Correlation of the Vibrational Spectra of Isotopomers: Theory and Application

Anan Wu and Dieter Cremer*

Department of Theoretical Chemistry, Göteborg University Reutersgatan 2, S-413 20 Göteborg, Sweden

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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.[1−8] 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[9−11] 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 **M**), and the electronic structure of the molecule as reflected by its force constant matrix **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.[2]

If one would be able to exactly identify changes in the vibrational spectra, which accompany a change in either N, **M**, X, or **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.[1−8] 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 **K** while N, X, and **M** are fixed: correlation of the vibrational spectra along a reaction path

(2) changes in **K** and X while N and **M** are fixed: correlation of the vibrational spectra of isomers and conformers

(3) changes in **M** and X while N and **K** are fixed: correlation of isotopomer spectra

(4) changes in **K**, **M**, and X while N is fixed: correlation of the vibrational spectra of valence isomers

(5) Changes in N, **K**, **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[12] and the unified reaction valley approach.[13,14] 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[15]). The problem of correlating the generalized normal modes along the reaction path were solved with a diabatic ordering of the vibrational modes (DMOD),[16] which was used already in a number of reaction mechanism studies.[13,14,17,18]

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 **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).

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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.[1−5,19−25] Best known are the Teller−Redlich product rules[19] or the various sum rules for the vibrational frequencies of isotopomers.[20−22] Teller and later Wilson[23] 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.[24,25] 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[1−5] 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[16] 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;[23−25] 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,[16] 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 $N_{\mathrm{vib}} = 3K - L$ ($L = 5$ 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 Δm. At a given point t_a of the mass reaction path, defined by the path coordinate t, the generalized normal modes $l_\mu^{\mathrm{g}}(t_a)$ and the associated normal-mode frequencies, $\omega_\mu(t_a)$, are calculated by solving

$$\mathbf{K}(t_a) l_\mu^{\mathrm{g}}(t_a) = \omega_\mu{}^2(t)\, l_\mu^{\mathrm{g}}(t_a) \tag{1}$$

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

$$\Delta m_k = \frac{m_k^{\mathrm{iso2}} - m_k^{\mathrm{iso1}}}{f} \tag{2}$$

(m^{iso1}, m^{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 Δm_k are collected in the vector $\Delta\mathbf{m}$, which defines the mass

reaction coordinate) eq 1 is solved:

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

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

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_{vib}) matrices **A** and **B**:

$$\mathbf{A} = (\mathbf{a}_1, \mathbf{a}_2, ..., \mathbf{a}_\mu, ..., \mathbf{a}_{N_{vib}}) \tag{4a}$$

$$\mathbf{B} = (\mathbf{b}_1, \mathbf{b}_2, ..., \mathbf{b}_\mu, ..., \mathbf{b}_{N_{vib}}) \tag{4b}$$

then the overlap matrix between **A** and **B** will be defined as

$$\mathbf{S}_{BA} = \mathbf{B}^+\mathbf{A} \tag{5a}$$

with elements

$$\mathbf{S}_{ab} = \mathbf{b}_\mu^+\mathbf{a}_\nu \tag{5b}$$

With the overlap matrix $\mathbf{S}_{AB}$, a transformation matrix **T** is defined[16]

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

which fulfills the condition

$$\mathrm{Tr}(\mathbf{B}^+\mathbf{B}') = \max \tag{7}$$

with

$$\mathbf{B} \approx \mathbf{B}' = \mathbf{AT} \tag{8}$$

and

$$\mathbf{TT}^+ = \mathbf{I} \tag{9}$$

The transformation **T** leads to an image **B′** of matrix **B** in the space V^A. It is not possible to find such a transformation **T** that **B′** = **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

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

has been defined. Those N_i normal mode vectors $\mathbf{b}_\mu$ with largest amplitude values A_λ^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

