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Vibrational isotope effect by the low rank perturbation method

Case study: out-of-plane vibrations of benzene (H,D)-isotopomers

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Abstract   Mathematical formalism of the Low Rank Perturbation method (LRP) is applied to the vibrational isotope effect in the harmonic approximation with a standard assumption that force field does not change under isotopic substitutions. A pair of two n-atom isotopic molecules **A** and **B** which are identical except for isotopic substitutions at ρ atomic sites is considered. In the LRP approach vibrational frequencies ω_k and normal modes $|\Psi_k\rangle$ of the isotopomer **B** are expressed in terms of the vibrational frequencies ν_i and normal modes $|\Phi_i\rangle$ of the parent molecule **A**. In those relations complete specification of the normal modes $|\Phi_i\rangle$ is not required. Only amplitudes $\langle \tau s|\Phi_i\rangle$ at sites τ affected by the isotopic substitutions and in the coordinate direction s ($s = x, y, z$) are needed. Out-of-plane vibrations of the (H,D)-benzene isotopomers are considered. Standard error of the LRP frequencies with respect to the DFT frequencies is on average $\Delta \approx 0.48\,\mathrm{cm}^{-1}$. This error is due to the uncertainty of the input data ($\pm 0.5\,\mathrm{cm}^{-1}$) and in the absence of those uncertainties and in the harmonic approximation it should disappear. In comparing with experiment, one finds that LRP frequencies reproduces experimental frequencies of (H,D)-benzene isotopomers better ($\Delta_{LRP} \approx 4.74\,\mathrm{cm}^{-1}$) than scaled DFT frequencies ($\Delta_{DFT} \approx 6.79\,\mathrm{cm}^{-1}$) which are designed to minimize (by frequency scaling technique) this error. In addition, LRP is conceptually and numerically simple and it also provides a new insight in the vibrational isotope effect in the harmonic approximation.

Keywords   Low rank perturbation · Vibrational isotope effect ·
Harmonic approximation · Benzene isotopomers

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1 Introduction

Molecular vibrations can be relatively well described within the harmonic approximation [1,2]. In this approximation one uses the classical model of the molecule where the nuclei are represented by mathematical points with masses [1,3,4]. The displacements of nuclei from the equilibrium positions can be described with Cartesian coordinates. If the molecule contains n nuclei, there are $3n$ such generic coordinates:

$$\xi_1, \xi_2, \ldots, \xi_{3n}.$$

In the harmonic approximation [1,3,4] the potential energy is

$$V = \sum_{i<j} f_{ij}\xi_i\xi_j, \tag{1a}$$

where $f_{ij} = \left(\partial^2 V/\partial\xi_i\partial\xi_j\right)_0$ are force constants expressed in Cartesian coordinates.

Kinetic energy expressed in terms of Cartesian displacements from equilibrium is

$$T = \frac{1}{2}\sum_{i}^{3n} m_i \left(\frac{d\xi_i}{dt}\right)^2. \tag{1b}$$

The solution of the above system consisting of n masses connected by harmonic forces leads to the generalized eigenvalue equation

$$\mathbf{F}\,|\Phi_i\rangle = \lambda_i \mathbf{M}\,|\Phi_i\rangle, \tag{2a}$$

where $\mathbf{F}$ and $\mathbf{M}$ are force field and mass operators, respectively. Eigenstates $|\Phi_i\rangle$ of this equation can be orthonormalized according to

$$\langle\Phi_i|\mathbf{M}\,|\Phi_j\rangle = \delta_{ij}, \tag{2b}$$

while eigenvalues λ_i are related to the vibrational frequencies ν_i by

$$\lambda_i = 4\pi^2\nu_i^2. \tag{2c}$$

If in the original molecule $\mathbf{A}$ some or all atoms are replaced by an isotope, to a very high degree of accuracy force field is not affected by those replacements [1,3,4]. In this approximation the modified equation describing isotopically substituted molecule $\mathbf{B}$ is

$$\mathbf{F}\,|\Psi_k\rangle = \varepsilon_k(\mathbf{M} + \Delta\mathbf{M})\,|\Psi_k\rangle, \tag{3a}$$

where operator $\Delta\mathbf{M}$ describes isotope mass changes. In analogy to (2b), eigenstates $|\Psi_k\rangle$ of (3a) can be orthonormalized according to

$$\langle\Psi_k|\mathbf{M} + \Delta\mathbf{M}\,|\Psi_l\rangle = \delta_{kl}, \tag{3b}$$

while frequencies ω_k of **B** are related to the eigenvalues ε_k of (3a) by

$$\varepsilon_k = 4\pi^2 \omega_k^2. \tag{3c}$$

Eigenstates $|\Phi_i\rangle$ and $|\Psi_k\rangle$ have physical meaning of vibrations or normal modes, and those terms will be used interchangibly. When the emphasize is on mathematics it is appropriate to use the term *eigenstates*, however when the emphasize is on physics it is more appropriate to use the term *vibrations* or *normal modes*.

