

Vibrational isotope effect of linear and planar molecules: Deuterated bromoethenes

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Linear (planar) molecules A and B which are identical except for isotopic substitutions at the atomic sites τ are considered. Stretching (bending, out-of-plane) frequencies ω_k and normal modes Ψ_k of the isotopically perturbed molecule B are expressed in terms of stretching (bending, out-of-plane) frequencies ν_i and the corresponding normal modes Φ_i of the unperturbed molecule A . Complete specification of the unperturbed normal modes is not required. All that is needed are stretching (bending, out-of-plane) amplitudes $\langle \tau | \Phi_i \rangle$ of the normal modes Φ_i at those sites τ that are affected by isotopic substitution. The rule which interlaces frequencies ω_k of molecule A with frequencies ν_i of molecule B is derived. Given two isotopic molecules A and B_τ that differ by a single isotopic substitution at site τ , the inversion relation is derived. This relation expresses unperturbed stretching (bending, out-of-plane) amplitudes at the site τ in terms of stretching (bending, out-of-plane) frequencies of molecules A and B_τ . As an example, out-of-plane vibrations of deuterated bromoethene were considered. In the simplest method 12 out-of-plane frequencies of four polydeuterated bromoethenes were calculated from 12 out-of-plane frequencies of bromoethene and three monodeuterated bromoethenes. Standard deviation of thus calculated frequencies from experimental frequencies is $\Delta = 2.74 \text{ cm}^{-1}$. In another method, 15 out-of-plane frequencies of four polydeuterated bromoethenes and selected monodeuterated bromoethene are calculated from 9 out-of-plane frequencies of bromoethene and the remaining two monodeuterated bromoethenes. Depending on which monodeuterated bromoethene is selected (1-, *cis*- or *trans*-), standard deviation of thus obtained frequencies from experimental frequencies is $\Delta_1 = 2.84 \text{ cm}^{-1}$, $\Delta_c = 2.96 \text{ cm}^{-1}$ and $\Delta_t = 2.72 \text{ cm}^{-1}$.

KEY WORDS: vibrational isotope effect, harmonic approximation, stretching and bending vibrations, out-of-plane vibrations, deuterated bromoethenes

1. Introduction

The aim of this and previous paper [1] is to provide a simple method for the calculation of the vibrational isotope effect in the harmonic approximation. We assume the unperturbed molecule A to be rigid and to contain n atoms. The perturbed molecule B is obtained from the unperturbed molecule A by ρ isotopic substitutions at selected atomic sites. If potential and kinetic energy is expressed in terms of the Cartesian coordinates of atomic displacements, and in the harmonic approximation [2], vibrations of the un-

perturbed molecule can be described by the generalised eigenvalue equation

$$\mathbf{F}|\Phi_i\rangle = \lambda_i\mathbf{M}|\Phi_i\rangle, \quad (1)$$

where \mathbf{F} is a $3n \times 3n$ force field matrix, while \mathbf{M} is a $3n \times 3n$ diagonal matrix which on a diagonal contains atomic masses m_i . Eigenvalues λ_i of this eigenvalue equation are related to the unperturbed frequencies ν_i by

$$\lambda_i = 4\pi^2\nu_i^2. \quad (2)$$

In addition, unperturbed vibrations Φ_i can be orthonormalized according to

$$\langle\Phi_i|\mathbf{M}|\Phi_j\rangle = \delta_{i,j}. \quad (3)$$

Usually one assumes that the force field is not affected by isotope substitutions [2]. In this approximation the perturbed eigenvalue equation is

$$\mathbf{F}|\Psi_k\rangle = \varepsilon_k(\mathbf{M} + \Delta\mathbf{M})|\Psi_k\rangle, \quad (4)$$

where $\Delta\mathbf{M}$ represents perturbation. Eigenvalues ε_k of perturbed equation (4) are related to perturbed frequencies ω_k by the relation

$$\varepsilon_k = 4\pi^2\omega_k^2. \quad (2')$$

We distinguish cardinal $\varepsilon_k \notin \{\lambda_i\}$ and singular $\varepsilon_k \in \{\lambda_i\}$ solutions to the perturbed equation (4) [1]. Each singular eigenvalue ε_k coincides with some unperturbed eigenvalue λ_j , and such eigenvalues are relatively rare. Many systems have only cardinal and no singular eigenvalues. In addition, treatment of singular solutions is similar though not identical to the treatment of cardinal solutions [1]. Therefore, we will in this paper concentrate on cardinal solutions. We will consider singular solutions only when this is necessary in order to clarify some point in the discussion.

We use here the same notation as in [1]. In particular, Δm_μ denotes isotope mass change of atom μ , while $\langle\mu s|\Phi_i\rangle$ denotes the amplitude of the unperturbed vibration $|\Phi_i\rangle$ at atom μ in the s th coordinate direction.

2. Linear molecules

Relations obtained in [1] substantially simplify in the case of linear molecules. We choose x -axis to point in the direction of the molecular axis. Hence, $I_x = 0$ and $I_y = I_z = I$. Since each isotope atom τ is situated on the x -axis, one has $y_\tau = z_\tau = 0$. Further, relations (22) in [1] involve various terms of the type $y_\mu y_\tau / I_x$ and $y_\mu z_\tau / I_x$ which are formally $0/0$. Proper analysis shows that one should neglect all terms that contain moment of inertia I_x . In particular, this implies $R_x = 0$ in [1, equation (21b)]. In addition, due to symmetry, each vibration Φ_i can be chosen to have nonvanishing components either only along x -axis, only along y -axis, or only along z -axis. Hence, one can distinguish stretching vibrations, where all atom displacements are along x -axis, and bending vibrations, where all atom displacements are perpendicular to the x -axis, either

in the y - or in the z -direction. There are $n - 1$ stretching vibrations, since one degree of freedom along x -axis corresponds to translation in this direction. Due to rotational symmetry bending vibrations are doubly degenerate. There are $n - 2$ bending vibrations in the y -direction, and $n - 2$ bending vibrations in the z -direction. In each of these two directions one degree of freedom is consumed by translation in this direction, and one by rotation around another of these two axes. Due to this separation on bending and stretching vibrations and since $y_\tau = z_\tau = 0$, one obtains

$$\Omega_{\mu x, \tau y}(\varepsilon) = \Omega_{\mu x, \tau z}(\varepsilon) = \Omega_{\mu y, \tau z}(\varepsilon) = 0$$

for the matrix elements of matrix $\Omega(\varepsilon)$ defined in [1]. This matrix is, hence, block-diagonal matrix containing three blocks which refer to vibrations in the x -, y -, and z -direction, respectively. Related relations accordingly factorise into three relations.

One, thus, obtains that $\varepsilon_k^x \notin \{\lambda_i^x\}$ is a (cardinal) stretching eigenvalue of the perturbed system if and only if it is a root of the equation

$$f^x(\varepsilon) \equiv \left| \Omega^x(\varepsilon) + \frac{\Delta \mathbf{M}_\rho^{-1}}{\varepsilon} \right| = 0, \quad (5a)$$

where Ω^x is a $\rho \times \rho$ Hermitian matrix with matrix elements

$$\Omega_{\mu\tau}^x(\varepsilon) = \frac{1}{\varepsilon M} + \sum_i^{n-1} \frac{\langle \mu x | \Phi_i^x \rangle \langle \Phi_i^x | \tau x \rangle}{\varepsilon - \lambda_i^x}, \quad (6a)$$

while $\Delta \mathbf{M}_\rho^{-1}$ is a diagonal $\rho \times \rho$ matrix with matrix elements $(\Delta \mathbf{M}_\rho^{-1})_{\mu\tau} = \delta_{\mu\tau} / \Delta m_\tau$. Total mass of the unperturbed molecule is denoted by M .

Each stretching vibration Ψ_k^x corresponding to the eigenvalue $\varepsilon_k^x \notin \{\lambda_i^x\}$ is of the form

$$\Psi_k^x = \frac{1}{\varepsilon_k^x \sqrt{M}} \sum_\tau^\rho C_\tau |\Phi_{Tx}\rangle + \sum_i^{n-1} \frac{\sum_\tau^\rho \langle \Phi_i^x | \tau x \rangle C_\tau}{\varepsilon_k^x - \lambda_i^x} |\Phi_i^x\rangle, \quad (7a)$$

where ρ coefficients C_τ are components of the column vector \mathbf{C} , solution of the matrix equation

$$\left[\Omega^x(\varepsilon_k^x) + \frac{\Delta \mathbf{M}_\rho^{-1}}{\varepsilon_k^x} \right] \mathbf{C} = 0. \quad (8a)$$

Each linearly independent solution \mathbf{C} to a matrix equation (8a) generates the corresponding stretching vibration (7a). One finds that the degeneracy of the stretching eigenvalue $\varepsilon_k^x \notin \{\lambda_i^x\}$ equals the number of linearly independent solutions \mathbf{C} to (8a). Further, each perturbed stretching vibration Ψ^x is according to (7a) a linear combination of $(n - 1)$ unperturbed stretching vibrations Φ_i^x and a translation Φ_{Tx} in the x -direction along molecular axis. The role of this translation is to compensate for the change in the centre of mass caused by the isotope substitutions. The resulting vibration Ψ^x has no translational component in the x -direction, i.e., it satisfies $\langle \Phi_{Tx} | \mathbf{M} + \Delta \mathbf{M} | \Psi^x \rangle = 0$.

Similar relations are obtained for bending vibrations Ψ^y and Ψ^z . Thus, each perturbed bending eigenvalue $\varepsilon_k^y \notin \{\lambda_i^y\}$ is a root of the equation

$$f^y(\varepsilon) \equiv \left| \Omega^y(\varepsilon) + \frac{\Delta \mathbf{M}_\rho^{-1}}{\varepsilon} \right| = 0, \quad (5b)$$

where Ω^y is a $\rho \times \rho$ Hermitian matrix with matrix elements

$$\Omega_{\mu\tau}^y(\varepsilon) = \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{x_\mu x_\tau}{I} \right] + \sum_i^{n-2} \frac{\langle \mu y | \Phi_i^y \rangle \langle \Phi_i^y | \tau y \rangle}{\varepsilon - \lambda_i^y} \quad (6b)$$

and where $I \equiv I_y \equiv I_z$ is the moment of inertia of the unperturbed molecule. Each bending vibration Ψ_k^y corresponding to the eigenvalue $\varepsilon_k^y \notin \{\lambda_i^y\}$ is of the form

$$\Psi_k^y = \frac{1}{\varepsilon_k^y} \left[\frac{1}{\sqrt{M}} \sum_\tau^\rho C_\tau |\Phi_{Ty}\rangle + \frac{1}{\sqrt{I}} \sum_\tau^\rho x_\tau C_\tau |\Phi_{Rz}\rangle \right] + \sum_i^{n-2} \frac{\sum_\tau^\rho \langle \Phi_i^y | \tau y \rangle C_\tau}{\varepsilon_k^y - \lambda_i^y} |\Phi_i^y\rangle, \quad (7b)$$

where the coefficients C_τ are the components of the column vector \mathbf{C} , solution of the matrix equation

$$\left[\Omega^y(\varepsilon_k^y) + \frac{\Delta \mathbf{M}_\rho^{-1}}{\varepsilon_k^y} \right] \mathbf{C} = 0. \quad (8b)$$

Again, degeneracy of the perturbed bending eigenvalue $\varepsilon_k^y \notin \{\lambda_i^y\}$ equals the number of linearly independent solutions \mathbf{C} to this matrix equation.