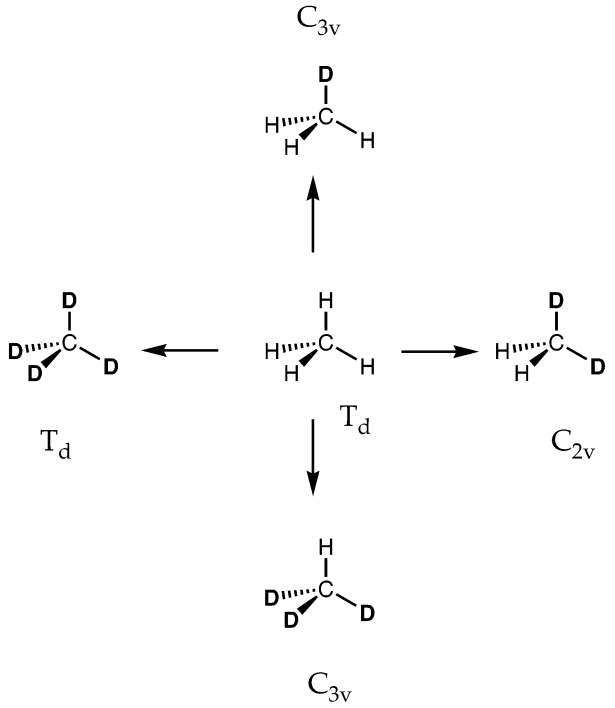


TABLE 1: Correlation of the Vibrational Mode Frequencies of the Five Isotopomers of Methane[a]

CH_4		CDH_3		CD_2H_2		CD_3H		CD_4	
ω_μ	T_d	ω_μ	C_{3v}	ω_μ	C_{2v}	ω_μ	C_{3v}	ω_μ	T_d
1357	t_2	1351	a_1	1061	a_1	1034	a_1	1025	t_2
1357	t_2	1198	e	1276	b_1	1063	e	1025	t_2
1357	t_2	1198	e	1126	b_2	1063	e	1025	t_2
1579	e	1517	e	1368	a_2	1330	e	1117	e
1579	e	1517	e	1480	a_1	1330	e	1117	e
3046	a_1	2291	a_1	2243	a_1	2198	a_1	2154	a_1
3162	t_2	3162	e	3162	b_2	2342	e	2342	t_2
3162	t_2	3162	e	2342	b_1	2342	e	2342	t_2
3162	t_2	3080	a_1	3110	a_1	3137	a_1	2342	t_2

[a] Unscaled frequencies in cm^{-1}. 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

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

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

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

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

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

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.

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

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

TABLE 2: Correlation of the Vibrational Frequencies of the 13 (H,D)-Isotopomers of Benzene[a]

