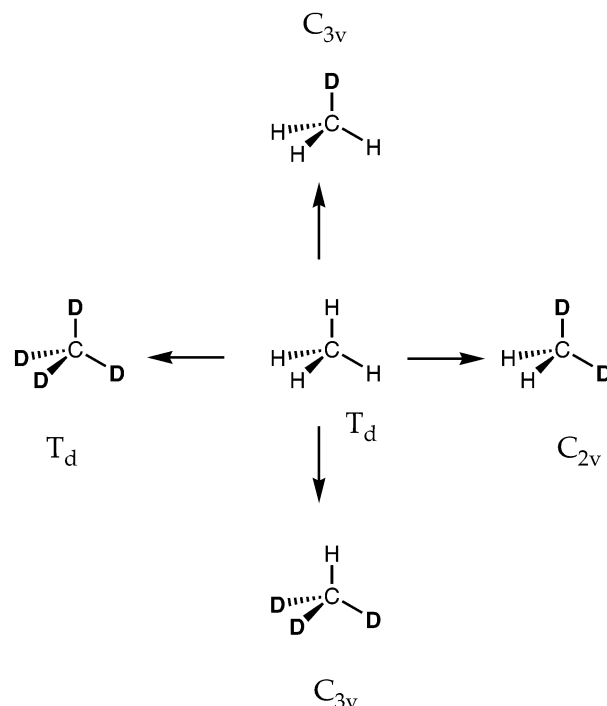
The transformation  $\mathbf{T}$  leads to an image  $\mathbf{B}'$  of matrix  $\mathbf{B}$  in the space  $V^A$ . It is not possible to find such a transformation  $\mathbf{T}$  that  $\mathbf{B}' = \mathbf{B}$  because vectors  $\mathbf{a}_\mu$  and  $\mathbf{b}_\mu$  span different spaces  $V^A$  and  $V^B$ , respectively.

For the purpose of relating  $N_i$  vectors  $\mathbf{b}_\mu$  of space  $V^B$  with subspace  $V_i^A$  of dimension  $N_i$  (1: nondegenerate vibrational modes; 2, 3, ...: degenerate vibrational modes), an amplitude

$$A_\lambda^i = \frac{1}{N_i} \sum_{\mu=1}^{N_i} T_{\mu i, \lambda}^2 \quad (10)$$

has been defined. Those  $N_i$  normal mode vectors  $\mathbf{b}_\mu$  with largest amplitude values  $A_\lambda^i$  can be assigned to space  $V_i^A$ . The procedure of finding image vectors  $\mathbf{b}'_\mu$ , which mimic vectors  $\mathbf{b}_\mu$  in space  $V^B$ , is the only way of connecting the vectors of space  $V^A$  and  $V^B$ .

## SCHEME 1



**TABLE 1: Correlation of the Vibrational Mode Frequencies of the Five Isotopomers of Methane<sup>a</sup>**

CH <sub>4</sub>		CDH <sub>3</sub>		CD <sub>2</sub> H <sub>2</sub>		CD <sub>3</sub> H		CD <sub>4</sub>	
$\omega_\mu$	$T_d$	$\omega_\mu$	$C_{3v}$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$C_{3v}$	$\omega_\mu$	$T_d$
1357	t <sub>2</sub>	1351	a <sub>1</sub>	1061	a <sub>1</sub>	1034	a <sub>1</sub>	1025	t <sub>2</sub>
1357	t <sub>2</sub>	1198	e	1276	b <sub>1</sub>	1063	e	1025	t <sub>2</sub>
1357	t <sub>2</sub>	1198	e	1126	b <sub>2</sub>	1063	e	1025	t <sub>2</sub>
1579	e	1517	e	1368	a <sub>2</sub>	1330	e	1117	e
1579	e	1517	e	1480	a <sub>1</sub>	1330	e	1117	e
3046	a <sub>1</sub>	2291	a <sub>1</sub>	2243	a <sub>1</sub>	2198	a <sub>1</sub>	2154	a <sub>1</sub>
3162	t <sub>2</sub>	3162	e	3162	b <sub>2</sub>	2342	e	2342	t <sub>2</sub>
3162	t <sub>2</sub>	3162	e	2342	b <sub>1</sub>	2342	e	2342	t <sub>2</sub>
3162	t <sub>2</sub>	3080	a <sub>1</sub>	3110	a <sub>1</sub>	3137	a <sub>1</sub>	2342	t <sub>2</sub>

<sup>a</sup> Unscaled frequencies in cm<sup>-1</sup>. B3LYP/6-31G(d,p) calculations. Frequencies in one row correlate with each other.

Finally, vectors  $\mathbf{a}_\mu$  in subspaces  $V_i^A$  are rotated according to

$$\mathbf{a}_{\mu i} = \sum_{\nu=1}^{N_i} \mathbf{a}_{\nu i} \mathbf{R}_{\nu i, \mu i}^i \quad (11)$$

where  $\mathbf{R}_i$  is the rotation matrix associated with space  $V_i^A$

$$\mathbf{R}^i = [(\mathbf{S}_{BA}^i)^+ \mathbf{S}_{BA}^i]^{-1/2} (\mathbf{S}_{BA}^i)^+ \quad (12)$$

and  $\mathbf{S}_{BA}^i$  is the overlap matrix for space  $V_i^A$  given by

$$(\mathbf{S}_{BA}^i)_{\mu i, \nu i} = \mathbf{b}_{\mu i}^+ \mathbf{a}_{\nu i} \quad \mu i, \nu i = 1, \dots, N_i \quad (13)$$

In this way, a correct ordering of degenerate modes spanning subspace  $V_i^A$  is guaranteed.