According to (7b) each bending vibration Ψ^y is a linear combination of $(n-2)$ unperturbed bending vibrations Φ_i^y , a translation Φ_{Ty} in the y -direction, and a rotation Φ_{Rz} around the z -axis. The role of these nonproper vibrations is to compensate for the change of the centre of mass and moment of inertia caused by the isotope substitutions. The resulting vibration Ψ^y has no translation component in the y -direction, and no component of the rotation around z -axis, i.e., it satisfies $\langle \Phi_{Ty} | \mathbf{M} + \Delta \mathbf{M} | \Psi^y \rangle = 0$ and $\langle \Phi_{Rz} | \mathbf{M} + \Delta \mathbf{M} | \Psi^y \rangle = 0$. While stretching vibrations Ψ^x contain only one translation which is required in order to compensate for the change of the centre of mass caused by the isotope substitutions, bending vibrations besides the translation in the direction of the bending contain also a rotation around the axis that is perpendicular to the direction of the bending. This difference is also reflected in the difference between matrix elements (6a) and (6b).

3. Single isotopic substitution of linear molecules: interlacing rule and inversion relations

Consider two linear isotopic molecules A and B_τ which are identical, except for a single isotopic substitution at the atomic site τ .

Relations (5) and (6) now reduce to

$$f^x(\varepsilon) \equiv \sum_i^{n-1} \frac{\langle \tau x | \Phi_i^x \rangle \langle \Phi_i^x | \tau x \rangle}{\varepsilon - \lambda_i^x} + \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{1}{\Delta m_\tau} \right] = 0, \quad (9a)$$

$$f^y(\varepsilon) \equiv \sum_i^{n-2} \frac{\langle \tau y | \Phi_i^y \rangle \langle \Phi_i^y | \tau y \rangle}{\varepsilon - \lambda_i^y} + \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{x_\tau^2}{I} + \frac{1}{\Delta m_\tau} \right] = 0, \quad (9b)$$

where x_τ is the x -coordinate of the isotope atom τ . Relation for $f^z(\varepsilon)$ is identical to the relation for $f^y(\varepsilon)$, except that everywhere y should be replaced by z .

Each root ε_k^x of $f^x(\varepsilon) = 0$ determines a stretching frequency $\omega_k^x = \sqrt{\varepsilon_k^x}/2\pi$ of the isotope molecule B_τ , while each root ε_k^y of $f^y(\varepsilon) = 0$ determines a bending frequency $\omega_k^y = \sqrt{\varepsilon_k^y}/2\pi$ of this molecule. In this way one obtains all cardinal frequencies $\omega_k^x \notin \{v_i^x\}$ and $\omega_k^y \notin \{v_i^y\}$ of the isotope molecule B_τ . In addition, relations (9) may produce some singular ($\omega_k \in \{v_i\}$) frequencies of the perturbed molecule B_τ . This may happen only if the corresponding unperturbed frequency v_j is passive.

Once a particular perturbed frequency is known, one can obtain the corresponding normal mode. Since quantities Ω^x , Ω^y and Ω^z are no more matrices, vector \mathbf{C} in relations (8) reduces to a vector with only one component, and without loss of generality this component can be chosen equal to one. With this choice relations (7) reduce to

$$|\Psi_k^x\rangle = \frac{1}{\varepsilon_k^x \sqrt{M}} |\Phi_{Tx}\rangle + \sum_i^{n-1} \frac{\langle \Phi_i^x | \tau x \rangle}{\varepsilon_k^x - \lambda_i^x} |\Phi_i^x\rangle, \quad (10a)$$

$$|\Psi_k^y\rangle = \frac{1}{\varepsilon_k^y} \left[\frac{1}{\sqrt{M}} |\Phi_{Ty}\rangle + \frac{x_\tau}{\sqrt{I}} |\Phi_{Rz}\rangle \right] + \sum_i^{n-2} \frac{\langle \Phi_i^y | \tau y \rangle}{\varepsilon_k^y - \lambda_i^y} |\Phi_i^y\rangle. \quad (10b)$$

In addition, one obtains [1]

$$\langle \tau x | \Psi_k^x \rangle = -\frac{1}{\varepsilon_k^x \Delta m_\tau}, \quad \langle \tau y | \Psi_k^y \rangle = -\frac{1}{\varepsilon_k^y \Delta m_\tau}. \quad (11)$$

According to relations (10), each root ε_k^x of $f^x(\varepsilon)$ as well as each root ε_k^y of $f^y(\varepsilon)$ produces exactly one normal mode. Each stretching cardinal frequency $\omega_k^y \notin \{v_i^y\}$ of B_τ is, hence, nondegenerate in the space of stretching frequencies. Of course, this frequency may coincide with some bending frequency $\omega_{k'}^y$ of this molecule, but it does not coincide with any other stretching frequency. Similarly, each bending cardinal frequency $\omega_k^y \notin \{v_i^y\}$ is nondegenerate in the space of bending frequencies $\{\omega_k^y\}$. Here again, this frequency may coincide with some stretching frequency. In addition, all bending frequencies are doubly degenerate, since bending frequencies corresponding to normal vibrations in directions y and z that are perpendicular to molecular axis are identical: $\{\omega_k^y\} \equiv \{\omega_k^z\}$. However, restricted to the set $\{\omega_k^y\}$ of bending frequencies in the y -direction, each cardinal frequency $\omega_k^y \notin \{v_i^y\}$ is nondegenerate. Similarly, restricted to the set $\{\omega_k^z\}$ of bending frequencies in the z -direction, each cardinal frequency $\omega_k^z \notin \{v_i^z\}$

is nondegenerate. In conclusion, in the case of single isotopic substitutions of linear molecules, only singular frequencies (if any) may be degenerate.

In order to analyse the general distribution of perturbed frequencies and properties of the corresponding normal modes, we have to complete the above analysis with detailed description of singular solutions. This was done in more detail and for a general case of an arbitrary molecule with a multiple isotopic substitutions in a previous paper. If those results are specified to the case considered here, the following results are obtained.

Consider first stretching vibrations. Let the unperturbed eigenvalue λ_j^x be η -degenerate and let $|\Phi_{j\kappa}^x\rangle$, $\kappa = 1, \dots, \eta$, be the corresponding normal modes.

If λ_j^x is passive, that is, if $\langle \tau x | \Phi_{j\kappa}^x \rangle = 0$, $\kappa = 1, \dots, \eta$, then all the unperturbed eigenstates $|\Phi_{j\kappa}^x\rangle$ are also the perturbed eigenstates. In addition, if $\varepsilon_k^x = \lambda_j^x$ is a root of $f^x(\varepsilon)$, there is an extra eigenstate of the type (10a). In conclusion, if the unperturbed eigenvalue λ_j^x is passive and η -degenerate, the perturbed eigenvalue $\varepsilon_k^x = \lambda_j^x$ is either η - or $(\eta + 1)$ -degenerate. It is η -degenerate if $f^x(\lambda_j^x) \neq 0$. Otherwise it is $(\eta + 1)$ -degenerate. In particular, one finds that all roots of $f^x(\varepsilon)$, not only cardinal roots $\varepsilon_k^x \notin \{\lambda_i^x\}$, are the eigenvalues of the perturbed equation, while (10a) are the corresponding eigenstates.

If λ_j^x is active and nondegenerate ($\eta = 1$), $\varepsilon_k^x = \lambda_j^x$ is not an eigenvalue of the perturbed system. Otherwise ($\eta > 1$), it is a $(\eta - 1)$ -degenerate eigenvalue of the perturbed system, and the corresponding eigenstates Ψ_k^x are linear combinations

$$\Psi_k^x = \sum_{\kappa}^{\eta} D_{\kappa} |\Phi_{j\kappa}^x\rangle, \quad (12a)$$

where coefficients D_{κ} satisfy

$$\sum_{\kappa}^{\eta} \langle \tau x | \Phi_{j\kappa}^x \rangle D_{\kappa} = 0. \quad (12b)$$

This completes the description of singular eigenvalues and eigenstates. In particular, degeneracy of each singular eigenvalue $\varepsilon_k^x = \lambda_j^x$ can decrease (increase) only by one relative to the degeneracy of the unperturbed eigenvalue λ_j^x , while each cardinal eigenvalue $\varepsilon_k^x \notin \{\lambda_i^x\}$ is nondegenerate. Identical results are obtained for the bending vibrations.

From equations (9) one can derive two important results. The first is the interlacing relation, which interlaces perturbed and unperturbed frequencies. The second is the inversion relation that enables calculation of unperturbed amplitudes at the site of isotopic substitution from known unperturbed and perturbed frequencies.

In general, if in a mechanical system that exhibits harmonic oscillations one increases the mass of one or few particles without changing the potential energy, the frequencies of normal vibrations do not increase [3]. These frequencies either decrease or remain the same. In particular, if frequencies ν_i of the initial molecule *A* are arranged

in the increasing order, and if frequencies ω_k of the heavier isotopic molecule B are also arranged in the increasing order, then [3]

$$\omega_1 \leq \nu_1, \quad \omega_2 \leq \nu_2, \quad \dots, \quad \omega_{3n-5} \leq \nu_{3n-5}. \quad (13)$$

The above order rule applies to such pairs of isotopic molecules A and B where all substituted isotopes in the molecule B are heavier than the corresponding isotopes in the molecule A . Relation (13) involves all frequencies of such isotopic molecules. However, since in the case of linear molecules stretching and bending vibrations separate, this rule applies separately to stretching and separately to bending frequencies.

We will now derive the so-called interlacing rule. It applies equally to stretching as well as to bending frequencies. The interlacing rule implies the order rule, but it also imposes much stronger restriction to the range of possible values of frequencies ν_i and ω_k .

Consider again linear isotopic molecules A and B_τ that differ in a single isotopic substitution at the site τ . Assume that molecule B_τ is heavier from molecule A , i.e., $\Delta m_\tau > 0$. Since $\langle \tau x | \Phi_i^x \rangle \langle \Phi_i^x | \tau x \rangle \geq 0$ function $f^x(\varepsilon)$ has a negative derivative for each $\varepsilon \notin \{\lambda_i^x\}$. In each point $\varepsilon = \lambda_i^x$ this function is singular, unless the unperturbed eigenvalue λ_i^x is passive. This function is also singular in the point $\varepsilon = 0$. There is, hence, exactly one root of $f^x(\varepsilon)$ in each open interval $(\lambda_i^x, \lambda_j^x)$ where $\lambda_i^x < \lambda_j^x$ are two consecutive active eigenvalues. This applies also to the interval $(0, \lambda_s^x)$, where λ_s^x is the smallest active eigenvalue. Hence, if all unperturbed proper eigenvalues λ_i^x are active and nondegenerate, one finds

$$0 < \varepsilon_1^x < \lambda_1^x < \varepsilon_2^x < \lambda_2^x < \dots < \varepsilon_{n-1}^x < \lambda_{n-1}^x.$$

The $(n - 1)$ eigenvalues ε_i^x of the perturbed equation are, thus, interlaced with the $(n - 1)$ eigenvalues λ_i^x of the unperturbed equation. Due to relations (2) and (2') this interlacing rule also holds for the corresponding stretching frequencies. Analogous rule is obtained for the bending frequencies.