C_6H_6		$C_6(DH)_3$		C_6D_6		C_6DH_5		1,2-$C_6D_2H_4$		1,3-$C_6D_2H_4$		1,4-$C_6D_2H_4$	
ω_μ	D_{6h}	ω_μ	D_{3h}	ω_μ	D_{6h}	ω_μ	C_{2v}	ω_μ	C_{2v}	ω_μ	C_{2v}	ω_μ	D_{2h}
414	e_{2u}	386	e″	361	e_{2u}	414	a_2	403	b_2	402	b_2	414	a_u
414	e_{2u}	386	e″	361	e_{2u}	393	b_2	384	a_2	386	a_2	374	b_{1u}
621	e_{2g}	607	e′	592	e_{2g}	618	b_1	609	b_1	610	a_1	615	b_{1g}
621	e_{2g}	607	e′	592	e_{2g}	614	a_1	612	a_1	612	b_1	608	a_g
694	a_{2u}	545	a_2''	509	a_{2u}	622	b_2	591	b_2	582	b_2	611	b_{1u}
718	b_{2g}	714	a_2''	615	b_{2g}	714	b_2	676	a_2	714	b_2	648	b_{3g}
865	e_{1g}	719	e″	673	e_{1g}	865	a_2	782	a_2	830	b_2	865	b_{2g}
865	e_{1g}	719	e″	673	e_{1g}	792	b_2	797	b_2	719	a_2	750	b_{3g}
974	e_{2u}	934	e″	791	e_{2u}	974	a_2	960	b_2	934	a_2	974	a_u
974	e_{2u}	934	e″	791	e_{2u}	934	b_2	900	a_2	934	b_2	879	b_{1u}
1013	b_{2g}	934	a_2''	837	b_{2g}	1003	b_2	998	a_2	991	b_2	978	b_{3g}
1018	b_{1u}	975	a_1'	978	b_{1u}	1003	a_1	891	b_1	854	a_1	1002	b_{2u}
1020	a_{1g}	1019	a_1'	972	a_{1g}	1019	a_1	858	a_1	990	a_1	1004	a_g
1067	e_{1u}	851	e′	831	e_{1u}	1063	a_1	1005	b_1	896	b_1	1059	b_{2u}
1067	e_{1u}	851	e′	831	e_{1u}	876	b_1	1002	a_1	1019	a_1	838	b_{3u}
1180	b_{2u}	928	a_2'	841	b_{2u}	1111	b_1	1079	a_1	1085	b_1	1134	b_{3u}
1203	e_{2g}	1125	e′	878	e_{2g}	1203	a_1	1158	b_1	1128	a_1	1203	a_g
1203	e_{2g}	1125	e′	878	e_{2g}	1188	b_1	1190	a_1	1196	b_1	927	b_{1g}
1356	b_{2u}	1303	a_2'	1346	b_{2u}	1344	b_1	1352	a_1	1323	b_1	1348	b_{3u}
1381	a_{2g}	1358	a_2'	1074	a_{2g}	1361	b_1	1305	b_1	1359	b_1	1338	b_{1g}
1525	e_{1u}	1461	e′	1373	e_{1u}	1519	a_1	1497	a_1	1503	b_1	1513	b_{2u}
1525	e_{1u}	1461	e′	1373	e_{1u}	1494	b_1	1481	b_1	1466	a_1	1454	b_{3u}
1653	e_{2g}	1633	e′	1610	e_{2g}	1648	a_1	1642	b_1	1640	b_1	1642	a_g
1653	e_{2g}	1633	e′	1610	e_{2g}	1646	b_1	1639	a_1	1639	a_1	1637	b_{1g}
3173	b_{1u}	2358	a_1'	2337	b_{1u}	2359	a_1	2348	b_1	2359	a_1	2358	b_{2u}
3182	e_{2g}	2359	e′	2349	e_{2g}	3182	b_1	2369	a_1	3178	a_1	3182	b_{1g}
3182	e_{2g}	2359	e′	2349	e_{2g}	3175	a_1	3177	b_1	2359	b_1	2360	a_g
3198	e_{1u}	3190	e′	2369	e_{1u}	3198	b_1	3195	b_1	3190	a_1	3198	b_{3u}
3198	e_{1u}	3190	e′	2369	e_{1u}	3190	a_1	3185	a_1	3190	b_1	3181	b_{2u}
3209	a_{1g}	3191	a_1'	2381	a_{1g}	3206	a_1	3204	a_1	3203	a_1	3200	a_g