In a standard treatment Eqs. 2a and 3a are expressed in a mass weighted coordinates where dependence on molecular masses is absorbed in the definition of related coordinates [1,3,4]. This simplifies mathematical treatment of a single molecule **A** and/or a single molecule **B** [1,3,4]. However, vibrational isotope effect involves changes in atomic masses from the original molecule **A** to the isotopomer **B**. In studding this effect it is more natural to retain explicit dependence on atomic masses, as this is done in expressions (2a) and (3a). This also results in a more transparent transition to the treatment of the vibrational isotope effect by the low rank perturbation (LRP) method [5–7]. As a consequence of the explicit dependence on atomic masses, normal modes as defined in a standard treatment slightly differ from normal modes as defined in the LRP approach. In the standard treatment based on mass weighted coordinates normal modes $\left|\Phi_i^*\right\rangle$ of the parent molecule **A** are orthonormalized according to $\left\langle \Phi_i^* | \Phi_j^* \right\rangle = \delta_{ij}$, while in the LRP approach those normal modes are orthonormalized according to (2b). Connection between normal modes $\left|\Phi_i^*\right\rangle$ and $|\Phi_i\rangle$ is $\left|\Phi_i^*\right\rangle = \mathbf{M}^{1/2} |\Phi_i\rangle$. The same applies to the corresponding normal modes $\left|\Psi_k^*\right\rangle$ and $|\Psi_k\rangle$ of the isotopomer **B**. Those normal modes are related to each other according to $\left|\Psi_k^*\right\rangle = (\mathbf{M} + \Delta\mathbf{M})^{1/2} |\Psi_k\rangle$.

An arbitrary molecule **A** containing n atoms has $3n$ vibrations $|\Phi_i\rangle$. In this general case and in a matrix form Eqs. 2a and 3a are $3n \times 3n$ matrix eigenvalue equations. If molecule **A** is linear (nonlinear), among those $3n$ vibrations there are 5 (6) non-proper vibrations that correspond to three translations and two (three) rotations. However, if the molecule is planar, in-plane and out-of-plane vibrations can be treated separately. In-plane vibrations of the parent molecule **A** are again described by the eigenvalue equation of a general type (2a), while in-plane vibrations of the isotopomer **B** are described by the eigenvalue equation of a general type (3a). The same applies to the out-of-plane vibrations. Each planar nonlinear molecule has n out-of-plane and $2n$ in-plane-vibrations. Only out-of-plane vibrations of planar molecules will be considered here. Three out-of-plane vibrations of planar molecules are non-proper. One non-proper vibration is a translation $|\Phi_T\rangle$ in the z-direction perpendicular to the molecular plane, while other two non-proper vibrations are rotations $|\Phi_{Rx}\rangle$ and $|\Phi_{Ry}\rangle$ around x- and y-axis which lie in the molecular plane. Remaining $n-3$ vibrations are proper vibrations. As an example, out-of-plane vibrations of (H,D)-benzene isotopomers will be considered.

2 LRP method

One can solve eigenvalue equation 3a using the LRP method [5,6]. This is a general mathematical formalism by which one can express the eigenvalues and the eigenstates

of the modified system **B** in terms of the eigenvalues and eigenstates of the initial system **A** [5–8]. In this respect LRP is similar to a standard perturbation expansion approach. However, unlike standard perturbation methods, LRP does not rely on any kind of a power series expansion, and it is reliable however large the operators that describe the difference between systems **A** and **B**, as long as those operators have finite rank [5,6]. In the Appendices is given an outline of the LRP method as applied to the vibrational isotope effect in the harmonic approximation. In the LRP approach one makes a distinction between *cardinal* and *singular* eigenvalues and eigenstates of the modified system **B**. By definition, an eigenvalue ε_k of the modified Eq. 3a is "cardinal" if it differs from all the eigenvalues λ_i of the initial Eq. 2a. Otherwise it is singular [6–8]. In other words, ε_k is cardinal if $\varepsilon_k \notin \{\lambda_i\}$ and singular if $\varepsilon_k \in \{\lambda_i\}$.