The above interlacing rule is derived under the assumption that all the unperturbed eigenvalues are active and mutually distinct. These conditions can be relaxed [4]. If the eigenvalue equation (1) has some degenerate and/or passive eigenvalues λ_i , one can always consider an infinitesimal variation of the matrix elements of the force field matrix \mathbf{F} such that the resulting eigenvalue equation has all eigenvalues distinct and active. According to the above analysis, all eigenvalues of this slightly perturbed eigenvalue equation should satisfy the above interlacing condition. However, each eigenvalue of the eigenvalue equation (1) is a continuous function of all the matrix elements of the matrix \mathbf{F} , and hence, one derives:

Interlacing rule. Consider two n -atom linear molecules A and B_τ , which differ by a single isotopic substitution at atomic site τ . Let molecule B_τ be heavier than molecule A , and let ν_i and ω_k be proper stretching (bending) frequencies of molecules A

and B_τ , respectively. Arrange these frequencies in the nondecreasing order. Then, these frequencies are interlaced according to

$$0 \leq \omega_1 \leq \nu_1 \leq \omega_2 \leq \nu_2 \leq \omega_3 \leq \nu_3 \leq \dots \quad (14a)$$

One easily finds the condition for a strict inequality to apply. If the two successive unperturbed stretching (bending) frequencies ν_i and ν_{i+1} are degenerate, one has $\nu_i = \omega_{i+1} = \nu_{i+1}$. If the two successive unperturbed stretching (bending) frequencies ν_i and ν_{i+1} are distinct and active, one has strict inequality $\nu_i < \omega_{i+1} < \nu_{i+1}$, etc.

One can generalise this interlacing rule to the case of the multiple isotopic substitutions. For example, if A and B are two linear isotopic molecules that differ by two isotopic substitutions, one can consider the transition from a molecule A to a molecule B in two steps: from molecule A to the intermediate molecule C , and from molecule C to molecule B . In each step only a single isotopic substitution is performed, and hence, to each step interlacing rule (14a) applies. Assume, for example, that both isotopes are heavier in molecule B . In this case molecule C is heavier from molecule A , and molecule B is heavier from molecule C . Hence, if ν'_i are nondecreasing stretching (bending) frequencies of molecule C , the interlacing rule (14a) implies $\nu_{k-1} \leq \nu'_k \leq \nu_k$ (transition from A to C) and $\nu'_{k-1} \leq \omega_k \leq \nu'_k$ (transition from C to B). Combining these two results one finds the interlacing condition $\nu_{k-2} \leq \omega_k \leq \nu_k$. Similarly, if one of these two isotopes is heavier in molecule A , while another is heavier in molecule B , one finds the interlacing condition $\nu_{k-1} \leq \omega_k \leq \nu_{k+1}$, etc. In this way one can generalise the interlacing rule to all multiple isotopic substitutions. Each such multiple isotopic substitution can be considered as a sequence of single isotopic substitutions. The introduction of each new isotope can shift (ordered) perturbed frequencies ω_k relative to the (ordered) unperturbed frequencies ν_i only by one place. The direction in which this shift is performed (lowering or increasing these frequencies) depends on whether the isotope mass change is positive or negative. One thus finds:

Generalised interlacing rule. Consider two n -atom linear molecules A and B which differ by ρ isotopic substitutions. Let η isotopes be heavier in molecule B , and let $(\rho - \eta)$ isotopes be heavier in molecule A . Let further ν_i and ω_k be proper stretching (bending) frequencies of molecules A and B , respectively. Arrange these frequencies in the nondecreasing order. Then, these frequencies are interlaced according to

$$\nu_{k-\eta} \leq \omega_k \leq \nu_{k+\rho-\eta}. \quad (14b)$$

For $\eta = \rho = 1$ this relation reduces to (14a).

The interlacing relation (14b) implies order rule (13). However, the interlacing relation is more restrictive. Thus, if A and B_τ are two linear molecules that differ by a single isotopic substitution at site τ , and if ω_k is k th perturbed frequency, the order rule restricts this frequency only from above ($\omega_k \leq \nu_k$), while the interlacing rule restricts it from above as well as from below ($\nu_{k-1} \leq \omega_k \leq \nu_k$). In addition, the order rule applies

Table 1
Experimental [3] frequencies (cm^{-1}) for acetylene
and deuterated acetylenes.

Vibration type		C_2H_2	C_2HD	C_2D_2
1	Σ_g^+	3372.5	3335.62	2703.8
2	Σ_g^+	1973.5	1853.78	1764.2
3	Σ_u^+	3287	2583.6	2427
4	Π_g	613.5	518.38	511.12
5	Π_r	729.1	677.77	539.1

only to such pairs of isotopic molecules A and B where all substituted isotopes in one molecule are heavier from the corresponding isotopes in another molecule. Generalised interlacing rule has no such restriction. This rule applies to all pairs of linear isotopic molecules A and B , regardless of the relative mass of various isotopic substitutions. Since it is more restrictive and more general, the interlacing rule can be used to facilitate frequency assignments of various isotopomers.

As an example of the validity of the interlacing rule, consider acetylene and deuterated acetylenes. Experimental stretching and bending frequencies of acetylene C_2H_2 (d0) and deuterated acetylenes C_2HD (d1) and C_2D_2 (d2) are shown in table 1.

Vibrations of the symmetry type Σ are stretching vibrations, while vibrations of the symmetry type Π are bending vibrations. One can easily verify that all these vibrations satisfy interlacing rule. For example, the stretching vibrations of acetylene C_2H_2 and deuterated acetylene C_2HD that differ by a single isotopic substitution satisfy $1853.78(\text{d1}) < 1973.5(\text{d0}) < 2583.6(\text{d1}) < 3287(\text{d0}) < 3335.62(\text{d1}) < 3372.5(\text{d0})$ in accord with (22a). Also, the bending frequencies of these two molecules satisfy $518.38(\text{d1}) < 613.5(\text{d0}) < 677.77(\text{d1}) < 729.1(\text{d0})$ in accord with (14a). Similar agreement is obtained if one compares stretching and bending frequencies of C_2HD and C_2D_2 . However, if one compares stretching frequencies of isotopic molecules C_2H_2 and C_2D_2 that differ by a double isotopic substitution, one finds that these frequencies do not satisfy the interlacing relation (14a) that applies to a single isotopic substitution: $1764.2(\text{d2}) < 1973.5(\text{d0}) < 2427(\text{d2}) < 3287(\text{d0}) < 2703.8(\text{d2}) < 3372.5(\text{d0})$. However, these frequencies do satisfy the generalised interlacing rule. Namely, one finds $1973.5(\text{d0}) < 2703.8(\text{d2}) < 3372.5(\text{d0})$, in accord with $\nu_{k-2} \leq \omega_k \leq \nu_k$, as required by (14b).

Inversion relations. Another consequence of the relations (9) are the inversion relations. Using these relations one can deduce squares of the unperturbed amplitudes $\langle \tau x | \Phi_i^x \rangle \langle \tau y | \Phi_i^y \rangle$ at the substitution site τ from the unperturbed and perturbed stretching (bending) frequencies of isotopic molecules A and B_τ .

Consider, for example, stretching frequencies. Assume that all the unperturbed eigenvalues λ_j^x are nondegenerate and active. In this case all perturbed eigenvalues ε_k^x are roots of $f^x(\varepsilon)$. There are exactly $(n - 1)$ mutually distinct unperturbed eigenvalues λ_j^x and also exactly $(n - 1)$ mutually distinct perturbed eigenvalues ε_k^x . In addition, all perturbed eigenvalues differ from all the unperturbed eigenvalues and these eigenvalues are interlaced according to (14a).

Define matrix \mathbf{A}^x and column vectors \mathbf{X}^x and Σ^x

$$\mathbf{A}_{k,i}^x = \frac{1}{\varepsilon_k^x - \lambda_i^x}, \quad \mathbf{X}_k^x = -\frac{1}{\varepsilon_k^x} \left[\frac{1}{M} + \frac{1}{\Delta m_\tau} \right], \quad \Sigma_i^x = \langle \tau x | \Phi_i^x \rangle \langle \Phi_i^x | \tau x \rangle. \quad (15a)$$

According to (9a), matrix $\mathbf{A} \equiv \mathbf{A}^x$ and vectors $\mathbf{X} \equiv \mathbf{X}^x$ and $\Sigma \equiv \Sigma^x$ satisfy $\mathbf{A}\Sigma = \mathbf{X}$. Hence, and provided matrix $\mathbf{A} \equiv \mathbf{A}^x$ is nonsingular,

$$\Sigma = \mathbf{A}^{-1}\mathbf{X}. \quad (16)$$

This is the inversion relation. Using this relation one can calculate squares $\Sigma_i \equiv \Sigma_i^x$ of the unperturbed stretching amplitudes at the isotope site τ from the stretching unperturbed frequencies ν_j^x and the stretching isotopic frequencies ω_k^x .

The inversion relation (16) is derived under the assumption that all the unperturbed frequencies are nondegenerate and active. These conditions can be relaxed. For example, if the unperturbed frequency ν_j^x is η -degenerate and if $|\Phi_{j\kappa}^x\rangle$, $\kappa = 1, \dots, \eta$, are the corresponding normal modes, one has to replace the coefficient Σ_j^x in relation (15a) with a more general expression

$$\Sigma_j^x = \sum_{\kappa}^{\eta} \langle \tau x | \Phi_{j\kappa}^x \rangle \langle \Phi_{j\kappa}^x | \tau x \rangle. \quad (17a)$$

Also it follows from the relation (9a) that if a particular unperturbed eigenvalue λ_j^x is passive, component Σ_j^x of a vector Σ^x equals zero, and this eigenvalue should not be included in the construction of a matrix \mathbf{A}^x and vectors \mathbf{X}^x and Σ^x .

In conclusion, in choosing the set $\{\lambda_i^x\}_\tau$ of unperturbed eigenvalues λ_i^x and the set $\{\varepsilon_k^x\}_\tau$ of perturbed eigenvalues ε_k^x that are required for the construction of the matrix \mathbf{A} and vector \mathbf{X} , the following rule applies: the set $\{\lambda_i^x\}_\tau$ should contain all mutually distinct and, relative to the substitution site τ , active unperturbed stretching eigenvalues. In particular, if all the unperturbed eigenvalues are active and nondegenerate, the set $\{\lambda_i^x\}_\tau$ coincides with the set $\{\lambda_i^x\}$. The set $\{\varepsilon_k^x\}_\tau$ should contain mutually distinct perturbed stretching eigenvalues that are strictly interlaced with the unperturbed eigenvalues $\lambda_j^x \in \{\lambda_i^x\}_\tau$. If between any two successive eigenvalues $\lambda_i^x < \lambda_{i+1}^x$ contained in the set $\{\lambda_i^x\}_\tau$ there are two or more perturbed eigenvalues $\varepsilon_k^x \in \{\varepsilon_k^x\}$, one should include in the set $\{\varepsilon_k^x\}_\tau$ the perturbed eigenvalue ε_k^x which does not coincide with any unperturbed eigenvalue $\lambda_j^x \in \{\lambda_i^x\}$. According to the above analysis there is at most one perturbed eigenvalue that satisfies this condition. We say that the set $\{\varepsilon_k^x\}_\tau$ obtained in this way is *complementary* to the set $\{\lambda_i^x\}_\tau$. Since the sets $\{\lambda_i^x\}_\tau$ and $\{\varepsilon_k^x\}_\tau$ are strictly interlaced they contain the same number of elements, and the matrix \mathbf{A} is a square matrix. The inversion relation now produces coefficients Σ_i^x (relation (17a)). Each coefficient Σ_i^x is a squared amplitude (or sum of such squared amplitudes) of the unperturbed normal mode (or modes) at the site τ of isotopic substitution.