1,2,3-$C_6D_3H_3$		1,2,4-$C_6D_3H_3$		1,2,3,4-$C_6D_4H_2$		1,2,3,5-$C_6D_4H_2$		1,2,4,5-$C_6D_4H_2$		C_6D_5H	
ω_μ	C_{2v}	ω_μ	C_s	ω_μ	C_{2v}	ω_μ	C_{2v}	ω_μ	D_{2h}	ω_μ	C_{2v}
386	a_2	400	*a*″	384	a_2	386	a_2	390	b_{1u}	376	b_2
383	b_2	370	*a*″	368	b_2	368	b_2	361	a_u	361	a_2
606	b_1	609	*a*′	602	b_1	603	b_1	599	b_{1g}	595	b_1
606	a_1	604	*a*′	599	a_1	600	a_1	604	a_g	598	a_1
558	b_2	573	*a*″	544	b_2	537	b_2	560	b_{1u}	526	b_2
670	b_2	647	*a*′	640	a_2	646	b_2	631	b_{3g}	628	b_2
790	b_2	718	*a*″	698	a_2	718	b_2	673	b_{2g}	673	a_2
719	a_2	782	*a*″	746	b_2	719	a_2	779	b_{3g}	719	b_2
934	a_2	934	*a*″	873	b_2	934	a_2	791	a_u	791	a_2
840	b_2	873	*a*″	822	a_2	810	b_2	931	b_{1u}	825	b_2
991	b_2	976	*a*′	976	a_2	934	b_2	936	b_{3g}	934	b_2
854	a_1	837	*a*′	863	b_1	851	a_1	835	b_{2u}	833	a_1
989	a_1	861	*a*′	836	a_1	975	a_1	880	a_g	879	a_1
860	b_1	990	*a*′	951	b_1	836	b_1	991	b_{2u}	974	a_1
1004	a_1	941	*a*′	858	a_1	1004	a_1	837	b_{3u}	836	b_1
908	b_1	1003	*a*′	988	a_1	866	b_1	1085	b_{3u}	858	b_1
1124	a_1	1169	*a*′	991	b_1	1121	a_1	988	a_g	990	a_1
1179	b_1	1083	*a*′	1165	a_1	965	b_1	984	b_{1g}	1003	b_1
1252	b_1	1299	*a*′	1347	a_1	1251	b_1	1346	b_{3u}	1198	b_1
1351	b_1	1348	*a*′	1214	b_1	1348	b_1	1286	b_{1g}	1346	b_1
1458	a_1	1491	*a*′	1415	a_1	1453	a_1	1391	b_{2u}	1382	a_1
1478	b_1	1435	*a*′	1466	b_1	1426	b_1	1474	b_{3u}	1435	b_1
1633	b_1	1635	*a*′	1628	a_1	1623	b_1	1628	b_{1g}	1616	a_1
1635	a_1	1630	*a*′	1625	b_1	1628	a_1	1621	a_g	1620	b_1
2344	a_1	2348	*a*′	2342	b_1	2344	a_1	2347	b_{2u}	2340	a_1
2359	b_1	2359	*a*′	2353	a_1	2359	b_1	2349	b_{1g}	2349	b_1
2374	a_1	2369	*a*′	2365	b_1	2359	a_1	2370	a_g	2359	a_1
3190	b_1	3191	*a*′	3182	b_1	2374	a_1	2369	b_{3u}	2369	b_1
3178	a_1	3182	*a*′	2376	a_1	3190	b_1	3190	b_{2u}	2378	a_1
3202	a_1	3199	*a*′	3199	a_1	3191	a_1	3191	a_g	3191	a_1

[a] Unscaled frequencies in cm^{-1}. 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.