One can test the assignments made by calculating the final overlap matrix  $\mathbf{S}_{BA}$  according to eq 14, which should be close to diagonal.

$$(\mathbf{S}_{BA})_{\mu \nu} = \mathbf{b}_{\mu i}^+ \mathbf{a}_{\nu i} \quad (14)$$

If the smallest value of  $\mathbf{S}_{BA}$  is smaller than a threshold value

**TABLE 2: Correlation of the Vibrational Frequencies of the 13 (H,D)-Isotopomers of Benzene<sup>a</sup>**

C <sub>6</sub> H <sub>6</sub>		C <sub>6</sub> (DH) <sub>3</sub>		C <sub>6</sub> D <sub>6</sub>		C <sub>6</sub> DH <sub>5</sub>		1,2-C <sub>6</sub> D <sub>2</sub> H <sub>4</sub>		1,3-C <sub>6</sub> D <sub>2</sub> H <sub>4</sub>		1,4-C <sub>6</sub> D <sub>2</sub> H <sub>4</sub>	
$\omega_\mu$	$D_{6h}$	$\omega_\mu$	$D_{3h}$	$\omega_\mu$	$D_{6h}$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$D_{2h}$
414	e <sub>2u</sub>	386	e''	361	e <sub>2u</sub>	414	a <sub>2</sub>	403	b <sub>2</sub>	402	b <sub>2</sub>	414	a <sub>u</sub>
414	e <sub>2u</sub>	386	e''	361	e <sub>2u</sub>	393	b <sub>2</sub>	384	a <sub>2</sub>	386	a <sub>2</sub>	374	b <sub>1u</sub>
621	e <sub>2g</sub>	607	e'	592	e <sub>2g</sub>	618	b <sub>1</sub>	609	b <sub>1</sub>	610	a <sub>1</sub>	615	b <sub>1g</sub>
621	e <sub>2g</sub>	607	e'	592	e <sub>2g</sub>	614	a <sub>1</sub>	612	a <sub>1</sub>	612	b <sub>1</sub>	608	a <sub>g</sub>
694	a <sub>2u</sub>	545	a <sub>2</sub> ''	509	a <sub>2u</sub>	622	b <sub>2</sub>	591	b <sub>2</sub>	582	b <sub>2</sub>	611	b <sub>1u</sub>
718	b <sub>2g</sub>	714	a <sub>2</sub> ''	615	b <sub>2g</sub>	714	b <sub>2</sub>	676	a <sub>2</sub>	714	b <sub>2</sub>	648	b <sub>3g</sub>
865	e <sub>1g</sub>	719	e <sub>2</sub> ''	673	e <sub>1g</sub>	865	a <sub>2</sub>	782	a <sub>2</sub>	830	b <sub>2</sub>	865	b <sub>2g</sub>
865	e <sub>1g</sub>	719	e <sub>2</sub> ''	673	e <sub>1g</sub>	792	b <sub>2</sub>	797	b <sub>2</sub>	719	a <sub>2</sub>	750	b <sub>3g</sub>
974	e <sub>2u</sub>	934	e <sub>2</sub> ''	791	e <sub>2u</sub>	974	a <sub>2</sub>	960	b <sub>2</sub>	934	a <sub>2</sub>	974	a <sub>u</sub>
974	e <sub>2u</sub>	934	e <sub>2</sub> ''	791	e <sub>2u</sub>	934	b <sub>2</sub>	900	a <sub>2</sub>	934	b <sub>2</sub>	879	b <sub>1u</sub>
1013	b <sub>2g</sub>	934	a <sub>2</sub> ''	837	b <sub>2g</sub>	1003	b <sub>2</sub>	998	a <sub>2</sub>	991	b <sub>2</sub>	978	b <sub>3g</sub>
1018	b <sub>1u</sub>	975	a <sub>1</sub> '	978	b <sub>1u</sub>	1003	a <sub>1</sub>	891	b <sub>1</sub>	854	a <sub>1</sub>	1002	b <sub>2u</sub>
1020	a <sub>1g</sub>	1019	a <sub>1</sub> '	972	a <sub>1g</sub>	1019	a <sub>1</sub>	858	a <sub>1</sub>	990	a <sub>1</sub>	1004	a <sub>g</sub>
1067	e <sub>1u</sub>	851	e <sub>1</sub> '	831	e <sub>1u</sub>	1063	a <sub>1</sub>	1005	b <sub>1</sub>	896	b <sub>1</sub>	1059	b <sub>2u</sub>
1067	e <sub>1u</sub>	851	e <sub>1</sub> '	831	e <sub>1u</sub>	876	b <sub>1</sub>	1002	a <sub>1</sub>	1019	a <sub>1</sub>	838	b <sub>3u</sub>
1180	b <sub>2u</sub>	928	a <sub>2</sub> '	841	b <sub>2u</sub>	1111	b <sub>1</sub>	1079	a <sub>1</sub>	1085	b <sub>1</sub>	1134	b <sub>3u</sub>