The inversion relation applies also to the bending frequencies of linear molecules. One finds that in the case of bending frequencies the matrix $\mathbf{A} \equiv \mathbf{A}^y$ and vectors $\mathbf{X} \equiv \mathbf{X}^y$ and $\mathbf{\Sigma} \equiv \mathbf{\Sigma}^y$ are

$$\mathbf{A}_{k,i}^y = \frac{1}{\varepsilon_k^y - \lambda_i^y}, \quad \mathbf{X}_k^y = -\frac{1}{\varepsilon_k^y} \left[\frac{1}{M} + \frac{x_\tau^2}{I} + \frac{1}{\Delta m_\tau} \right], \quad (15b)$$

$$\mathbf{\Sigma}_j^y = \sum_{\kappa}^{\eta} \langle \tau y | \Phi_{j\kappa}^y \rangle \langle \Phi_{j\kappa}^y | \tau y \rangle. \quad (17b)$$

The inversion relations suggest a systematic method to obtain frequencies and normal modes of all isotopomers of a given linear molecule. All one needs are experimental frequencies ν_i of unperturbed molecule, and various sets $\{\omega_k\}_\tau$ of experimental frequencies of monosubstituted molecules B_τ .

Consider a linear molecule A and a set of monosubstituted linear molecules B_τ , $\tau = 1, 2, \dots$. Each molecule B_τ is identical to the molecule A , except for a single isotopic substitution at site τ . Let $\{\nu_i\}_\tau$ be the set of all mutually distinct and (relative to the substitution site τ) active stretching (bending) frequencies of a molecule A . Let the set $\{\omega_k\}_\tau$ containing distinct stretching (bending) frequencies of a molecule B_τ be complementary to the set $\{\nu_i\}_\tau$. Each set $\{\omega_k\}_\tau$ contains the same number of elements as the corresponding unperturbed set $\{\nu_i\}_\tau$. Using the relation (16), where the matrix \mathbf{A} and vector \mathbf{X} are defined in terms of frequencies $\{\nu_i\}_\tau$ and $\{\omega_k\}_\tau$, one obtains vector $\mathbf{\Sigma}$ that determines amplitude squares $\langle \tau | \Phi_i \rangle^2$ (or, in the case of degeneracy, sum of such amplitudes) of unperturbed stretching (bending) normal modes at the substitution site τ . In this way, by using only experimental frequencies of monosubstituted molecules B_τ , one can obtain amplitude squares of unperturbed vibrations at all atomic sites of interest. According to relations (5)–(8), in order to obtain stretching (bending) frequencies and normal modes of a polysubstituted molecule with isotopic substitutions at sites μ and τ , one has to know a relative sign of amplitudes $\langle \tau | \Phi_i \rangle$ and $\langle \mu | \Phi_i \rangle$ at these sites, in addition to absolute values of these amplitudes. These relative signs can be obtained in various ways. In some cases relative signs of vibrational amplitudes are determined by the symmetry [4]. Further, the orthonormality relation (3) substantially restricts possible variations in these relative signs, and one can use these relations in order to single out relative signs which are acceptable. In addition, these relations can be utilised in order to decrease the number of experimental frequencies that are used in order to calculate amplitudes $\langle \tau | \Phi_i \rangle$. Finally, one can use relatively crude model which is not required to produce reliable absolute values of the amplitudes $\langle \tau | \Phi_i \rangle$ and $\langle \mu | \Phi_i \rangle$ at different sites, but which is nevertheless good enough to produce relative signs of these amplitudes. After these relative signs are obtained, one can calculate all stretching (bending) frequencies and vibrations for any isotopomer. Thus, monosubstituted frequencies in conjunction with molecular geometry and atomic masses completely determine all polysubstituted frequencies and vibrations.

We will postpone further discussion of the inversion relations to the treatment of out-of-plane vibrations of planar molecules. Planar molecules are more complex than linear molecules, and it is more instructive to see how this relation can be applied to the out-of-plane vibrations of planar molecules, than to see how this relation applies to the simpler case of stretching and bending vibrations of linear molecules.

4. Planar molecules

Consider now planar molecules. Choose z -axis to be perpendicular to the molecular plane. Out-of-plane vibrations in the z -direction separate from the vibrations in the xy -plane. There are $(n - 3)$ out-of-plane vibrations in the z -direction, and $(2n - 3)$ in-plane vibrations in the xy -plane. Since each isotope is in the molecular plane, one has $z_\tau = 0$, $\tau = 1, \dots, \rho$. Hence, the corresponding relations in [1] simplify. One obtains two sets of relations, one describing out-of-plane vibrations, and another describing in-plane vibrations.

5. Out-of-plane vibrations of planar molecules

The following results are obtained for the out-of-plane eigenvalues ε_k^z and the corresponding normal modes Ψ_k^z of a planar molecule.

Each perturbed out-of-plane eigenvalue $\varepsilon_k^z \notin \{\lambda_i^z\}$ is a root of the equation

$$f^z(\varepsilon) \equiv \left| \mathbf{\Omega}^z(\varepsilon) + \frac{\Delta \mathbf{M}_\rho^{-1}}{\varepsilon} \right| = 0, \quad (5c)$$

where $\mathbf{\Omega}^z(\varepsilon)$ is a $\rho \times \rho$ Hermitian matrix with matrix elements

$$\Omega_{\mu\tau}^z(\varepsilon) = \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{x_\mu x_\tau}{I_y} + \frac{y_\mu y_\tau}{I_x} \right] + \sum_i^{n-3} \frac{\langle \mu z | \Phi_i^z \rangle \langle \Phi_i^z | \tau z \rangle}{\varepsilon - \lambda_i^z}, \quad (6c)$$

while $\Delta \mathbf{M}_\rho^{-1}$ is $\rho \times \rho$ diagonal matrix with diagonal matrix elements $1/\Delta m_\tau$. Conversely, each root of $f^z(\varepsilon)$ is a perturbed out-of-plane eigenvalue.

If $\varepsilon_k^z \notin \{\lambda_i^z\}$ is an out-of-plane eigenvalue, each normal mode corresponding to this eigenvalue is of the form

$$|\Psi_k^z\rangle = \frac{1}{\varepsilon_k^z} [T_z |\Phi_{Tz}\rangle + R_x |\Phi_{Rx}\rangle + R_y |\Phi_{Ry}\rangle] + \sum_i^{n-3} \frac{\sum_\tau^\rho \langle \Phi_i^z | \tau z \rangle C_\tau}{\varepsilon_k^z - \lambda_i^z} |\Phi_i^z\rangle, \quad (7c)$$

where coefficients T_z , R_x and R_y are [1]

$$T_z = \frac{1}{\sqrt{M}} \sum_\tau^\rho C_\tau, \quad R_x = \frac{1}{\sqrt{I_x}} \sum_\tau^\rho y_\tau C_\tau, \quad R_y = \frac{(-1)}{\sqrt{I_y}} \sum_\tau^\rho x_\tau C_\tau, \quad (7d)$$

and where C_τ are components of the nontrivial vector \mathbf{C} that is a solution of the matrix equation

$$\left[\boldsymbol{\Omega}^z(\varepsilon_k^z) + \frac{\Delta \mathbf{M}_\rho^{-1}}{\varepsilon_k^z} \right] \mathbf{C} = 0. \quad (8c)$$

The above relations produce all cardinal ($\varepsilon_k^z \notin \{\lambda_i^z\}$) eigenvalues and all the corresponding normal modes of the perturbed system. In addition, these relations may produce some singular ($\varepsilon_k^z \in \{\lambda_i^z\}$) eigenvalues. This may happen if the corresponding unperturbed eigenvalue $\lambda_j^z = \varepsilon_k^z$ is passive. In this case the corresponding normal mode or normal modes is also of the type (7c). In addition, there may exist some other singular eigenvalues and normal modes.

If there is only a single atom substituted by an isotope, the above relations simplify, and one obtains

$$f^z(\varepsilon) \equiv \sum_i^{n-3} \frac{\langle \tau z | \Phi_i^z \rangle \langle \Phi_i^z | \tau z \rangle}{\varepsilon - \lambda_i^z} + \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{x_\tau^2}{I_y} + \frac{y_\tau^2}{I_x} + \frac{1}{\Delta m_\tau} \right] = 0 \quad (9c)$$

in analogy to (9a) and (9b). Similarly, the relation (7c) simplifies to

$$|\Psi_k^z\rangle = \frac{1}{\varepsilon_k^z} \left[\frac{1}{\sqrt{M}} |\Phi_{Tz}\rangle + \frac{y_\tau}{\sqrt{I_x}} |\Phi_{Rx}\rangle - \frac{x_\tau}{\sqrt{I_y}} |\Phi_{Ry}\rangle \right] + \sum_i^{n-3} \frac{\langle \Phi_i^z | \tau z \rangle}{\varepsilon_k^z - \lambda_i^z} |\Phi_i^z\rangle \quad (10c)$$

in analogy to (10a) and (10b).

One finds that the out-of-plane frequencies of the planar molecules also satisfy interlacing rule. In particular, if A and B_τ are two planar molecules which differ by a single isotope substitution at an atomic site τ , and if molecule B_τ is heavier than molecule A , then the out-of-plane frequencies ν_i^z of the molecule A and the out-of-plane frequencies ω_k^z of the heavier molecule B_τ are interlaced according to the relation (22a). More generally, if planar molecules A and B differ by ρ ($\rho > 1$) isotopic substitutions, these frequencies are interlaced according to (14b). One also finds that the inversion relation (16) applies to the out-of-plane vibrations. In the case of out-of-plane vibrations matrix $\mathbf{A} \equiv \mathbf{A}^z$ and column vectors $\mathbf{X} \equiv \mathbf{X}^z$ and $\boldsymbol{\Sigma} \equiv \boldsymbol{\Sigma}^z$ are defined as

$$\mathbf{A}_{k,i}^z = \frac{1}{\varepsilon_k^z - \lambda_i^z}, \quad (15c)$$

$$\mathbf{X}_k = -\frac{1}{\varepsilon_k^z} \left[\frac{1}{M} + \frac{x_\tau^2}{I_y} + \frac{y_\tau^2}{I_x} + \frac{1}{\Delta m_\tau} \right],$$

$$\boldsymbol{\Sigma}_i^z = \sum_{\kappa}^{\eta} \langle \tau z | \Phi_{i\kappa}^z \rangle \langle \Phi_{i\kappa}^z | \tau z \rangle. \quad (17c)$$

As in the case of linear molecules, the inversion relation suggests a systematic method to obtain out-of-plane frequencies and normal modes of all isotopomers of a given planar molecule. All one needs are the experimental out-of-plane frequencies ν_i of

the unperturbed molecule A , and various complementary sets $\{\omega_k\}_\tau$ of the out-of-plane frequencies of monosubstituted molecules B_τ . For example, in the case of the benzene molecule there are nine out-of-plane normal modes. Due to the symmetry, all hydrogen positions are equivalent, and there is only one type of monodeuterated benzene. Hence, the set of only 18 frequencies, nine benzene out-of-plane frequencies and nine monodeuterated benzene out-of-plane frequencies, is sufficient to calculate the out-of-plane frequencies and normal modes for all bideuterated, trideuterated etc. benzene molecules. In fact, due to high symmetry of benzene molecule, even that much information is not needed, and it suffices to know only three out of nine monodeuterated frequencies [5].