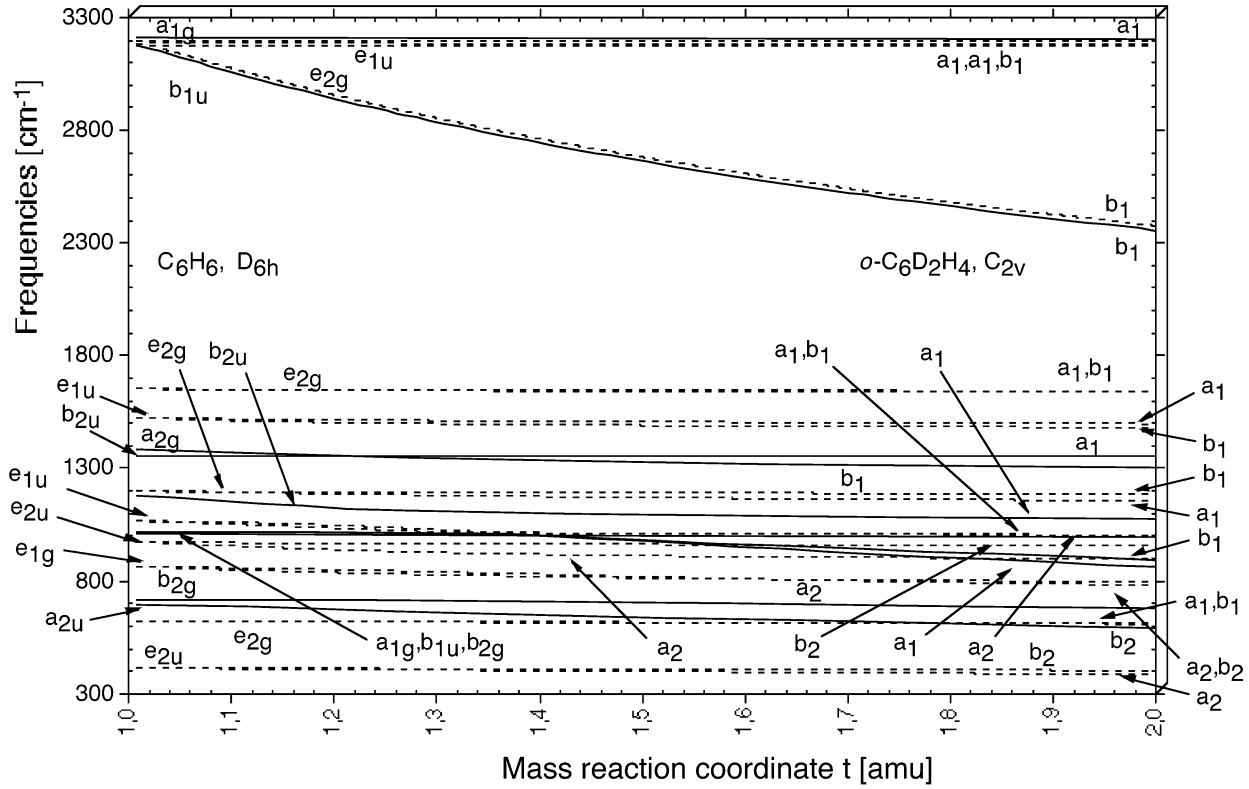
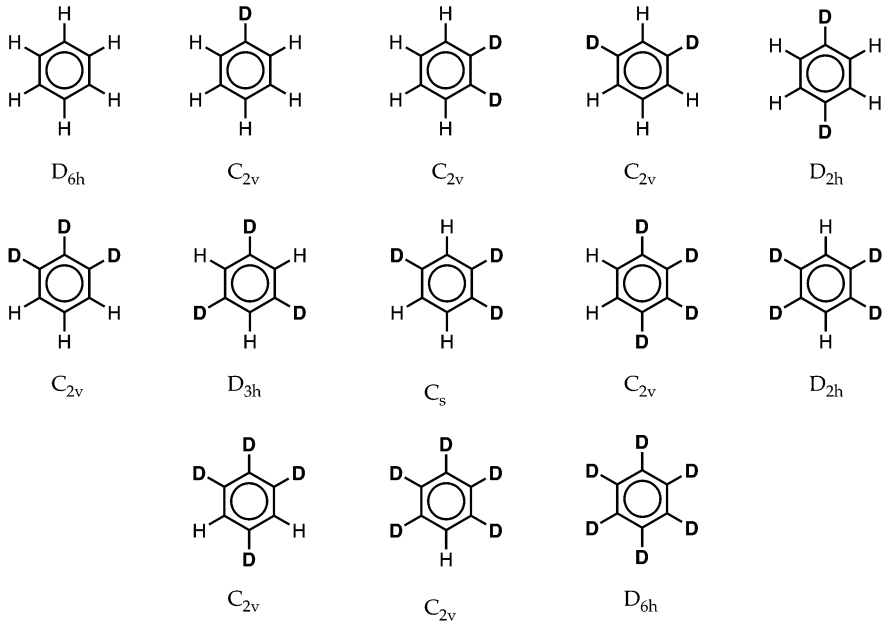