In the case of planar molecules, one can apply LRP approach separately to in-plane and separately to out-of-plane vibrations. Accordingly, general expressions given in the Appendix simplify.

Let **A** be a planar molecule containing n atoms. Put the origin of the coordinate system in the centre of mass of this molecule and let x-, y- and z-axis coincide with principal axis of **A**. Without loss of generality one can choose z-axis to be perpendicular to the molecular plane and x- and y-axis to lie in this plane. According to lemma 1 (see Appendix), with this choice non-proper vibrations (translations and rotations) of a molecule **A** are all mutually orthogonal.

If one replaces $\rho \leq n$ atoms in molecule **A** with an isotope, one obtains an isotopomer **B**. In general, all vibrations of the initial molecule **A** change. A key quantity in the LRP description of the modified molecule **B** is matrix $\boldsymbol{\Omega}(\varepsilon)$ with matrix elements given by the expression (B2a). This matrix depends on a real parameter ε. In a general case $\boldsymbol{\Omega}(\varepsilon)$ is a $3\rho \times 3\rho$ matrix. However, in the case of out-of-plane vibrations of planar molecules one has to consider only atom displacements in the z-direction. Hence $\boldsymbol{\Omega}(\varepsilon)$ reduces to a $\rho \times \rho$ matrix. Using explicit expressions (C4) and since there are no displacements in the x- and y-directions, one finds [7,8]

$$\boldsymbol{\Omega}_{\mu\tau}(\varepsilon) = \frac{1}{\varepsilon}\left[\frac{1}{M} + \frac{x_\mu x_\tau}{I_y} + \frac{y_\mu y_\tau}{I_x}\right] + \sum_{i(\lambda_i \neq \varepsilon)}^{n-3} \frac{\langle\mu|\Phi_i\rangle\langle\Phi_i|\tau\rangle}{\varepsilon - \lambda_i}, \quad \mu,\tau = 1,\dots,\rho.$$

(4)

where M is molecular mass of the molecule **A**, while I_x and I_y are moments of inertia of this molecule around x- and y-axis, respectively. Further, x_μ and y_μ are x- and y-coordinates of the μ-th isotope atom, $\langle\mu|\Phi_i\rangle$ is the amplitude of the normalized (out-of-plane) vibration $|\Phi_i\rangle$ of molecule **A** at the position μ, while λ_i is the corresponding eigenvalue related to the frequency ν_i according to (2c). The summation in the above expression is performed over all i such that $\lambda_i \neq \varepsilon$. In particular, if $\varepsilon \notin \{\lambda_i\}$ this summation is performed over all $n-3$ terms. Since all displacements are in the z-direction, in the above and in the following expressions is used simplified notation $\langle\mu z|\Phi_i\rangle \equiv \langle\mu|\Phi_i\rangle$, $\boldsymbol{\Omega}_{\mu z,\tau z}(\varepsilon) \equiv \boldsymbol{\Omega}_{\mu\tau}(\varepsilon)$, etc. (See Appendices).

In the LRP approach [7,8] the solution to the vibrational isotope effect in the harmonic approximation is given by Theorems 1 and 2 (see Appendix). In the case of out-of-plane vibrations Theorem 1 reduces to [8].

Theorem 1a (cardinal out-of-plane vibrations) *Let (2a) be the initial isotope eigen-value equation describing out-of-plane vibrations of planar molecule* **A**. *Let further out-of-plane vibrations $|\Phi_i\rangle$ of this molecule be orthonormalized according to (2b). Then:*

(a) $\varepsilon_k \notin \{\lambda_i\}$ is (cardinal) eigenvalue of the modified isotope eigenvalue equation 3a that describes out-of-plane vibrations of isotopomer **B** if and only if $\varepsilon = \varepsilon_k$ satisfies matrix equation

$$\left[\mathbf{\Omega}(\varepsilon_k) + \frac{\Delta\mathbf{M}^{-1}}{\varepsilon_k} \right] \mathbf{C} = 0, \quad \varepsilon_k \notin \{\lambda_i\}, \tag{5a}$$

where $\mathbf{\Omega}(\varepsilon)$ is a $\rho \times \rho$ matrix with matrix elements (4), while $\Delta\mathbf{M}^{-1}$ is a $\rho \times \rho$ diagonal matrix with matrix elements

$$\Delta\mathbf{M}_{\mu\tau}^{-1} = \frac{\delta_{\mu\tau}}{\Delta m_\tau}, \quad \mu, \tau = 1, \ldots, \rho, \tag{5b}$$

and where Δm_τ is isotope mass change of the atom τ.