It should be noted that another type of connection between vibrational frequencies of isotopic molecules can be obtained by various isotopic rules. Of such rules are known the product rule [6,7], the sum rule [8] and the complete isotopic rule [9,10]. For example, the complete isotopic rule concerns three isotopic molecules (A , B and C). These molecules must be in a special relation: molecule A is a plane molecule in which two definite atoms form a symmetrically equivalent set. B is identical to A except that one of these two atoms is exchanged for an isotope, and C is identical to A and B except that both of these two atoms are exchanged for this isotope [9,10]. An example is the set of three molecules: ethylene, ethylene-d1 and *trans*-ethylene-d2. From the known frequencies of the compounds A and C one can now calculate frequencies of the compound B .

There are important differences between isotopic rules and suggested method. All isotopic rules provide only the information about frequencies, while the suggested method determines in addition the corresponding normal modes. Further, this method produces in a systematic way out-of-plane (stretching, bending) frequencies of all isotopomers of a given planar (linear) molecule. All what is required are out-of-plane (stretching, bending) frequencies of the unperturbed molecule and of the selected monosubstituted molecules. In order to apply, for example, the complete isotopic rule, one has to know frequencies of two isotopic molecules A and C . These molecules differ in a very special way. Only then one can obtain the frequencies of the third molecule B which is intermediate between molecules A and C . Similar restrictions apply to other isotopic rules.

6. Out-of-plane vibrations of deuterated bromoethenes

As an example of the application of the above results, consider the out-of-plane vibrations of bromoethene and deuterated bromoethenes. The following bromoethene parameters were used [3]:

$$r_{CC} = 1.34 \text{ \AA}, \quad r_{CBr} = 1.86 \text{ \AA}, \quad r_{CH} = 1.07 \text{ \AA}, \quad \alpha(CBr) = \alpha(CCH) = 120^\circ.$$

In conjuncture with atomic masses as expressed in atomic units ($m_H = 1.0087$, $m_C = 12.011$, and $m_{Br} = 79.909$), these parameters determine molecular mass, molecular geometry and moments of inertia of bromoethene molecule. We will express all required quantities in the units of atomic masses and angstroms. In these units one finds

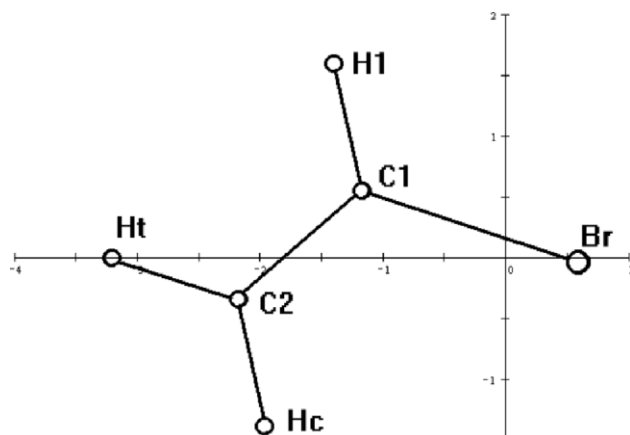


Figure 1. Bromoethene molecule. The origin of the coordinate system is in the molecular center of mass, and x - and y -axes coincide with molecular principal axes. Coordinate units are in angstroms.

Table 2
Experimental [3] out-of-plane frequencies (cm^{-1}) for bromoethene and monodeuterated bromoethenes.

Vibration	$\text{C}_2\text{H}_3\text{Br}$	CH_2CDBr	<i>trans</i> -CHDCHBr	<i>cis</i> -CHDCHBr
10	942	802	485	541 544*
11	902 906*	906 908*	940	918*
12	583	551	811 808*	797

* liquid.

$M = 106.9544$, $I_x = 9.6435$ and $I_y = 117.4137$, where I_x and I_y are the moments of inertia with respect to the two in-plane principal axes. In figure 1 bromoethene molecule is shown with the centre of mass situated in the origin of the coordinate system, and x - and y -axes chosen to be principal in-plane axes. In the following expressions we will use notation as in figure 1 when referring to various atoms. For example, $\langle \text{H1} | \Phi_i^z \rangle$ will denote the amplitude of the out-of-plane vibration Φ_i^z at the position of the hydrogen atom H1, etc.

There are three out-of-plane vibrations of bromoethene and deuterated bromoethenes. The corresponding frequencies are denoted as ν_{10} , ν_{11} and ν_{12} [3]. In table 2 are given the experimental out-of-plane frequencies of bromoethene and monodeuterated bromoethenes.

Using the inversion relation (16) with expressions (15c) for matrix \mathbf{A} and a vector \mathbf{X} , those frequencies determine the amplitude squares Σ_i of the unperturbed out-of-plane vibrations at the positions of the three hydrogen atoms. In particular, the out-of-plane frequencies of bromoethene $\text{C}_2\text{H}_3\text{Br}$ and monodeuterated bromoethene

CH_2CDBr determine squares $\langle \text{H1} | \Phi_i^z \rangle^2$, the out-of-plane frequencies of bromoethene and *cis*- CHDCHBr determine squares $\langle \text{Hc} | \Phi_i^z \rangle^2$, while the out-of-plane frequencies of bromoethene and *trans*- CHDCHBr determine squares $\langle \text{Ht} | \Phi_i^z \rangle^2$.

For some vibrations in table 2 two experimental frequencies are reported, one for a liquid phase, and another for a gas phase. Given a choice, we use frequency obtained in a gas phase as more reliable. Accordingly, in the following calculation we use gas frequencies from table 2, with a single exception of the frequency $\nu_{11} = 918 \text{ cm}^{-1}$ in the case of *cis*- CHDCHBr . This frequency is obtained in a liquid phase, and in [3] only this value is reported. Using these experimental frequencies one first constructs matrix \mathbf{A} and vector \mathbf{X} according to (23c). Next one applies the inversion relation (16) to obtain amplitude squares at the positions of the three hydrogen atoms. The corresponding amplitudes are:

$$\begin{aligned} \langle \text{H1} | \Phi_{10}^z \rangle &= 0.7215, & \langle \text{Hc} | \Phi_{10}^z \rangle &= 0.6013, & \langle \text{Ht} | \Phi_{10}^z \rangle &= -0.1755, \\ \langle \text{H1} | \Phi_{11}^z \rangle &= 0.2085, & \langle \text{Hc} | \Phi_{11}^z \rangle &= -0.4292, & \langle \text{Ht} | \Phi_{11}^z \rangle &= -0.6591, \\ \langle \text{H1} | \Phi_{12}^z \rangle &= 0.3437, & \langle \text{Hc} | \Phi_{12}^z \rangle &= -0.3923, & \langle \text{Ht} | \Phi_{12}^z \rangle &= 0.6337. \end{aligned} \quad (18a)$$

Inversion relation (16) determines only absolute values of the above amplitudes, but not their signs. Without loss of generality, one can choose amplitudes $\langle \text{H1} | \Phi_i^z \rangle$ at the position of the H1 hydrogen to be positive. Relative signs of the amplitudes on the other two hydrogen atoms can be obtained in various ways. For example, normal mode $|\Phi_{10}^z\rangle$ is of the approximate vibration type $\chi_{\text{CH}_2}^{\text{CHBr}}$ [3]. This suggests the amplitude $\langle \text{Hc} | \Phi_{10}^z \rangle$ to be positive, and the amplitude $\langle \text{Ht} | \Phi_{10}^z \rangle$ to be negative, in accord with relative signs chosen in (18a). In this way relative signs of all amplitudes of the normal mode $|\Phi_{10}^z\rangle$ are fixed. In a similar way approximate vibration types of other two out-of-plane vibrations may suggest possible relative signs for the amplitudes of these vibrations. There is, however, a more systematic way to determine these relative signs.

Each out-of-plane vibration Φ_i^z that appears in the equations (6c) and (7c) is by assumption normalised and orthogonal to all other vibrations. In particular, each vibration Φ_i^z is normalised and orthogonal to nonproper vibrations Φ_{Tz} , Φ_{Rx} and Φ_{Ry} :

$$\langle \Phi_{Tz} | \mathbf{M} | \Phi_i^z \rangle = 0, \quad \langle \Phi_{Rx} | \mathbf{M} | \Phi_i^z \rangle = 0, \quad \langle \Phi_{Ry} | \mathbf{M} | \Phi_i^z \rangle = 0, \quad (19a)$$

$$\langle \Phi_i^z | \mathbf{M} | \Phi_i^z \rangle = 1. \quad (19b)$$

Also, the three out-of-plane vibrations are mutually orthogonal:

$$\langle \Phi_{10}^z | \mathbf{M} | \Phi_{11}^z \rangle = 0, \quad \langle \Phi_{10}^z | \mathbf{M} | \Phi_{12}^z \rangle = 0, \quad \langle \Phi_{11}^z | \mathbf{M} | \Phi_{12}^z \rangle = 0. \quad (19c)$$

In order to give a complete description of the three out-of-plane bromoethene vibrations, we have to determine 18 quantities, the amplitudes at six atoms for each of the three out-of-plane vibrations. The inversion relation (16) provides absolute values of nine amplitudes (18a), while relations (19) provide additional 15 conditions. Thus, we have a mathematically overdetermined system. If there is no error in experimental frequencies utilised to obtain amplitudes (18a) and provided harmonic approximation is valid, all relations (19) must be satisfied exactly. Thus, the degree to which these

relations can be simultaneously satisfied is a measure of the mutual consistency of experimental data and/or validity of the harmonic approximation.

Fifteen conditions (19) are more than sufficient to fix relative signs of hydrogen amplitudes (18a). In addition, besides amplitudes (18a) on hydrogen atoms, these conditions determine the remaining vibrational amplitudes on two carbon atoms and on the bromium atom.