Figure 1. Correlation of the vibrational frequencies of benzene, C_6H_6, and 1,2-dideuteriobenzene, $C_6D_2H_4$, using a mass reaction path and the DMOD algorithm.

SCHEME 2



3. Implementation and Application

The approach described above was programmed and inserted into the diabatic mode ordering DMOD of the program package COLOGNE 2003.[26] Input for the program is the set of vibrational modes and vibrational frequencies calculated for the parent molecule. In addition, the isotopomer is specified by indicating the atoms, which will adopt a new isotope mass. A default scale factor f of 1000 (see eq 2) is used, and the threshold for degenerate vibrational modes is set to 10^{-3} cm^{-1}. Following the f points along the mass reaction path the isotopomer spectrum is stewise derived from the vibrational spectrum of the parent molecule. For each new path point procedures 1−6 are carried out:

(1) First, the new vectors stored in **B** are rotated into **B′** using the unitary transformation (8). In the simplest case (now projection of the gradient along the mass path), **A** and **B′** match perfectly, but in the general case (see above) the two spaces spanned by the vectors of **A** and **B′** are different and the vecors **b′** just mimic the old vectors **a**. (2) The new vectors **b** are grouped in subspaces possessing dimensions one larger than one in the case of degenerate vibrational modes. (3) The same is done for the old vectors mimicked by vectors **b′**. (4) The

TABLE 3: Comparison of Scaled Vibrational Frequencies and Experimental Frequencies for the (H,D)-Isotopomers of Benzene[a]