1203	e <sub>2g</sub>	1125	e <sub>2</sub> '	878	e <sub>2g</sub>	1203	a <sub>1</sub>	1158	b <sub>1</sub>	1128	a <sub>1</sub>	1203	a <sub>g</sub>
1203	e <sub>2g</sub>	1125	e <sub>2</sub> '	878	e <sub>2g</sub>	1188	b <sub>1</sub>	1190	a <sub>1</sub>	1196	b <sub>1</sub>	927	b <sub>1g</sub>
1356	b <sub>2u</sub>	1303	a <sub>2</sub> '	1346	b <sub>2u</sub>	1344	b <sub>1</sub>	1352	a <sub>1</sub>	1323	b <sub>1</sub>	1348	b <sub>3u</sub>
1381	a <sub>2g</sub>	1358	a <sub>2</sub> '	1074	a <sub>2g</sub>	1361	b <sub>1</sub>	1305	b <sub>1</sub>	1359	b <sub>1</sub>	1338	b <sub>1g</sub>
1525	e <sub>1u</sub>	1461	e <sub>1</sub> '	1373	e <sub>1u</sub>	1519	a <sub>1</sub>	1497	a <sub>1</sub>	1503	b <sub>1</sub>	1513	b <sub>2u</sub>
1525	e <sub>1u</sub>	1461	e <sub>1</sub> '	1373	e <sub>1u</sub>	1494	b <sub>1</sub>	1481	b <sub>1</sub>	1466	a <sub>1</sub>	1454	b <sub>3u</sub>
1653	e <sub>2g</sub>	1633	e <sub>2</sub> '	1610	e <sub>2g</sub>	1648	a <sub>1</sub>	1642	b <sub>1</sub>	1640	b <sub>1</sub>	1642	a <sub>g</sub>
1653	e <sub>2g</sub>	1633	e <sub>2</sub> '	1610	e <sub>2g</sub>	1646	b <sub>1</sub>	1639	a <sub>1</sub>	1639	a <sub>1</sub>	1637	b <sub>1g</sub>
3173	b <sub>1u</sub>	2358	a <sub>1</sub> '	2337	b <sub>1u</sub>	2359	a <sub>1</sub>	2348	b <sub>1</sub>	2359	a <sub>1</sub>	2358	b <sub>2u</sub>
3182	e <sub>2g</sub>	2359	e <sub>2</sub> '	2349	e <sub>2g</sub>	3182	b <sub>1</sub>	2369	a <sub>1</sub>	3178	a <sub>1</sub>	3182	b <sub>1g</sub>
3182	e <sub>2g</sub>	2359	e <sub>2</sub> '	2349	e <sub>2g</sub>	3175	a <sub>1</sub>	3177	b <sub>1</sub>	2359	b <sub>1</sub>	2360	a <sub>g</sub>
3198	e <sub>1u</sub>	3190	e <sub>1</sub> '	2369	e <sub>1u</sub>	3198	b <sub>1</sub>	3195	b <sub>1</sub>	3190	a <sub>1</sub>	3198	b <sub>3u</sub>
3198	e <sub>1u</sub>	3190	e <sub>1</sub> '	2369	e <sub>1u</sub>	3190	a <sub>1</sub>	3185	a <sub>1</sub>	3190	b <sub>1</sub>	3181	b <sub>2u</sub>
3209	a <sub>1g</sub>	3191	a <sub>1</sub> '	2381	a <sub>1g</sub>	3206	a <sub>1</sub>	3204	a <sub>1</sub>	3203	a <sub>1</sub>	3200	a <sub>g</sub>
1,2,3-C <sub>6</sub> D <sub>3</sub> H <sub>3</sub>		1,2,4-C <sub>6</sub> D <sub>3</sub> H <sub>3</sub>		1,2,3,4-C <sub>6</sub> D <sub>4</sub> H <sub>2</sub>		1,2,3,5-C <sub>6</sub> D <sub>4</sub> H <sub>2</sub>		1,2,4,5-C <sub>6</sub> D <sub>4</sub> H <sub>2</sub>		C <sub>6</sub> D <sub>5</sub> H			
$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$C_s$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$D_{2h}$	$\omega_\mu$	$C_{2v}$		
386	a <sub>2</sub>	400	a <sub>2</sub> ''	384	a <sub>2</sub>	386	a <sub>2</sub>	390	b <sub>1u</sub>	376	b <sub>2</sub>		
383	b <sub>2</sub>	370	a <sub>2</sub> ''	368	b <sub>2</sub>	368	b <sub>2</sub>	361	a <sub>u</sub>	361	a <sub>2</sub>		
606	b <sub>1</sub>	609	a <sub>1</sub> '	602	b <sub>1</sub>	603	b <sub>1</sub>	599	b <sub>1g</sub>	595	b <sub>1</sub>		
606	a <sub>1</sub>	604	a <sub>1</sub> '	599	a <sub>1</sub>	600	a <sub>1</sub>	604	a <sub>g</sub>	598	a <sub>1</sub>		
558	b <sub>2</sub>	573	a <sub>2</sub> ''	544	b <sub>2</sub>	537	b <sub>2</sub>	560	b <sub>1u</sub>	526	b <sub>2</sub>		