After some algebra one finds that conditions (19a) are equivalent to the matrix relation

$$\mathbf{Y} = \mathbf{\Lambda}^{-1}\mathbf{U}\mathbf{H}, \quad (20a)$$

where

$$\mathbf{H} = \begin{pmatrix} \text{H1} \\ \text{Hc} \\ \text{Ht} \end{pmatrix}, \quad \mathbf{Y} = \begin{pmatrix} \text{C1} \\ \text{C2} \\ \text{Br} \end{pmatrix}, \quad (20b)$$

$$\mathbf{\Lambda} = \begin{bmatrix} m_{\text{C}} & m_{\text{C}} & m_{\text{Br}} \\ x_{\text{C1}}m_{\text{C}} & x_{\text{C2}}m_{\text{C}} & x_{\text{Br}}m_{\text{Br}} \\ y_{\text{C1}}m_{\text{C}} & y_{\text{C2}}m_{\text{C}} & y_{\text{Br}}m_{\text{Br}} \end{bmatrix}, \quad \mathbf{U} = \begin{bmatrix} 1 & 1 & 1 \\ x_{\text{H}} & x_{\text{Hc}} & x_{\text{Ht}} \\ y_{\text{H}} & y_{\text{Hc}} & y_{\text{Ht}} \end{bmatrix}$$

and where we use simplified notation $\text{H1} = \langle \text{H1} | \Phi_i^z \rangle$, $\text{Hc} = \langle \text{Hc} | \Phi_i^z \rangle$, $\text{Ht} = \langle \text{Ht} | \Phi_i^z \rangle$, $\text{C1} = \langle \text{C1} | \Phi_i^z \rangle$, $\text{C2} = \langle \text{C2} | \Phi_i^z \rangle$ and $\text{Br} = \langle \text{Br} | \Phi_i^z \rangle$ in order to denote amplitudes of the i th out-of-plane vibration Φ_i^z at various atomic sites. The condition $|\mathbf{U}| = 0$ is the condition of the colinearity of the three hydrogen atoms, while the condition $|\mathbf{\Lambda}| = 0$ is the condition of the colinearity of two carbon atoms and a bromium atom. In the case of bromoethene it is obviously $|\mathbf{U}| \neq 0$ and $|\mathbf{\Lambda}| \neq 0$ and the matrices \mathbf{U} and $\mathbf{\Lambda}$ are, hence, nonsingular. This guarantees the existence of the inverse $\mathbf{\Lambda}^{-1}$.

Relations (20) express amplitudes at the positions of two carbon atoms and bromium atom in terms of the amplitudes at the positions of the three hydrogen atoms. However, absolute values of the amplitudes at the positions of hydrogen atoms are obtained from the inversion relation. We determine relative signs of these amplitudes using remaining normalisation conditions (19b) and orthogonality conditions (19c). Since without loss of generality amplitudes $\langle \text{H1} | \Phi_i^z \rangle$ at the position of the H1 hydrogen can be assumed to be positive, one has only to determine relative signs of the amplitudes $\langle \text{Hc} | \Phi_i^z \rangle$ and $\langle \text{Ht} | \Phi_i^z \rangle$ at the positions of *cis*- and *trans*-hydrogens, respectively.

The simplest way to proceed is to calculate norms $N_i = \langle \Phi_i^z | \mathbf{M} | \Phi_i^z \rangle$ for each possible combination of hydrogen amplitude signs, and to see how much these norms differ from unity. Acceptable are only those sign combinations for which the norms do not differ substantially from unity. For example, in the case of the vibration Φ_{10}^z one obtains the following results for various possible sign combinations on *cis*- and *trans*-positions: *cis*⁺*trans*⁺, $N = 1.042$; *cis*⁺*trans*⁻, $N = 0.981$; *cis*⁻*trans*⁺, $N = 1.704$; *cis*⁻*trans*⁻, $N = 1.712$. Norms $N = 1.704$ and $N = 1.712$ are obviously in error, while norms $N = 1.042$ and $N = 0.981$ are both in principle acceptable, since the deviation from unity is not significant, and this deviation can be attributed to the experimental error. Thus, we dismiss the signs combinations *cis*⁻*trans*⁺ and *cis*⁻*trans*⁻ as

unacceptable, while there is still ambiguity between the sign combinations cis^+trans^+ and cis^+trans^- . Similar results are obtained for the vibrations Φ_{11}^z and Φ_{12}^z . In this way the majority of the possible 64 sign combinations are eliminated. In order to make a final choice between remaining ambiguous possibilities, we use the remaining orthogonality conditions (19c). For example, in the case of the vibration Φ_{12}^z , there is an ambiguity between amplitude signs cis^-trans^+ ($N = 0.947$) and cis^-trans^- ($N = 0.982$). These results taken alone suggest that the sign combination cis^-trans^- is preferable to the sign combination cis^-trans^+ . However, if for both options one calculates overlaps with remaining two vibrations, one obtains $\langle \Phi_{10}^z | \mathbf{M} | \Phi_{12}^z \rangle = 0.145$ and $\langle \Phi_{11}^z | \mathbf{M} | \Phi_{12}^z \rangle = 0.940$ for the first sign choice, and $\langle \Phi_{10}^z | \mathbf{M} | \Phi_{12}^z \rangle = 0.004$ and $\langle \Phi_{11}^z | \mathbf{M} | \Phi_{12}^z \rangle = -0.030$ for the second sign choice. The sign choice cis^-trans^- is obviously in error. Such analysis finally leads to the sign combination as given in equation (18a). Once the amplitudes on hydrogen atoms are determined, the amplitudes on the remaining three atoms are obtained from relation (20). In this way one finds

$$\begin{aligned} \langle C1 | \Phi_{10}^z \rangle &= -0.0659, & \langle C2 | \Phi_{10}^z \rangle &= -0.0277, & \langle Br | \Phi_{10}^z \rangle &= -0.0004, \\ \langle C1 | \Phi_{11}^z \rangle &= -0.0592, & \langle C2 | \Phi_{11}^z \rangle &= 0.1341, & \langle Br | \Phi_{11}^z \rangle &= -0.0001, \\ \langle C1 | \Phi_{12}^z \rangle &= -0.1443, & \langle C2 | \Phi_{12}^z \rangle &= 0.0291, & \langle Br | \Phi_{12}^z \rangle &= 0.0099. \end{aligned} \quad (18b)$$

The above simple method of determining relative signs of vibrational amplitudes can be done in a more systematic way. As a quantitative measure of the deviation from the conditions (19b) and (19c) one can define a quantity

$$\Delta^2 = \frac{\sum_i (\langle \Phi_i^z | \mathbf{M} | \Phi_i^z \rangle - 1)^2 + \langle \Phi_{10}^z | \mathbf{M} | \Phi_{11}^z \rangle^2 + \langle \Phi_{10}^z | \mathbf{M} | \Phi_{12}^z \rangle^2 + \langle \Phi_{11}^z | \mathbf{M} | \Phi_{12}^z \rangle^2}{6}. \quad (21)$$

Due to (20) remaining conditions (19a) are guaranteed to be satisfied. We now investigate in a systematic way all possible combinations of amplitude signs at *cis*- and *trans*-hydrogens for all three vibrations, and we choose the absolute minimum. There are 64 such combinations, and one obtains a minimum value of $\Delta = 0.041$ for the sign combination: Φ_{10}^z : cis^+trans^- , Φ_{11}^z : cis^-trans^- and Φ_{12}^z : cis^-trans^+ . This result is in accord with the above more simple approach. All other possible sign combinations produce substantially larger values for Δ . The next smallest value is $\Delta = 0.090$.

In conclusion, in this simple method one obtains vibrational amplitudes (18) from the experimental out-of-plane frequencies of bromoethene and three monodeuterated bromoethene molecules.

Once the vibration amplitudes (18) are obtained, one can use relations (5c)–(8c) to derive frequencies and vibrations for all possible bromoethene isotopomers. In particular, if vibrations for deuterated bromoethenes are required, only amplitudes (18a) on hydrogen atoms are needed.

Table 3 gives the frequencies of deuterated isotopomers that were calculated in this way. Thus, all theoretical frequencies of polydeuterated bromoethenes in table 3

Table 3

Comparison of theoretical (LRP) and experimental [3] out-of-plane frequencies (cm^{-1}) for polydeuterated bromoethenes. LRP frequencies were calculated using 12 out-of-plane frequencies of bromoethene and monodeuterated bromoethenes (see table 2).

	10			11			12		
	Exp.	Calc.	Diff.	Exp.	Calc.	Diff.	Exp.	Calc.	Diff.
CD ₂ CHBr	465	464.1	-0.9	724 723*	730.8	6.8	871	870.0	-1.0
<i>cis</i> -CHDCDBr	719 716*	719.1	0.1	872 864*	871.2	-0.8	476	476.6	0.6
<i>trans</i> -CHDCDBr	691	692.9	1.9	856	858.3	2.3	532 533*	531.3	-0.7
CD ₂ CDBr	462	461.4	-0.6	732 730*	737.6	5.6	691	691.2	0.2

* liquid.

were obtained using the experimental frequencies of bromoethene and monodeuterated bromoethenes given in table 2.

The agreement between theoretical and experimental frequencies is very good. Especially good is the agreement with experimental gas frequencies, which is consistent with acceptance of these frequencies as more reliable. A standard error for all calculated frequencies in table 3 from the experimental gas frequencies is only $\Delta = 2.74 \text{ cm}^{-1}$.

Once a particular perturbed eigenvalue is calculated, one can obtain the corresponding vibration or vibrations from relations (7c) and (8c). For the sake of simplicity, we do not report these perturbed vibrations here.

In the above derivation of theoretical frequencies in table 3, the six conditions (19b) and (19c) were used only as auxiliary conditions for the sole purpose of determining relative signs of various nonperturbed vibrational amplitudes. This is not very economical, and these conditions can be used in a much more efficient way. This leads to a more powerful method, albeit mathematically more complex.

Assume, for example, that we know out-of-plane frequencies of C₂H₃Br and *cis*- and *trans*-CHDCDBr, but we have no knowledge of the out-of-plane frequencies of CH₂CDBr isotope. We can use the inversion relation in order to obtain amplitude squares $\langle \text{Hc} | \Phi_i^z \rangle^2$ and $\langle \text{Ht} | \Phi_i^z \rangle^2$ of the three out-of-plane vibrations at the positions of *cis*- and *trans*-hydrogen atoms. Relations (20) eliminate all amplitudes at the two carbon atoms and at the bromium atom, and we are left with six conditions (19b) and (19c) in three unknown amplitudes $\langle \text{Hl} | \Phi_i^z \rangle$. We solve these equations by minimizing standard deviation (21). Since the inversion relation does not give any clue about signs of the amplitudes $\langle \text{Hc} | \Phi_i^z \rangle$ and $\langle \text{Ht} | \Phi_i^z \rangle$, one has to repeat this calculation for all possible sign combinations. Each sign combination produces a different value for a standard deviation (21). From all possible sign combinations one chooses that one which produces the smallest value of Δ . One, thus, again obtains a sign combination as given in relation (18a). For this sign combination one finds $\Delta = 0.028$,

Table 4

Comparison of theoretical (LRP) and experimental [3] out-of-plane frequencies (cm^{-1}) for monodeuterated bromoethene CH_2CDBr and polydeuterated bromoethenes. LRP frequencies were calculated using nine experimental out-of-plane frequencies of bromoethene $\text{C}_2\text{H}_3\text{Br}$ and *cis*- and *trans*-monodeuterated bromoethenes CHDCHBr (see table 2).