According to (5a), each out-of-plane cardinal eigenvalue $\varepsilon_k \notin \{\lambda_i\}$ of isotopomer **B** is a root of a function $f(x)$

$$f(\varepsilon) = \left| \mathbf{\Omega}(\varepsilon) + \frac{\Delta M^{-1}}{\varepsilon} \right|. \tag{5c}$$

(b) Each cardinal out-of-plane vibration $|\Psi_k\rangle$ of isotopomer **B** that has eigenvalue $\varepsilon_k \notin \{\lambda_i\}$ is a linear combination

$$|\Psi_k\rangle = \frac{1}{\varepsilon_k} \left[T^{(k)} |\Phi_T\rangle + R_x^{(k)} |\Phi_{Rx}\rangle + R_y^{(k)} |\Phi_{Ry}\rangle \right] + \sum_i^{n-3} \frac{\sum_\tau^\rho \langle\Phi_i|\tau\rangle \, C_\tau^{(k)}}{\varepsilon_k - \lambda_i} |\Phi_i\rangle, \tag{6a}$$

where $|\Phi_i\rangle$ are proper out-of-plane vibrations of the parent molecule **A**, while $|\Phi_T\rangle$, $|\Phi_{Rx}\rangle$ and $|\Phi_{Ry}\rangle$ are non-proper vibrations of this molecule, translation in the z-direction perpendicular to the molecular plane and rotations around in-plane x- and y-axis, respectively (see Appendix):

$$|\Phi_T\rangle = \frac{1}{\sqrt{M}} \sum_\alpha^n |\alpha\rangle, \quad |\Phi_{Rx}\rangle = \frac{1}{\sqrt{I_x}} \sum_\alpha^n y_\alpha |\alpha\rangle, \quad |\Phi_{Ry}\rangle = \frac{-1}{\sqrt{I_y}} \sum_\alpha^n x_\alpha |\alpha\rangle, \tag{6b}$$

Coefficients $C_\tau^{(k)}$ in (6a) are components of a column vector $\mathbf{C}^{(k)}$, eigenvector of the matrix Eq. 5a, while coefficients $T^{(k)}$, $R_x^{(k)}$ and $R_y^{(k)}$ are [7,8]

$$T^{(k)} = \frac{1}{\sqrt{M}} \sum_\tau^\rho C_\tau^{(k)}, \quad R_x^{(k)} = \frac{1}{\sqrt{I_x}} \sum_\tau^\rho y_\tau C_\tau^{(k)}, \quad R_y^{(k)} = \frac{(-1)}{\sqrt{I_y}} \sum_\tau^\rho x_\tau C_\tau^{(k)}, \quad (6c)$$

(c) Coefficients $C_\tau^{(k)}$ that determine cardinal vibration $|\Psi_k\rangle$ of $\mathbf{B}$ satisfy [7,8]

$$C_\tau^{(k)} = -\varepsilon_k \langle\tau|\Delta\mathbf{M}|\Psi_k\rangle = -\varepsilon_k \Delta m_\tau \langle\tau|\Psi_k\rangle, \quad \tau = 1, \dots, \rho. \quad (6d)$$

(d) Degeneracy of the cardinal eigenvalue $\varepsilon_k \notin \{\lambda_i\}$ of $\mathbf{B}$ equals nullity of the matrix $\mathbf{H}(\varepsilon_k) = \mathbf{\Omega}(\varepsilon_k) - \Delta\mathbf{M}^{-1}/\varepsilon_k$.