670	b <sub>2</sub>	647	a <sub>2</sub> '	640	a <sub>2</sub>	646	b <sub>2</sub>	631	b <sub>3g</sub>	628	b <sub>2</sub>		
790	b <sub>2</sub>	718	a <sub>2</sub> ''	698	a <sub>2</sub>	718	b <sub>2</sub>	673	b <sub>2g</sub>	673	a <sub>2</sub>		
719	a <sub>2</sub>	782	a <sub>2</sub> ''	746	b <sub>2</sub>	719	a <sub>2</sub>	779	b <sub>3g</sub>	719	b <sub>2</sub>		
934	a <sub>2</sub>	934	a <sub>2</sub> ''	873	b <sub>2</sub>	934	a <sub>2</sub>	791	a <sub>u</sub>	791	a <sub>2</sub>		
840	b <sub>2</sub>	873	a <sub>2</sub> ''	822	a <sub>2</sub>	810	b <sub>2</sub>	931	b <sub>1u</sub>	825	b <sub>2</sub>		
991	b <sub>2</sub>	976	a <sub>2</sub> '	976	a <sub>2</sub>	934	b <sub>2</sub>	936	b <sub>3g</sub>	934	b <sub>2</sub>		
854	a <sub>1</sub>	837	a <sub>1</sub> '	863	b <sub>1</sub>	851	a <sub>1</sub>	835	b <sub>2u</sub>	833	a <sub>1</sub>		
989	a <sub>1</sub>	861	a <sub>1</sub> '	836	a <sub>1</sub>	975	a <sub>1</sub>	880	a <sub>g</sub>	879	a <sub>1</sub>		
860	b <sub>1</sub>	990	a <sub>1</sub> '	951	b <sub>1</sub>	836	b <sub>1</sub>	991	b <sub>2u</sub>	974	a <sub>1</sub>		
1004	a <sub>1</sub>	941	a <sub>1</sub> '	858	a <sub>1</sub>	1004	a <sub>1</sub>	837	b <sub>3u</sub>	836	b <sub>1</sub>		
908	b <sub>1</sub>	1003	a <sub>1</sub> '	988	a <sub>1</sub>	866	b <sub>1</sub>	1085	b <sub>3u</sub>	858	b <sub>1</sub>		
1124	a <sub>1</sub>	1169	a <sub>1</sub> '	991	b <sub>1</sub>	1121	a <sub>1</sub>	988	a <sub>g</sub>	990	a <sub>1</sub>		
1179	b <sub>1</sub>	1083	a <sub>1</sub> '	1165	a <sub>1</sub>	965	b <sub>1</sub>	984	b <sub>1g</sub>	1003	b <sub>1</sub>		
1252	b <sub>1</sub>	1299	a <sub>1</sub> '	1347	a <sub>1</sub>	1251	b <sub>1</sub>	1346	b <sub>3u</sub>	1198	b <sub>1</sub>		
1351	b <sub>1</sub>	1348	a <sub>1</sub> '	1214	b <sub>1</sub>	1348	b <sub>1</sub>	1286	b <sub>1g</sub>	1346	b <sub>1</sub>		
1458	a <sub>1</sub>	1491	a <sub>1</sub> '	1415	a <sub>1</sub>	1453	a <sub>1</sub>	1391	b <sub>2u</sub>	1382	a <sub>1</sub>		
1478	b <sub>1</sub>	1435	a <sub>1</sub> '	1466	b <sub>1</sub>	1426	b <sub>1</sub>	1474	b <sub>3u</sub>	1435	b <sub>1</sub>		
1633	b <sub>1</sub>	1635	a <sub>1</sub> '	1628	a <sub>1</sub>	1623	b <sub>1</sub>	1628	b <sub>1g</sub>	1616	a <sub>1</sub>		
1635	a <sub>1</sub>	1630	a <sub>1</sub> '	1625	b <sub>1</sub>	1628	a <sub>1</sub>	1621	a <sub>g</sub>	1620	b <sub>1</sub>		
2344	a <sub>1</sub>	2348	a <sub>1</sub> '	2342	b <sub>1</sub>	2344	a <sub>1</sub>	2347	b <sub>2u</sub>	2340	a <sub>1</sub>		
2359	b <sub>1</sub>	2359	a <sub>1</sub> '	2353	a <sub>1</sub>	2359	b <sub>1</sub>	2349	b <sub>1g</sub>	2349	b <sub>1</sub>		
2374	a <sub>1</sub>	2369	a <sub>1</sub> '	2365	b <sub>1</sub>	2359	a <sub>1</sub>	2370	a <sub>g</sub>	2359	a <sub>1</sub>		
3190	b <sub>1</sub>	3191	a <sub>1</sub> '	3182	b <sub>1</sub>	2374	a <sub>1</sub>	2369	b <sub>3u</sub>	2369	b <sub>1</sub>		
3178	a <sub>1</sub>	3182	a <sub>1</sub> '	2376	a <sub>1</sub>	3190	b <sub>1</sub>	3190	b <sub>2u</sub>	2378	a <sub>1</sub>		
3202	a <sub>1</sub>	3199	a <sub>1</sub> '	3199	a <sub>1</sub>	3191	a <sub>1</sub>	3191	a <sub>g</sub>	3191	a <sub>1</sub>		