	10			11			12		
	Exp.	Calc.	Diff.	Exp.	Calc.	Diff.	Exp.	Calc.	Diff.
CH_2CDBr	802	801.0	-1.0	906 908*	907.3	1.3	551	546.7	-4.3
CD_2CHBr	465	464.1	-0.9	724 723*	730.7	6.7	871	869.9	-1.1
<i>cis</i> - CHDCDBr	719 716*	716.7	-2.3	872 864*	875.7	3.7	476	476.7	0.7
<i>trans</i> - CHDCDBr	691	695.8	4.8	856	857.1	1.1	532 533*	530.2	-1.8
CD_2CDBr	462	460.5	-1.5	732 730*	733.5	1.5	691	691.1	0.1

* liquid.

and the corresponding amplitudes are

$$\begin{aligned}
 \langle \text{H1} | \Phi_{10}^z \rangle &= 0.7192, & \langle \text{Hc} | \Phi_{10}^z \rangle &= 0.6013, & \langle \text{Hr} | \Phi_{10}^z \rangle &= -0.1755, \\
 \langle \text{H1} | \Phi_{11}^z \rangle &= 0.2443, & \langle \text{Hc} | \Phi_{11}^z \rangle &= -0.4292, & \langle \text{Hr} | \Phi_{11}^z \rangle &= -0.6591, \\
 \langle \text{H1} | \Phi_{12}^z \rangle &= 0.3685, & \langle \text{Hc} | \Phi_{12}^z \rangle &= -0.3923, & \langle \text{Hr} | \Phi_{12}^z \rangle &= 0.6337, \\
 \langle \text{C1} | \Phi_{10}^z \rangle &= -0.0655, & \langle \text{C2} | \Phi_{10}^z \rangle &= -0.0278, & \langle \text{Br} | \Phi_{10}^z \rangle &= -0.0004, \\
 \langle \text{C1} | \Phi_{11}^z \rangle &= -0.0663, & \langle \text{C2} | \Phi_{11}^z \rangle &= 0.1364, & \langle \text{Br} | \Phi_{11}^z \rangle &= 0.0001, \\
 \langle \text{C1} | \Phi_{12}^z \rangle &= -0.1492, & \langle \text{C2} | \Phi_{12}^z \rangle &= 0.0307, & \langle \text{Br} | \Phi_{12}^z \rangle &= 0.0101.
 \end{aligned} \tag{22}$$

The above amplitudes were obtained using only 9 experimental frequencies. Those amplitudes slightly differ from the amplitudes (18) which were obtained using 12 experimental frequencies. In particular, since in both approaches amplitudes $\langle \text{Hc} | \Phi_i^z \rangle$ and $\langle \text{Hr} | \Phi_i^z \rangle$ were derived from the inversion relation using the same experimental data, those amplitudes are the same in (18) and (22). However, amplitudes $\langle \text{H1} | \Phi_i^z \rangle$ at the H1 hydrogen atoms slightly differ in (18) and (22). Also, all amplitudes on the remaining three atoms that were obtained using relation (20) slightly differ in these two approaches.

Once the amplitudes (22) are derived, one can calculate the out-of-plane frequencies and the corresponding normal modes for all bromoethene isotopomers.

The obtained results for deuterated bromoethenes are shown in table 4. The agreement between thus obtained theoretical and experimental frequencies is again very good. Though, unlike in the first simple method, in order to obtain theoretical frequencies in table 4 we did not use experimental out-of-plane frequencies of CH_2CDBr , standard deviation of all thus obtained frequencies from the experimental values is $\Delta 1 = 2.84 \text{ cm}^{-1}$. This differs insignificantly from the standard deviation $\Delta = 2.74 \text{ cm}^{-1}$ of theoretical

frequencies in table 3. In addition, in this improved method we obtain out-of-plane frequencies of CH_2CDBr as a theoretical result.

The identical approach can be followed if we have no knowledge of the out-of-plane frequencies of either *cis*- or *trans*-CHDCHBr. In the former case in addition to the out-of-plane frequencies of poly-deuterated bromoethenes one also obtains out-of-plane frequencies of *cis*-CHDCHBr. Standard deviation of all thus obtained theoretical frequencies from the experimental frequencies is $\Delta c = 2.96 \text{ cm}^{-1}$. In the latter case in addition to the out-of-plane frequencies of poly-deuterated bromoethenes one also obtains the out-of-plane frequencies of *trans*-CHDCHBr. Standard deviation of all thus obtained theoretical frequencies from the experimental frequencies is $\Delta t = 2.72 \text{ cm}^{-1}$. The comparison of thus obtained standard deviations $\Delta l = 2.84 \text{ cm}^{-1}$, $\Delta c = 2.96 \text{ cm}^{-1}$ and $\Delta t = 2.72 \text{ cm}^{-1}$ with a standard deviation $\Delta = 2.74 \text{ cm}^{-1}$ shows that by neglecting one set of the three monodeuterated out-of-plane frequencies one does not deteriorate the precision of the calculated frequencies in any significant way.

One can even further decrease the number of required experimental frequencies [5]. In the above example we have found three unknown amplitudes $\langle \text{H}1 | \Phi_i^z \rangle$ by using six conditions (19b) and (19c). This was done by minimising the quantity (21). However, since there are six conditions and only three unknowns, this suggests that we can dismiss additional three experimental frequencies. This can be really done. However, some caution is required.

The simplest idea is to use three out-of-plane frequencies of bromoethene $\text{C}_2\text{H}_3\text{Br}$ and, for example, three out-of-plane frequencies of *cis*-CHDCHBr. However, one finds that these six experimental frequencies are mutually dependent [5], and this method does not work. Dependence of these frequencies follows from the product rule [6] that relates product of the three bromoethene out-of-plane frequencies with the three *cis*-CHDCHBr out-of-plane frequencies. Instead of three out-of-plane frequencies of the same deuterated bromoethene, one has to use three out-of-plane frequencies of at least two mutually different deuterated bromoethenes. Since the number of unknowns now matches the number of equations, conditions (19) are satisfied exactly, and the standard deviation (21) vanishes. Depending on the choice of experimental frequencies taken into account, the standard error of thus calculated frequencies varies, but it is in most cases approximately $\Delta \approx 5 \text{ cm}^{-1}$. Thus, the precision of the theoretical frequencies deteriorates from approximately $\Delta \approx 3 \text{ cm}^{-1}$ to approximately $\Delta \approx 5 \text{ cm}^{-1}$. This is the price one has to pay if there is a paucity of experimental frequencies and if one wants to calculate various theoretical frequencies from the minimum number of experimental frequencies. Nevertheless, this is still an acceptable result. The details of this approach will be given elsewhere [5].

The crucial point in the above approach is derivation of vibrational amplitudes of bromoethene $\text{C}_2\text{H}_3\text{Br}$. Once these amplitudes are obtained, one easily derives frequencies and normal modes of all bromoethene isotopomers. We have shown in tables 3 and 4 how thus obtained frequencies agree with the experimental out-of-plane frequencies of various deuterated bromoethenes. In a similar way out-of-plane frequencies for all other bromoethene isotopomers can be obtained. Also, using relations (7c) and (8c)

one obtains in this way all the corresponding normal modes. For the sake of simplicity we omit the calculation of those normal modes, but it is straightforward.

Using data in tables 2–4 one can also verify that out-of-plane frequencies of bromoethene and deuterated bromoethenes satisfy interlacing rule. For example, experimental out-of-plane frequencies of bromoethene $\text{C}_2\text{H}_3\text{Br}$ (d0) and deuterated bromoethene CH_2CDBr (d1) that differ by a single isotopic substitution satisfy $551(\text{d1}) < 583(\text{d0}) < 802(\text{d1}) < 902(\text{d0}) < 906(\text{d1}) < 942(\text{d0})$ in accord with (14a). Similar agreement is obtained if one compares out-of-plane frequencies of all other bromoethene isotopomers that differ by a single isotopic substitution.

7. In-plane vibrations of planar molecules

In the case of in-plane vibrations of planar molecules, relations obtained in [1] similarly simplify. Thus, one finds that $\varepsilon_k^{xy} \notin \{\lambda_i^{xy}\}$ is an in-plane eigenvalue of the perturbed system if and only if it is a root of $f^{xy}(\varepsilon) \equiv |\mathbf{\Omega}^{xy}(\varepsilon) + \Delta\mathbf{M}_{2\rho}^{-1}/\varepsilon| = 0$, where $\mathbf{\Omega}^{xy}(\varepsilon)$ and $\Delta\mathbf{M}_{2\rho}^{-1}$ are now $2\rho \times 2\rho$ Hermitian matrices. In particular, concerning matrix elements of $\mathbf{\Omega}^{xy}(\varepsilon)$ [1], one should take into account that in the case of planar molecules all z -coordinates of various isotope atoms vanish ($z_\mu = 0$). Also, corresponding summations are performed over $(2n - 3)$ in-plane vibrations Φ_i^{xy} and eigenvalues λ_i^{xy} . Once a particular in-plane eigenvalue $\varepsilon_k^{xy} \notin \{\lambda_i^{xy}\}$ is obtained, each perturbed normal mode Ψ_k^{xy} corresponding to this eigenvalue is of the form

$$\begin{aligned} |\Psi_k^{xy}\rangle = & \frac{1}{\varepsilon_k^{xy}} [T_x |\Phi_{Tx}\rangle + T_y |\Phi_{Ty}\rangle + R_z |\Phi_{Rz}\rangle] \\ & + \sum_i^{n-3} \frac{\sum_\tau^\rho [\langle \Phi_i^{xy} | \tau x \rangle C_{\tau x} + \langle \Phi_i^{xy} | \tau y \rangle C_{\tau y}]}{\varepsilon_k^{xy} - \lambda_i^{xy}} |\Phi_i^{xy}\rangle \end{aligned} \quad (23)$$

in accord with [1, equation (21a)]. Note that in the case of in-plane vibrations, the components $C_{\tau z}$ of the column vector \mathbf{C} vanish, which implies $T_z = 0$, $R_x = 0$ and $R_y = 0$. Hence, [1, equation (21a)] simplifies to (23). Also, the coefficients $C_{\tau x}$ and $C_{\tau y}$ are components of a 2ρ column vector, solution of the matrix equation $[\mathbf{\Omega}(\varepsilon_k^{xy}) - \Delta\mathbf{M}_{2\rho}^{-1}/\varepsilon_k^{xy}]\mathbf{C} = 0$.