C_6H_6		$C_6(DH)_3$			C_6D_6			C_6DH_5		1,2-$C_6D_2H_4$		1,3-$C_6D_2H_4$	
ω_μ	D_{6h}	ω_μ	ω_{exp}	D_{3h}	ω_μ	ω_{exp}	D_{6h}	ω_μ	C_{2v}	ω_μ	C_{2v}	ω_μ	C_{2v}
398	e_{2u}	371	368	e″	347	345	e_{2u}	398	a_2	387	b_2	386	b_2
398	e_{2u}	371	368	e″	347	345	e_{2u}	378	b_2	369	a_2	371	a_2
606	e_{2g}	592	592	e′	578	579	e_{2g}	603	b_1	594	b_1	595	a_1
606	e_{2g}	592	592	e′	578	579	e_{2g}	599	a_1	597	a_1	597	b_1
673	a_{2u}	528	531	a_2''	494	496	a_{2u}	603	b_2	573	b_2	564	b_2
707	b_{2g}	703	697	a_2''	606	599	b_{2g}	703	b_2	666	a_2	703	b_2
846	e_{1g}	703	708	e″	658	660	e_{1g}	846	a_2	765	a_2	812	b_2
846	e_{1g}	703	708	e″	658	660	e_{1g}	775	b_2	780	b_2	703	a_2
967	e_{2u}	927	924	e″	785	787	e_{2u}	967	a_2	953	b_2	927	a_2
967	e_{2u}	927	924	e″	785	787	e_{2u}	927	b_2	894	a_2	927	b_2
990	b_{2g}	913	917	a_2''	818	829	b_{2g}	980	b_2	975	a_2	968	b_2
1010	b_{1u}	967	1004	a_1'	970	970	b_{1u}	995	a_1	884	b_1	847	a_1
993	a_{1g}	992	956	a_1'	946	945	a_{1g}	992	a_1	835	a_1	964	a_1
1037	e_{1u}	827	833	e′	808	814	e_{1u}	1033	a_1	977	b_1	871	b_1
1037	e_{1u}	827	833	e′	808	814	e_{1u}	851	b_1	974	a_1	990	a_1
1146	b_{2u}	901	912	a_2''	817	824	b_{2u}	1079	b_1	1048	a_1	1054	b_1
1178	e_{2g}	1102	1101	e′	860	869	e_{2g}	1178	a_1	1134	b_1	1105	a_1
1178	e_{2g}	1102	1101	e′	860	869	e_{2g}	1163	b_1	1165	a_1	1171	b_1
1309	b_{2u}	1258	1259	a_2'	1299	1282	b_{2u}	1297	b_1	1305	a_1	1277	b_1
1350	a_{2g}	1328	1321	a_2'	1050	1059	a_{2g}	1330	b_1	1276	b_1	1328	b_1
1482	e_{1u}	1420	1414	e′	1334	1333	e_{1u}	1476	a_1	1455	a_1	1461	b_1
1482	e_{1u}	1420	1414	e′	1334	1333	e_{1u}	1452	b_1	1439	b_1	1425	a_1
1599	e_{2g}	1580	1580	e′	1557	1557	e_{2g}	1594	a_1	1588	b_1	1586	b_1
1599	e_{2g}	1580	1580	e′	1557	1557	e_{2g}	1592	b_1	1585	a_1	1585	a_1
3057	b_{1u}	2272	2294	a_2''	2252	2284	b_{1u}	2273	a_1	2262	b_1	2273	a_1
3056	e_{2g}	2266	2282	e′	2256	2274	e_{2g}	3056	b_1	2275	a_1	3052	a_1
3056	e_{2g}	2266	2282	e′	2256	2274	e_{2g}	3049	a_1	3051	b_1	2266	b_1
3064	e_{1u}	3056	3063	e′	2270	2288	e_{1u}	3064	b_1	3061	b_1	3056	a_1
3064	e_{1u}	3056	3063	e′	2270	2288	e_{1u}	3056	a_1	3052	a_1	3056	b_1
3073	a_{1g}	3056	3065	a_1'	2280	2303	a_{1g}	3070	a_1	3068	a_1	3067	a_1