Note that expressions (6b) imply

$$M = \frac{1}{|\langle\alpha|\Phi_T\rangle|^2}, \quad I_x = \frac{y_\alpha^2}{|\langle\alpha|\Phi_{Rx}\rangle|^2}, \quad I_y = \frac{x_\alpha^2}{|\langle\alpha|\Phi_{Ry}\rangle|^2}. \quad \alpha = 1, \dots, n. \quad (7)$$

Global quantities M, I_x and I_y that enter expression (4) can be hence eliminated and expressed in terms of the amplitudes $\langle\alpha|\Phi_T\rangle$, $\langle\alpha|\Phi_{Rx}\rangle$ and $\langle\alpha|\Phi_{Ry}\rangle$ of non-proper vibrations $|\Phi_T\rangle$, $|\Phi_{Rx}\rangle$ and $|\Phi_{Ry}\rangle$ at atomic site α. With the exception of those atomic sites (if any) where the corresponding amplitude vanishes, α can be any atomic site of parent molecule $\mathbf{A}$. In particular, one can chose α to be an atomic site τ subject to the isotopic substitution.

According to Theorem 1a, as far as cardinal out-of-plane vibrations are considered, LRP replaces initial eigenvalue equation 3a acting in the n-dimensional vibrational space X_n with the Eq. 5a acting in the ρ-dimensional isotope substitution space $X_\rho^b \subseteq X_n$. If $\rho < n$, which is usually the case, this results in a substantial reduction of the computational complexity.

Concerning singular out-of-plane solutions that satisfy $\varepsilon_k \in \{\lambda_i\}$, one may have two kinds of such solutions: *strongly singular* and *weakly singular*. By definition, strongly singular vibration has no component on all those atoms that are effected by the isotopic substitutions (i.e. it has no component in isotope substitution space X_ρ^b), while weakly singular vibration has at least one such non-vanishing component (see Appendix). One has:

Theorem 2a (singular out-of-plane vibrations) *Let λ_j be a η_j-degenerate out-of-plane eigenvalue of the parent molecule $\mathbf{A}$ and let $|\Phi_{jl}\rangle$ ($l = 1, \dots, \eta_j$) be the corresponding out-of-plane vibrations orthonormalized according to (2b). Then:*

(a) Each strongly singular vibration of the isotopomer $\mathbf{B}$ that has eigenvalue $\varepsilon_k = \lambda_j$ is a linear combination

$$|\Psi_k\rangle = \sum_l^{\eta_j} D_l^{(j)} |\Phi_{jl}\rangle, \quad (8a)$$

where the coefficients $D_l^{(j)}$ satisfy

$$\sum_l^{\eta_j} \langle \mu | \Phi_{jl} \rangle D_l^{(j)} = 0, \quad \mu = 1, \ldots, \rho. \tag{8b}$$

(b) Each weakly singular vibration of **B** that has eigenvalue $\varepsilon_k = \lambda_j$ is a linear combination

$$|\Psi_k\rangle = \frac{1}{\lambda_j} \left[T^{(k)} |\Phi_T\rangle + R_x^{(k)} |\Phi_{Rx}\rangle + R_y^{(k)} |\Phi_{Ry}\rangle \right]$$
$$+ \sum_{i(\lambda_i \neq \lambda_j)}^{n-3} \frac{\sum_\tau^\rho \langle \Phi_i | \tau \rangle C_\tau^{(k)}}{\varepsilon_k - \lambda_i} |\Phi_i\rangle + \sum_l^{\eta_j} D_l^{(j)} |\Phi_{jl}\rangle \tag{9a}$$

where the coefficients $C_\tau^{(k)}$ and $D_l^{(j)}$ satisfy

$$\sum_\tau^\rho \langle \Phi_{jl} | \tau \rangle C_\tau^{(j)} = 0, \quad l = 1, \ldots, \eta_j, \quad \mathbf{C}^{(j)} \neq 0, \tag{9b}$$

$$\lambda_j \sum_\tau^\rho \Omega_{\mu\tau}(\lambda_j) C_\tau^{(j)} + \frac{C_\mu^{(j)}}{\Delta m_\mu} - \frac{1}{\Delta m_\mu} \sum_l^{\eta_j} \langle \mu | \Phi_{jl} \rangle D_l^{(j)} = 0, \quad \mu = 1, \ldots, \rho, \tag{9c}$$

and where the coefficients $T^{(k)}$, $R_x^{(k)}$ and $R_y^{(k)}$ are given in terms of the coefficients $C_\tau^{(k)}$ according to (6c). In addition, each weakly singular vibration (9a) must be orthogonal to all strongly singular vibrations (8a).