In the case of a single isotope substitution function $f^{xy}(\varepsilon)$ further simplifies to

$$f^{xy}(\varepsilon) \equiv \begin{vmatrix} \mathbf{\Omega}_{xx}(\varepsilon) + \frac{1}{\varepsilon \Delta m_\tau} & \mathbf{\Omega}_{xy}(\varepsilon) \\ \mathbf{\Omega}_{yx}(\varepsilon) & \mathbf{\Omega}_{yy}(\varepsilon) + \frac{1}{\varepsilon \Delta m_\tau} \end{vmatrix} = 0, \quad (24a)$$

where

$$\begin{aligned}\Omega_{xx}(\varepsilon) &= \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{y_\tau y_\tau}{I_z} \right] + \sum_i^{2n-3} \frac{\langle \tau x | \Phi_i^{xy} \rangle \langle \Phi_i^{xy} | \tau x \rangle}{\varepsilon - \lambda_i^{xy}}, \\ \Omega_{yy}(\varepsilon) &= \frac{1}{\varepsilon} \left[\frac{1}{M} + \frac{x_\tau x_\tau}{I_z} \right] + \sum_i^{2n-3} \frac{\langle \tau y | \Phi_i^{xy} \rangle \langle \Phi_i^{xy} | \tau y \rangle}{\varepsilon - \lambda_i^{xy}}, \\ \Omega_{xy}(\varepsilon) &= -\frac{x_\tau y_\tau}{\varepsilon I_z} + \sum_i^{2n-3} \frac{\langle \tau x | \Phi_i^{xy} \rangle \langle \Phi_i^{xy} | \tau y \rangle}{\varepsilon - \lambda_i^{xy}}.\end{aligned}\quad (24b)$$

Similarly, the relation (23) reduces to

$$\begin{aligned}|\Psi_k^{xy}\rangle &= \frac{1}{\varepsilon_k^{xy}} \left[\frac{C_x}{\sqrt{M}} |\Phi_{T_x}\rangle + \frac{C_y}{\sqrt{M}} |\Phi_{T_y}\rangle + \frac{x_\tau C_y - y_\tau C_x}{\sqrt{I_z}} |\Phi_{R_z}\rangle \right] \\ &+ \sum_i^{n-3} \frac{\langle \Phi_i^{xy} | \tau x \rangle C_x + \langle \Phi_i^{xy} | \tau y \rangle C_y}{\varepsilon_k^{xy} - \lambda_i^{xy}} |\Phi_i^{xy}\rangle,\end{aligned}$$

where ε_k^{xy} is a root of $f^{xy}(\varepsilon)$, and where (C_x, C_y) is a (nontrivial) solution of a matrix equation

$$\begin{bmatrix} \Omega_{xx}(\varepsilon_k^{xy}) + \frac{1}{\varepsilon_k^{xy} \Delta m_\tau} & \Omega_{xy}(\varepsilon_k^{xy}) \\ \Omega_{yx}(\varepsilon_k^{xy}) & \Omega_{yy}(\varepsilon_k^{xy}) + \frac{1}{\varepsilon_k^{xy} \Delta m_\tau} \end{bmatrix} \begin{bmatrix} C_x \\ C_y \end{bmatrix} = 0.$$

The above relations again express the perturbed frequencies and normal modes in terms of the unperturbed frequencies and normal modes. Thus, if the unperturbed frequencies and amplitudes of the unperturbed normal modes at the sites of isotopic substitutions are known, one can obtain frequencies and normal modes of all isotopomers. However, in the case of in-plane vibrations, there is no analogy to a simple inversion relation (16) by which one can obtain amplitudes of the unperturbed vibrations at the selected isotopic site. Unlike out-of-plane vibrations Φ_i^z , each in-plane vibration Φ_i^{xy} has at the atomic site τ two components, an amplitude $\langle \tau x | \Phi_i^{xy} \rangle$ and an amplitude $\langle \tau y | \Phi_i^{xy} \rangle$. This is double as many amplitudes as in the case of the out-of-plane vibrations, and accordingly Ω^{xy} is a $2\rho \times 2\rho$ matrix. Since there are $(2n - 3)$ proper in-plane vibrations, one has to determine $2(2n - 3)$ in-plane amplitudes at atomic site τ . In the case of a single isotope substitution at the atomic site τ , the relation (24a) is satisfied by $(2n - 3)$ planar isotope vibrations, and this is not sufficient to determine all in-plane amplitudes. However, if we have two isotope substitutions at the same site τ , for example, deuterium and tritium substituting hydrogen, then we have at the disposal $2(2n - 3)$ experimental planar isotope frequencies, and this should be sufficient to invert relation (24a) in order to determine planar amplitudes. However, the obtained relations are much more complicated than a simple inversion relation (16). Nevertheless, this shows that one can obtain in-plane amplitudes at a site τ if one knows experimental in-plane frequencies of two isotopomers that differ from the unperturbed molecule at a single site. In

many cases molecular symmetry may help to determine in-plane vibrational amplitudes. Alternatively, one can obtain the necessary information from in-plane frequencies of selected bi-substituted isotopomers, etc. [5]. Finally, one can deduce these amplitudes in a standard way using some force field model. Once these amplitudes are obtained in either way, the LRP approach provides a simple and a straightforward method to derive in-plane frequencies and the corresponding normal modes for all isotopomers.

Unlike inversion relation, there is a simple and straightforward generalisation of the interlacing rule to in-plane frequencies of planar molecules, and more generally, to frequencies of arbitrary (nonplanar) molecule.

Consider two planar molecules A and B_τ that are identical, except for a single isotopic substitution at site τ . Let molecule B_τ be heavier than molecule A . Relation (24) relates in-plane frequencies of a molecule A with in-plane frequencies of a molecule B_τ . Transition from A to B_τ is in this relation due to the increase Δm_τ of the isotopic mass. The same mass increase is associated with x - and with y -direction. Formally, one can consider transition from A to B_τ in two steps, transition from A to intermediate “molecule” C , and transition from C to B_τ . Molecule C has an “isotope” at the site τ with mass increase Δm_τ associated with x -direction, but no mass increase associated with the y -direction. This molecule is a mathematical construct, but not a real molecule. Nevertheless, transition from A to C is described by the relations analogous to relations (9), which imply interlacing rule (14a). Hence, as far as interlacing rule for in-plane vibrations is concerned, transition from A to B_τ is equivalent to a sequence of two simple transitions: a transition from A to C and a subsequent transition from C to B_τ . It follows that, if ν_k^{xz} and ω_k^{xz} are in-plane frequencies of a molecules A and B_τ , respectively, and if these frequencies are arranged in the nondecreasing order, then

$$\nu_{k-2}^{xz} \leq \omega_k^{xz} \leq \nu_k^{xz}. \quad (14c)$$

In a similar way one finds that frequencies of arbitrary (nonplanar) isotopic molecules A and B_τ that differ by a single isotopic substitution such that molecule B_τ is heavier than molecule A , are interlaced according to

$$\nu_{k-3} \leq \omega_k \leq \nu_k. \quad (14d)$$

Relations (14c) and (14d) apply to a single isotopic substitution. It is straightforward to generalise these relations to arbitrary isotopic molecules A and B that differ by multiple isotopic substitutions. Relations thus obtained are very similar to relations (14b). In the case of interlacing in-plane vibrations of planar molecules one should replace quantities ρ and η in (14b) with 2ρ and 2η , respectively, while in the case of interlacing vibrations of arbitrary (nonplanar) molecules one should replace these quantities with 3ρ and 3η , respectively.

8. Conclusion

The general theory of vibrational isotope effect developed in the previous [1] is applied to the vibrational isotope effect of linear and planar molecules. Stretching and

bending vibrations of linear molecules and out-of-plane vibrations of planar molecules were explicitly considered. The interlacing rule which interlaces the frequencies of the perturbed system and the frequencies of the unperturbed system is derived. This rule applies to the stretching (bending) frequencies of linear molecules, as well as to the out-of-plane frequencies of the planar molecules. The rule is particularly simple if molecules A and B_τ differ by a single isotopic substitution at the site τ , but it applies also to a general case of two isotopic molecules A and B that differ by an arbitrary number of isotopic substitutions. The rule is also generalised to in-plane vibrations of planar molecules, as well as to arbitrary (nonplanar) molecules.

Given a pair of linear (planar) isotopic molecules A and B_τ that differ by a single isotopic substitution at the site τ , inversion relation that expresses squares of the unperturbed vibrational amplitudes at the site τ in terms of the vibrational frequencies of molecules A and B_τ are derived. The inversion relation applies to the stretching and bending vibrations of linear molecules, as well as to the out-of-plane vibrations of planar molecules. Thus, using only experimental quantities, for example, out-of-plane frequencies of molecules A and B_τ , one can calculate squares of unperturbed out-of-plane amplitudes at the selected atomic sites τ . By using some additional information, such as the requirement that all vibrations be normalised and mutually orthogonal, one can derive also relative signs of these amplitudes at different atomic sites. In this way isotopic molecule B_τ , or rather out-of-plane frequencies of this molecule, serve as a probe to determine unperturbed amplitudes at this site. Thus, using various isotopic molecules B_τ as a probe, one can obtain unperturbed out-of-plane amplitudes at selected atomic sites. Once these amplitudes are known, one can calculate out-of-plane frequencies and the corresponding normal modes for all isotopomers that involve these selected sites.

As an example we have considered out-of-plane vibrations of bromoethene and deuterated bromoethenes. Two methods were explicitly considered. In the first method three inversion relations were used in order to obtain bromoethene out-of-plane vibrational amplitudes at three hydrogen atoms. This requires 12 experimental out-of-plane frequencies, three bromoethene out-of-plane frequencies, and three out-of-plane frequencies for each of the three monodeuterated bromoethenes CH_2CDBr , *cis*- CHDCHBr and *trans*- CHDCHBr . Relative signs of these amplitudes were obtained by imposing the requirement that these vibrations be normalised and mutually orthogonal. In addition, requirement of the orthogonality of these out-of-plane vibrations to three nonproper vibrations produces vibrational amplitudes at the sites of the two carbon atoms and a bromium atom. In this way all amplitudes of the bromoethene out-of-plane vibrations were derived. Once these amplitudes are obtained, one can calculate frequencies and normal modes for all bromoethene isotopomers. We have done this for deuterated bromoethenes. In this way the out-of-plane frequencies of CD_2CHBr , *cis*- CHDCDBr , *trans*- CHDCDBr and CD_2CDBr were calculated. Standard deviation of thus obtained theoretical frequencies from experimental frequencies is only $\Delta = 2.74 \text{ cm}^{-1}$. In the second method only out-of-plane experimental frequencies of bromoethene and *cis*- CHDCHBr and *trans*- CHDCHBr were used, but out-of-plane frequencies of CH_2CDBr were assumed unknown. In this method in addition to the out-of-plane frequencies of all

polydeuterated bromoethenes, one obtains as a bonus out-of-plane frequencies of monodeuterated bromoethene CH_2CDBr . Standard deviation of thus obtained theoretical frequencies from experimental frequencies is $\Delta l = 2.84 \text{ cm}^{-1}$. The same method can be applied to the case when we have no knowledge of the *cis*-CHDCCHBr out-of-plane frequencies ($\Delta c = 2.96 \text{ cm}^{-1}$), or no knowledge of *trans*-CHDCCHBr out-of-plane frequencies ($\Delta t = 2.72 \text{ cm}^{-1}$). In all three cases nine experimental out-of-plane frequencies were used in order to calculate 15 out-of-plane frequencies. Theoretical frequencies thus obtained are in very good agreement with experimental frequencies, standard deviation in all three cases being less than $\Delta = 3 \text{ cm}^{-1}$.

It is possible to decrease the number of required experimental frequencies even further, and to use only six experimental frequencies in order to calculate 18 out-of-plane frequencies. If this is done one finds that the standard deviation of thus calculated frequencies from experimental frequencies is approximately $\Delta \approx 5 \text{ cm}^{-1}$. This deterioration of theoretical results from $\Delta \approx 3 \text{ cm}^{-1}$ to $\Delta \approx 5 \text{ cm}^{-1}$ is a price one has to pay in order to decrease the number of experimental frequencies which are used as input data as much as possible.

Once the amplitudes of the unperturbed vibrations are obtained in either way, besides frequencies of various isotopomers one can also obtain all the corresponding normal modes. For the sake of simplicity this is not done in the present paper. However, the use of formulas (7) and (8) in the case of linear and planar molecules, as well as corresponding formulas in the case of arbitrary molecules [1] is straightforward.

In conclusion, the suggested LRP method provides a general formalism to treat vibrational isotopic effect in the harmonic approximation. This treatment is particularly simple in the case of linear molecules and in the case of out-of-plane vibrations of planar molecules.

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