<sup>a</sup> Unscaled frequencies in cm<sup>-1</sup>. B3LYP/6-31G(d,p) calculations. Frequencies in one row correlate with each other.

$S_{\min} = 0.95$ , the assignment will be considered weak and diabatic mode ordering is repeated for smaller mass increments.

In case of a change in symmetry, the condition that the subspaces conserve all their dimensions  $N_1$  along the reaction

path and map one to one on each other was relieved and instead only the overlap criterion kept. In this way it is possible to correlate degenerate vibrational eigenstates of a given symmetry with nondegenerate eigenstates of lower symmetry.





**TABLE 3: Comparison of Scaled Vibrational Frequencies and Experimental Frequencies for the (H,D)-Isotopomers of Benzene<sup>a</sup>**

C <sub>6</sub> H <sub>6</sub>		C <sub>6</sub> (DH) <sub>3</sub>			C <sub>6</sub> D <sub>6</sub>			C <sub>6</sub> DH <sub>5</sub>		1,2-C <sub>6</sub> D <sub>2</sub> H <sub>4</sub>		1,3-C <sub>6</sub> D <sub>2</sub> H <sub>4</sub>	
$\omega_\mu$	$D_{6h}$	$\omega_\mu$	$\omega_{\text{exp}}$	$D_{3h}$	$\omega_\mu$	$\omega_{\text{exp}}$	$D_{6h}$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$C_{2v}$
398	e <sub>2u</sub>	371	368	e''	347	345	e <sub>2u</sub>	398	a <sub>2</sub>	387	b <sub>2</sub>	386	b <sub>2</sub>
398	e <sub>2u</sub>	371	368	e''	347	345	e <sub>2u</sub>	378	b <sub>2</sub>	369	a <sub>2</sub>	371	a <sub>2</sub>
606	e <sub>2g</sub>	592	592	e'	578	579	e <sub>2g</sub>	603	b <sub>1</sub>	594	b <sub>1</sub>	595	a <sub>1</sub>
606	e <sub>2g</sub>	592	592	e'	578	579	e <sub>2g</sub>	599	a <sub>1</sub>	597	a <sub>1</sub>	597	b <sub>1</sub>
673	a <sub>2u</sub>	528	531	a <sub>2</sub> '	494	496	a <sub>2u</sub>	603	b <sub>2</sub>	573	b <sub>2</sub>	564	b <sub>2</sub>
707	b <sub>2g</sub>	703	697	a <sub>2</sub> '	606	599	b <sub>2g</sub>	703	b <sub>2</sub>	666	a <sub>2</sub>	703	b <sub>2</sub>
846	e <sub>1g</sub>	703	708	e''	658	660	e <sub>1g</sub>	846	a <sub>2</sub>	765	a <sub>2</sub>	812	b <sub>2</sub>
846	e <sub>1g</sub>	703	708	e''	658	660	e <sub>1g</sub>	775	b <sub>2</sub>	780	b <sub>2</sub>	703	a <sub>2</sub>
967	e <sub>2u</sub>	927	924	e''	785	787	e <sub>2u</sub>	967	a <sub>2</sub>	953	b <sub>2</sub>	927	a <sub>2</sub>
967	e <sub>2u</sub>	927	924	e''	785	787	e <sub>2u</sub>	927	b <sub>2</sub>	894	a <sub>2</sub>	927	b <sub>2</sub>
990	b <sub>2g</sub>	913	917	a <sub>2</sub> '	818	829	b <sub>2g</sub>	980	b <sub>2</sub>	975	a <sub>2</sub>	968	b <sub>2</sub>
1010	b <sub>1u</sub>	967	1004	a <sub>1</sub> '	970	970	b <sub>1u</sub>	995	a <sub>1</sub>	884	b <sub>1</sub>	847	a <sub>1</sub>
993	a <sub>1g</sub>	992	956	a <sub>1</sub> '	946	945	a <sub>1g</sub>	992	a <sub>1</sub>	835	a <sub>1</sub>	964	a <sub>1</sub>
1037	e <sub>1u</sub>	827	833	e'	808	814	e <sub>1u</sub>	1033	a <sub>1</sub>	977	b <sub>1</sub>	871	b <sub>1</sub>
1037	e <sub>1u</sub>	827	833	e'	808	814	e <sub>1u</sub>	851	b <sub>1</sub>	974	a <sub>1</sub>	990	a <sub>1</sub>
1146	b <sub>2u</sub>	901	912	a <sub>2</sub> '	817	824	b <sub>2u</sub>	1079	b <sub>1</sub>	1048	a <sub>1</sub>	1054	b <sub>1</sub>
1178	e <sub>2g</sub>	1102	1101	e'	860	869	e <sub>2g</sub>	1178	a <sub>1</sub>	1134	b <sub>1</sub>	1105	a <sub>1</sub>
1178	e <sub>2g</sub>	1102	1101	e'	860	869	e <sub>2g</sub>	1163	b <sub>1</sub>	1165	a <sub>1</sub>	1171	b <sub>1</sub>
1309	b <sub>2u</sub>	1258	1259	a <sub>2</sub> '	1299	1282	b <sub>2u</sub>	1297	b <sub>1</sub>	1305	a <sub>1</sub>	1277	b <sub>1</sub>
1350	a <sub>2g</sub>	1328	1321	a <sub>2</sub> '	1050	1059	a <sub>2g</sub>	1330	b <sub>1</sub>	1276	b <sub>1</sub>	1328	b <sub>1</sub>
1482	e <sub>1u</sub>	1420	1414	e'	1334	1333	e <sub>1u</sub>	1476	a <sub>1</sub>	1455	a <sub>1</sub>	1461	b <sub>1</sub>
1482	e <sub>1u</sub>	1420	1414	e'	1334	1333	e <sub>1u</sub>	1452	b <sub>1</sub>	1439	b <sub>1</sub>	1425	a <sub>1</sub>
1599	e <sub>2g</sub>	1580	1580	e'	1557	1557	e <sub>2g</sub>	1594	a <sub>1</sub>	1588	b <sub>1</sub>	1586	b <sub>1</sub>
1599	e <sub>2g</sub>	1580	1580	e'	1557	1557	e <sub>2g</sub>	1592	b <sub>1</sub>	1585	a <sub>1</sub>	1585	a <sub>1</sub>
3057	b <sub>1u</sub>	2272	2294	a <sub>2</sub> '	2252	2284	b <sub>1u</sub>	2273	a <sub>1</sub>	2262	b <sub>1</sub>	2273	a <sub>1</sub>
3056	e <sub>2g</sub>	2266	2282	e'	2256	2274	e <sub>2g</sub>	3056	b <sub>1</sub>	2275	a <sub>1</sub>	3052	a <sub>1</sub>
3056	e <sub>2g</sub>	2266	2282	e'	2256	2274	e <sub>2g</sub>	3049	a <sub>1</sub>	3051	b <sub>1</sub>	2266	b <sub>1</sub>
3064	e <sub>1u</sub>	3056	3063	e'	2270	2288	e <sub>1u</sub>	3064	b <sub>1</sub>	3061	b <sub>1</sub>	3056	a <sub>1</sub>