(c) Coefficients $C_\tau^{(j)}$ and $D_l^{(j)}$ that determine weakly singular vibration $|\Psi_k\rangle$ according to (9a) and strongly singular vibration $|\Psi_k\rangle$ according to (8a) satisfy

$$C_\tau^{(j)} = -\varepsilon_k \langle \tau | \Delta \mathbf{M} | \Psi_k \rangle = -\varepsilon_k \Delta m_\tau \langle \tau | \Psi_k \rangle,$$
$$D_l^{(j)} = \langle \Phi_{jl} | \mathbf{M} | \Psi_k \rangle, \quad \tau = 1, \ldots, \rho, \quad l = 1, \ldots, \eta_j. \tag{9d}$$

According to (9b) weakly singular vibrations satisfy $\mathbf{C}^{(j)} \neq 0$, and expressions (9d) hence imply that those vibrations have a nonzero component in the isotope substitution space X_ρ^b. On the other hand, strongly singular vibrations satisfies $\mathbf{C}^{(j)} = 0$, and they have no nonzero component in this space.

Above two theorems produce all out-of-plane vibrations of isotopomer **B**. Note that (8b) is a set of ρ homogenous linear equations in η_j unknowns $D_l^{(j)}$. Hence If $\eta_j > \rho$ one has at least $\eta_j - \rho$ strongly singular vibrations with the eigenvalue $\varepsilon_k = \lambda_j$. However, if $\eta_j \leq \rho$ one has usually no such vibration. An exceptional case is the case when the eigenvalue $\varepsilon_k \equiv \lambda_j$ is passive, in which case isotopomer **B** has maximum possible number of η_j strongly singular vibrations $|\Psi_k\rangle$ with this eigenvalue

(see Appendices). Concerning weakly singular vibrations, expressions (9b) and (9c) have usually no solution that satisfies $\mathbf{C}^{(j)} \neq 0$, and weakly singular vibrations are hence exceptionally rare (see Appendices). Accordingly, as far as singular out-of-plane vibrations are considered, LRP approach essentially replaces $n \times n$ eigenvalue equation 3a with a $\eta_j \times \eta_j$ matrix Eq. 8b that describes strongly singular vibrations. Since usually $\eta_j \ll n$, this again results in a substantial reduction of computational complexity.

Vibrations (6a), (8a) and (9a) are not normalized. If required, those vibrations can be easily normalized using matrix elements $\langle \Phi_i | \Delta M | \Phi_j \rangle$ and orthonormality relation (2b) of vibrations $|\Phi_i\rangle$ (see Appendices).

In addition to the above two theorems, out-of-plane frequencies ν_i of the parent molecule **A** and out-of-plane frequencies ω_i of the isotopomer **B** satisfy the

Interlacing rule [7–9]. Let κ substituted isotopes be heavier in the isotopomer **B**, and let remaining $(\rho - \kappa)$ substituted isotopes be heavier in the parent molecule **A**. Let further ν_i and ω_k be proper out-of-plane frequencies of **A** and **B**, respectively. Arrange those frequencies in a nondecreasing order. Then, these frequencies are interlaced according to

$$\nu_{k-\kappa} \leq \omega_k \leq \nu_{k+\rho-\kappa}, \quad k = \kappa, \kappa + 1, \kappa + 2, \ldots, \tag{10a}$$

where by definition $\nu_0 = 0$. Due to (2c) and (3c), the same relation applies to the corresponding eigenvalues λ_i and ε_k.

Interlacing rule (10a) generalizes well known order rule [1–4]. It provides a substantial help for the correct assignment of experimental frequencies to vibrational modes and it can be efficiently used in order to verify consistency of theoretical and/or experimental out-of-plane frequencies of planar molecules [9]. Interlacing rule (10a) applies to out-of-plane frequencies of planar molecules. There is a similar rule that applies to in-plane frequencies of those molecules, and also interlacing rule that applies to arbitrary (non-planar) molecules [8,9].