1,4-$C_6D_2H_4$		1,2,3-$C_6D_3H_3$		1,2,4-$C_6D_3H_3$		1,2,3,4-$C_6D_4H_2$		1,2,3,5-$C_6D_2H_4$		1,2,4,5-$C_6D_4H_2$		C_6D_5H	
ω_μ	D_{2h}	ω_μ	C_{2v}	ω_μ	C_s	ω_μ	C_{2v}	ω_μ	C_{2v}	ω_μ	D_{2h}	ω_μ	C_{2v}
398	a_u	382	a_2	385	a″	369	a_2	371	a_2	375	b_{1u}	363	b_2
360	b_{1u}	379	b_2	356	a″	354	b_2	354	b_2	347	a_u	347	a_2
600	b_{1g}	591	b_1	594	a′	587	b_1	588	b_1	585	b_{1g}	581	b_1
593	a_g	591	a_1	589	a′	585	a_1	586	a_1	589	a_g	584	a_1
592	b_{1u}	541	b_2	556	a″	528	b_2	521	b_2	543	b_{1u}	510	b_2
638	b_{3g}	656	b_2	637	a′	630	a_2	636	b_2	621	b_{3g}	618	b_2
846	b_{2g}	775	b_2	702	a″	683	a_2	702	b_2	658	b_{2g}	658	a_2
734	b_{3g}	706	a_2	765	a″	730	b_2	703	a_2	762	b_{3g}	703	b_2
967	a_u	935	a_2	927	a″	867	b_2	927	a_2	785	a_u	785	a_2
873	b_{1u}	841	b_2	867	a″	816	a_2	804	b_2	924	b_{1u}	819	b_2
956	b_{3g}	973	b_2	954	a′	954	a_2	913	b_2	915	b_{3g}	913	b_2
994	b_{2u}	847	a_1	830	a′	856	b_1	844	a_1	828	b_{2u}	826	a_1
977	a_g	962	a_1	838	a′	814	a_1	949	a_1	857	a_g	856	a_1
1029	b_{2u}	837	b_1	962	a′	924	b_1	812	b_1	963	b_{2u}	947	a_1
814	b_{3u}	977	a_1	915	a′	834	a_1	976	a_1	813	b_{3u}	812	b_1
1101	b_{3u}	885	b_1	974	a′	960	a_1	841	b_1	1054	b_{3u}	833	b_1
1178	a_g	1101	a_1	1145	a′	970	b_1	1098	a_1	967	a_g	969	a_1
908	b_{1g}	1154	b_1	1060	a′	1141	a_1	945	b_1	964	b_{1g}	982	b_1
1301	b_{3u}	1210	b_1	1254	a′	1300	a_1	1208	b_1	1299	b_{3u}	1156	b_1
1308	b_{1g}	1297	b_1	1318	a′	1187	b_1	1318	b_1	1257	b_{1g}	1316	b_1
1470	b_{2u}	1421	a_1	1449	a′	1375	a_1	1412	a_1	1352	b_{2u}	1343	a_1
1413	b_{3u}	1440	b_1	1395	a′	1425	b_1	1386	b_1	1432	b_{3u}	1395	b_1
1588	a_g	1577	b_1	1582	a′	1575	a_1	1570	b_1	1575	b_{1g}	1563	a_1
1584	b_{1g}	1579	a_1	1577	a′	1572	b_1	1575	a_1	1568	a_g	1567	b_1
2272	b_{2u}	2266	a_1	2262	a′	2256	b_1	2258	a_1	2261	b_{2u}	2254	a_1
3056	b_{1g}	2259	b_1	2266	a′	2260	a_1	2266	b_1	2256	b_{1g}	2256	b_1
2267	a_g	2273	a_1	2275	a′	2271	b_1	2266	a_1	2276	a_g	2266	a_1
3064	b_{3u}	3055	b_1	3057	a′	3049	b_1	2275	a_1	2270	b_{3u}	2270	b_1
3048	b_{2u}	3044	a_1	3049	a′	2276	a_1	3056	b_1	3056	b_{2u}	2278	a_1
3064	a_g	3055	a_1	3063	a′	3063	a_1	3056	a_1	3056	a_g	3056	a_1

[a] Scaled frequencies in cm^{-1}. B3LYP/6-31G(d,p) calculations. The ratios between experimental[31] and calculated frequencies of each mode in C_6H_6 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 rotatetd 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[27−29] and Pople's 6-31G(d,p) basis set.[30] 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 ($CH_4 \rightarrow CD_4$) and with a change of symmetry are encountered ($CH_4 \rightarrow CH_2D_2$, etc.). In the second case, the symmetry change occurs when adding $\Delta \boldsymbol{m}$ (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.[1] For example, the t_2-modes of CH_4 must correlate with the e- and a_1-symmetrical modes of C_{3v}-symmetrical CDH_3 or the a_1-, b_1-, and b_2-symmetrical modes of the C_{2v}-symmetrical CD_2H_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 C_6H_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.[31,32]

Experimental and scaled B3LYP frequencies are in close agreement deviating only for the a_{1g}- and b_{1u}-symmetrical modes close to 1000 cm^{-1} by more than 30 cm^{-1} (1,3,5-trideuteriobenzene) and in the case of the CH-stretching modes by 15 to 20 cm^{-1} (both 1,3,5-trideuteriobenzene and hexadeuteriobenzene). However, the calculated standard deviation for 1,3,5-trideuteriobenzene is 11.9 cm^{-1} and for hexadeuteriobenzene 9.8 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.[16] 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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