3064	e <sub>1u</sub>	3056	3063	e'	2270	2288	e <sub>1u</sub>	3056	a <sub>1</sub>	3052	a <sub>1</sub>	3056	b <sub>1</sub>
3073	a <sub>1g</sub>	3056	3065	a <sub>1</sub> '	2280	2303	a <sub>1g</sub>	3070	a <sub>1</sub>	3068	a <sub>1</sub>	3067	a <sub>1</sub>
1,4-C <sub>6</sub> D <sub>2</sub> H <sub>4</sub>		1,2,3-C <sub>6</sub> D <sub>3</sub> H <sub>3</sub>		1,2,4-C <sub>6</sub> D <sub>3</sub> H <sub>3</sub>		1,2,3,4-C <sub>6</sub> D <sub>4</sub> H <sub>2</sub>		1,2,3,5-C <sub>6</sub> D <sub>2</sub> H <sub>4</sub>		1,2,4,5-C <sub>6</sub> D <sub>4</sub> H <sub>2</sub>		C <sub>6</sub> D <sub>5</sub> H	
$\omega_\mu$	$D_{2h}$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$C_s$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$C_{2v}$	$\omega_\mu$	$D_{2h}$	$\omega_\mu$	$C_{2v}$
398	a <sub>u</sub>	382	a <sub>2</sub>	385	a''	369	a <sub>2</sub>	371	a <sub>2</sub>	375	b <sub>1u</sub>	363	b <sub>2</sub>
360	b <sub>1u</sub>	379	b <sub>2</sub>	356	a''	354	b <sub>2</sub>	354	b <sub>2</sub>	347	a <sub>u</sub>	347	a <sub>2</sub>
600	b <sub>1g</sub>	591	b <sub>1</sub>	594	a'	587	b <sub>1</sub>	588	b <sub>1</sub>	585	b <sub>1g</sub>	581	b <sub>1</sub>
593	a <sub>g</sub>	591	a <sub>1</sub>	589	a'	585	a <sub>1</sub>	586	a <sub>1</sub>	589	a <sub>g</sub>	584	a <sub>1</sub>
592	b <sub>1u</sub>	541	b <sub>2</sub>	556	a''	528	b <sub>2</sub>	521	b <sub>2</sub>	543	b <sub>1u</sub>	510	b <sub>2</sub>
638	b <sub>3g</sub>	656	b <sub>2</sub>	637	a'	630	a <sub>2</sub>	636	b <sub>2</sub>	621	b <sub>3g</sub>	618	b <sub>2</sub>
846	b <sub>2g</sub>	775	b <sub>2</sub>	702	a''	683	a <sub>2</sub>	702	b <sub>2</sub>	658	b <sub>2g</sub>	658	a <sub>2</sub>
734	b <sub>3g</sub>	706	a <sub>2</sub>	765	a''	730	b <sub>2</sub>	703	a <sub>2</sub>	762	b <sub>3g</sub>	703	b <sub>2</sub>
967	a <sub>u</sub>	935	a <sub>2</sub>	927	a''	867	b <sub>2</sub>	927	a <sub>2</sub>	785	a <sub>u</sub>	785	a <sub>2</sub>
873	b <sub>1u</sub>	841	b <sub>2</sub>	867	a''	816	a <sub>2</sub>	804	b <sub>2</sub>	924	b <sub>1u</sub>	819	b <sub>2</sub>
956	b <sub>3g</sub>	973	b <sub>2</sub>	954	a'	954	a <sub>2</sub>	913	b <sub>2</sub>	915	b <sub>3g</sub>	913	b <sub>2</sub>
994	b <sub>2u</sub>	847	a <sub>1</sub>	830	a'	856	b <sub>1</sub>	844	a <sub>1</sub>	828	b <sub>2u</sub>	826	a <sub>1</sub>
977	a <sub>g</sub>	962	a <sub>1</sub>	838	a'	814	a <sub>1</sub>	949	a <sub>1</sub>	857	a <sub>g</sub>	856	a <sub>1</sub>
1029	b <sub>2u</sub>	837	b <sub>1</sub>	962	a'	924	b <sub>1</sub>	812	b <sub>1</sub>	963	b <sub>2u</sub>	947	a <sub>1</sub>
814	b <sub>3u</sub>	977	a <sub>1</sub>	915	a'	834	a <sub>1</sub>	976	a <sub>1</sub>	813	b <sub>3u</sub>	812	b <sub>1</sub>
1101	b <sub>3u</sub>	885	b <sub>1</sub>	974	a'	960	a <sub>1</sub>	841	b <sub>1</sub>	1054	b <sub>3u</sub>	833	b <sub>1</sub>
1178	a <sub>g</sub>	1101	a <sub>1</sub>	1145	a'	970	b <sub>1</sub>	1098	a <sub>1</sub>	967	a <sub>g</sub>	969	a <sub>1</sub>
908	b <sub>1g</sub>	1154	b <sub>1</sub>	1060	a'	1141	a <sub>1</sub>	945	b <sub>1</sub>	964	b <sub>1g</sub>	982	b <sub>1</sub>
1301	b <sub>3u</sub>	1210	b <sub>1</sub>	1254	a'	1300	a <sub>1</sub>	1208	b <sub>1</sub>	1299	b <sub>3u</sub>	1156	b <sub>1</sub>
1308	b <sub>1g</sub>	1297	b <sub>1</sub>	1318	a'	1187	b <sub>1</sub>	1318	b <sub>1</sub>	1257	b <sub>1g</sub>	1316	b <sub>1</sub>
1470	b <sub>2u</sub>	1421	a <sub>1</sub>	1449	a'	1375	a <sub>1</sub>	1412	a <sub>1</sub>	1352	b <sub>2u</sub>	1343	a <sub>1</sub>
1413	b <sub>3u</sub>	1440	b <sub>1</sub>	1395	a'	1425	b <sub>1</sub>	1386	b <sub>1</sub>	1432	b <sub>3u</sub>	1395	b <sub>1</sub>
1588	a <sub>g</sub>	1577	b <sub>1</sub>	1582	a'	1575	a <sub>1</sub>	1570	b <sub>1</sub>	1575	b <sub>1g</sub>	1563	a <sub>1</sub>
1584	b <sub>1g</sub>	1579	a <sub>1</sub>	1577	a'	1572	b <sub>1</sub>	1575	a <sub>1</sub>	1568	a <sub>g</sub>	1567	b <sub>1</sub>
2272	b <sub>2u</sub>	2266	a <sub>1</sub>	2262	a'	2256	b <sub>1</sub>	2258	a <sub>1</sub>	2261	b <sub>2u</sub>	2254	a <sub>1</sub>
3056	b <sub>1g</sub>	2259	b <sub>1</sub>	2266	a'	2260	a <sub>1</sub>	2266	b <sub>1</sub>	2256	b <sub>1g</sub>	2256	b <sub>1</sub>
2267	a <sub>g</sub>	2273	a <sub>1</sub>	2275	a'	2271	b <sub>1</sub>	2266	a <sub>1</sub>	2276	a <sub>g</sub>	2266	a <sub>1</sub>
3064	b <sub>3u</sub>	3055	b <sub>1</sub>	3057	a'	3049	b <sub>1</sub>	2275	a <sub>1</sub>	2270	b <sub>3u</sub>	2270	b <sub>1</sub>
3048	b <sub>2u</sub>	3044	a <sub>1</sub>	3049	a'	2276	a <sub>1</sub>	3056	b <sub>1</sub>	3056	b <sub>2u</sub>	2278	a <sub>1</sub>
3064	a <sub>g</sub>	3055	a <sub>1</sub>	3063	a'	3063	a <sub>1</sub>	3056	a <sub>1</sub>	3056	a <sub>g</sub>	3056	a <sub>1</sub>