In order to obtain frequencies and normal modes of isotopomer **B** by the LRP method, no information about force constants is required. According to relations (4–9), frequencies $\omega_k = \sqrt{\varepsilon_k}/2\pi$ of **B** depend only on the frequencies $\nu_i = \sqrt{\lambda_i}/2\pi$ of the parent molecule **A**, on the mass changes Δm_τ of atoms τ that are substituted by an isotope, on positions (x_τ, y_τ) of those atoms, on the amplitudes $\langle \tau | \Phi_i \rangle$ of the vibrations $|\Phi_i\rangle$ at those atoms, and on three global properties of the parent molecule **A**: molecular mass M and moments of inertia I_x and I_y of this molecule. No knowledge of the amplitudes $\langle \alpha | \Phi_i \rangle$ of the vibrations $|\Phi_i\rangle$ at atoms α that are not substituted by an isotope is required. Accordingly, vibrational isotope effect does not depend on any fine details of molecules **A** and **B** outside the region affected by the isotopic substitutions. In particular, frequencies ω_k of **B** do not depend in any direct way on atomic masses and force constants outside this region. All the potentially huge information about the molecular structure outside this region is succinctly concentrated into the global information about frequencies ν_i of **A** and about only three global quantities of this molecule: molecular mass M and two moments of inertia, I_x and I_y. According to the expression (7), dependence on global quantities M, I_x and I_y can be also eliminated and replaced with dependence on strictly local quantities defined on the

region subject to the isotopic substitution. In conclusion, the only global quantities on which frequencies and normal modes of isotopomer **B** depend are frequencies ν_i of the parent molecule **A**. All other quantities are local in the sense that they all relate to the region subject to the isotopic substitutions.

What applies to the frequencies ω_k, applies also to the vibrations $|\Psi_k\rangle$ of the isotopomer **B**. In the LRP approach each such (properly normalized) vibration is expressed as a linear combination $|\Psi_k\rangle = \sum_i a_i |\Phi_i\rangle$ of vibrations $|\Phi_i\rangle$ of the parent molecule **A**. Expansion coefficients a_i depend exactly on the same quantities as frequencies ω_k of this isotopomer. Hence, if one knows matrix elements $\langle \Phi_i |\mathbf{O}| \Phi_j \rangle$ of some observable **O** between vibrations $|\Phi_i\rangle$ of the parent molecule **A**, using these matrix elements one can obtain matrix elements $\langle \Psi_k |\mathbf{O}| \Psi_l \rangle = \sum_{ij} a_i^* a_j \langle \Phi_i |\mathbf{O}| \Phi_j \rangle$ of this observable between any two vibrations $|\Psi_k\rangle$ and $|\Psi_l\rangle$ of **B**. For example, if one knows probability amplitudes for the transitions between vibrations $|\Phi_i\rangle$ of a parent molecule **A** (which can be obtained, for example, as experimental quantities), one can derive transition probabilities between vibrations $|\Psi_k\rangle$ of the isotopomer **B**. For this it not necessary to know any details (such as force constants, geometry, atomic masses, amplitudes $\langle \alpha |\Phi_i\rangle$, etc.) of the potentially huge region not effected by the isotopic substitutions.

Solution of the vibrational isotope effect by the LRP method usually requires much less data than solution of this effect in a standard way using eigenvalue equation 3a. Consider as an example a planar molecule **B** containing 100 atoms which differs by a single isotopic substitution from the corresponding parent molecule **A**. In a standard approach, in order to obtain out-of-plane frequencies of **B** one has to specify $101 * 100/2 = 5,050$ force constants f_{ij}. In addition, one has to know masses of all 100 atoms in this molecule. Accordingly, one has to know 5,150 quantities in order to specify eigenvalue equation 3a. In the LRP approach one has to know 97 out-of-plane frequencies ν_i of the parent molecule **A**, 97 amplitudes $\langle \mu |\Phi_i\rangle$ of the proper vibrations $|\Phi_i\rangle$ of this molecule at the position μ of the isotope substitution, three global quantities, M, I_x and I_y, one isotope mass change Δm_μ, and the position (x_μ, y_μ) of the isotope substitution. This amounts to only 200 quantities. Accordingly, in this particular case in the LRP approach one has to specify only 200 instead of 5,150 quantities. All remaining quantities are redundant. One can argue that there are many schemas where one neglects force constants that are sufficiently small, and this can substantially reduce the number of data required to solve vibrational isotope effect in the standard way. However, all such schemas are only approximate, and unlike LRP they can never provide an exact solution of the vibrational isotope effect in the harmonic approximation.