<sup>a</sup> Scaled frequencies in cm<sup>-1</sup>. B3LYP/6-31G(d,p) calculations. The ratios between experimental<sup>31</sup> and calculated frequencies of each mode in C<sub>6</sub>H<sub>6</sub> were taken as individual scaling factors.

new vectors **b** are rotated, but only within the subspaces with dimension larger than one, to obtain the perfect match between degenerate modes (see eqs 11–13). If there are no degenerate vibrational modes, this step is skipped. (5) Finally, the rotated

vectors **b** are rearranged so that they appear in the same order as the set of old vectors **a** mimicked by vectors **b'**. All quantities connected to the vibrational modes (frequencies and symmetry assignments, etc.) are ordered at the same time. (6) The ordering

is tested according to eq 14. If the assignment of one or more ordered vectors **b** is weak, the mass increment from eq 2 will be reduced, a new set of **b** vectors calculated, and the ordering procedure repeated. This will happen frequently if scaling factors lower than 1000 are used.

Test calculations were made for methane and benzene using density functional theory (DFT) with the hybrid functional B3LYP<sup>27–29</sup> and Pople's 6-31G(d,p) basis set.<sup>30</sup> First, the equilibrium geometry, the corresponding force constant matrix, and the vibrational frequencies of these molecules were determined. Then, the algorithm described above was utilized to correlate the vibrational frequencies of the parent compounds stepwise with those of their deuterium isotopomers as indicated in Scheme 1 for methane.

For the methane isotopomers, both situations with conservation of symmetry ( $\text{CH}_4 \rightarrow \text{CD}_4$ ) and with a change of symmetry are encountered ( $\text{CH}_4 \rightarrow \text{CH}_2\text{D}_2$ , etc.). In the second case, the symmetry change occurs when adding  $\Delta m$  (eq 2) to the starting masses and making the first step along the mass reaction path. For a sufficiently large factor  $f$  (eq 2) the change in the vibrational frequencies will be tiny, but large enough to reflect the change in symmetry as detected by stringent symmetry criteria.

Calculations are carried out in the way that a change in symmetry will be always from the higher to the lower symmetry (or the same symmetry; see Scheme 1). Therefore, an avoided crossing of the vibrational mode eigenstates is not possible in the first step. The overlap criterion guarantees that all vibrational modes of the high symmetry form are correctly associated with the vibrational modes of the low symmetry form; in particular in the case of degenerate modes that are converted into nondegenerate modes because of symmetry reduction, a correct correlation is obtained after appropriate rotation among the degenerate modes (see Chapter 2).

After the first step along the mass reaction path the symmetry of the mass reaction complex is retained until the correct masses and the vibrational eigenstates of the isotopomer in question are reached. In this part of the correlation avoided and nonavoided crossings are possible, which are correctly resolved by the diabatic ordering algorithm discussed in the previous chapter.

In Table 1, the vibrational frequencies of the five (H,D)-isotopomers of methane are correlated. The frequencies of the four isotopomers (Scheme 1) were obtained by stepwise conversion of the methane frequencies. Symmetries of the normal modes are automatically determined by the computer program used. This gives an independent test possibility to see whether the symmetries of the correlated isotopomer modes comply with the symmetry correlation tables.<sup>1</sup> For example, the  $t_2$ -modes of  $\text{CH}_4$  must correlate with the  $e$ - and  $a_1$ -symmetrical modes of  $C_{3v}$ -symmetrical  $\text{CDH}_3$  or the  $a_1$ -,  $b_1$ -, and  $b_2$ -symmetrical modes of the  $C_{2v}$ -symmetrical  $\text{CD}_2\text{H}_2$ , which is fulfilled after diabatic mode ordering (see Table 1).

In Table 2, the vibrational frequencies of the 13 (H,D)-isotopomers of benzene (Scheme 2) are correlated, which are all related to the B3LYP/6-31G(d,p) frequencies of  $\text{C}_6\text{H}_6$ . Again, the frequencies are given in the way as the correlation procedure has ordered them; i.e., they are no longer ordered according to magnitude. In Figure 1, a correlation diagram for the frequencies of benzene and *o*-dideuteriobenzene is given as it was generated by the program DMOD. Although many frequencies  $\omega_\mu(t)$  cross, these are exclusively allowed crossings, as can be verified by the symmetry notations given in Figure 1. Avoided crossings will appear if the vibrational eigenstates of low symmetry forms

are directly correlated with each other. These were also carried out in this work to verify the high symmetry–low symmetry correlations and to further test the program DMOD. There was not a single case in which the two different procedures led to different correlation assignments.

The procedure taken in this work (pairwise correlation of all deuterium isotopomers with the parent molecule) does not lead to any avoided crossings, which means that the character of the vibrational modes is largely retained. This gives the chance of predicting the isotopomer frequencies with considerable accuracy using individual mode scaling factors that accurately reproduce the vibrational frequencies of benzene. In Table 3, scaled isotopomer frequencies obtained in this way are listed and compared in the case of 1,2,3-trideuteriobenzene and hexadeuteriobenzene with the available experimental frequencies.<sup>31,32</sup>

Experimental and scaled B3LYP frequencies are in close agreement deviating only for the  $a_{1g}$ - and  $b_{1u}$ -symmetrical modes close to 1000  $\text{cm}^{-1}$  by more than 30  $\text{cm}^{-1}$  (1,3,5-trideuteriobenzene) and in the case of the CH-stretching modes by 15 to 20  $\text{cm}^{-1}$  (both 1,3,5-trideuteriobenzene and hexadeuteriobenzene). However, the calculated standard deviation for 1,3,5-trideuteriobenzene is 11.9  $\text{cm}^{-1}$  and for hexadeuteriobenzene 9.8  $\text{cm}^{-1}$ . Therefore, we consider the frequencies listed in Table 3 as a set of reliable frequencies for all (H,D)-isotopomers of benzene.

#### 4. Conclusions

A general algorithm has been developed, which makes it possible to correlate the vibrational frequencies of isotopomers independent of whether they possess the same or different point group symmetry. The algorithm is based on the mass reaction coordinate connecting isotopomers of different masses and the diabatic mode ordering of Konkoli, Kraka, and Cremer.<sup>16</sup> Although the mass reaction path does not show any curvature, which makes various simplifications possible, the algorithm was kept in a general form to be used also for rotations of the reaction complex around a curved reaction path. In this way it can be extended to a more general goal, namely, the correlation of the vibrational frequencies of configurational isomers, valence isomers, or even structurally related molecules of different symmetries and different numbers of atoms.

The application of the new method implemented in the DMOD program showed that irrespective of symmetry the vibrational frequencies of isotopomers can easily be correlated. Complete sets of isotopomer frequencies for methane and benzene were obtained. Individual scaling of the calculated harmonic frequencies of the parent molecule benzene leads to reliable isotopomer frequencies, which can be used by experimentalists for the assignment of measured infrared and Raman spectra.

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