3 Single isotopic substitution

Consider out-of-plane vibrations of planar molecules **A** and **B**$_\tau$ which are identical except for a single isotopic substitution at atomic site τ. Since $\rho = 1$ expressions (4–10) simplify. In particular, if molecule **B**$_\tau$ is heavier than molecule **A** (which can be assumed without loss of generality) one has $\kappa = 1$ and interlacing rule (10a) simplifies to

$$0 \leq \omega_1 \leq \nu_1 \leq \omega_2 \leq \nu_2 \leq \cdots \leq \omega_{n-3} \leq \nu_{n-3}. \tag{10b}$$

According to this expression, a single isotopic substitution in a planar molecule can change (increase or decrease) degeneracy of each particular out-of-plane frequency ν_j at most by one. For example, if planar molecule **A** has doubly degenerate frequency ν_j ($\eta_j = 2$), planar molecule $\mathbf{B}_\tau$ has at least one and at most three vibrations with this frequency.

In the case of a single isotopic substitution expressions (5) and (6) describing cardinal out-of-plane vibrations of $\mathbf{B}_\tau$ simplify to

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

(11a)

$$|\Psi_k\rangle = \frac{1}{\varepsilon_k} \left[\frac{1}{\sqrt{M}} |\Phi_T\rangle + \frac{y_\tau}{\sqrt{I_x}} |\Phi_{Rx}\rangle - \frac{x_\tau}{\sqrt{I_y}} |\Phi_{Ry}\rangle \right] + \sum_i^{n-3} \frac{\langle \Phi_i | \tau \rangle}{\varepsilon_k - \lambda_i} |\Phi_i\rangle.$$

(11b)

In the above expressions Δm_τ is the isotope mass change of the atom τ, (x_τ, y_τ) is its coordinate position, while $\langle \Phi_i | \tau \rangle$ are amplitudes of the out-of-plane vibrations $|\Phi_i\rangle$ at this atom.

Each root $\varepsilon = \varepsilon_k \notin \{\lambda_i\}$ of (11a) is a (cardinal) out-of-plane eigenvalue of the isotopomer $\mathbf{B}_\tau$. Once $\varepsilon = \varepsilon_k$ is obtained as a root of (11a), the corresponding vibration $|\Psi_k\rangle$ is given by (11b). Unlike in a general case of multiple isotopic substitutions (expressions (5–6)), in a case of a single isotopic substitution each cardinal vibration $|\Psi_k\rangle$ is nondegenerate, i.e. there is only one out-of-plane vibration $|\Psi_k\rangle$ of $\mathbf{B}_\tau$ with the eigenvalue $\varepsilon_k \notin \{\lambda_i\}$.

Consider now singular solutions of $\mathbf{B}_\tau$. Each strongly singular vibration $|\Psi_k\rangle$ that corresponds to the eigenvalue $\varepsilon_k \equiv \lambda_j$ is a linear combination (8a) where coefficients $D_l^{(j)}$ satisfy (8b). In the case of single isotopic substitution ρ conditions (8b) reduce to a single condition

$$\sum_l^{\eta_j} \langle \tau | \Phi_{jl} \rangle D_l^{(j)} = 0.$$

(12)

If all η_j amplitudes $\langle \tau | \Phi_{jl} \rangle$ ($l = 1, \ldots, \eta_j$) vanish, eigenvalue $\varepsilon_k \equiv \lambda_j$ is passive (see Appendices), and in this case one has η_j strongly singular out-of-plane vibrations with this eigenvalue. Otherwise (eigenvalue $\varepsilon_k \equiv \lambda_j$ is active) one has $\eta_j - 1$ such vibrations. In particular, if λ_j is nondegenerate ($\eta_j = 1$) and if $\langle \tau | \Phi_j \rangle \neq 0$, then there is no strongly singular vibration with this eigenvalue.

Concerning weakly singular solutions, in the case of a single isotopic substitution expressions (9b) reduce to $\langle \Phi_{jl} | \tau \rangle C_\tau^{(j)} = 0$ ($l = 1, \ldots, \eta_j$). Since $C_\tau^{(j)} \neq 0$, this implies $\langle \Phi_{jl} | \tau \rangle = 0$ for each $l = 1, \ldots, \eta_j$. Accordingly, expressions (9b) and (9c)

reduce to

$$\langle \Phi_{jl} | \tau \rangle = 0, \quad l = 1, \ldots, \eta_j, \tag{13a}$$

$$\lambda_j \Omega_{\tau\tau}(\lambda_j) + \frac{1}{\Delta m_\tau} = 0. \tag{13b}$$

The corresponding weakly singular eigenstate is

$$|\Psi_k\rangle = \frac{1}{\lambda_j} \left[\frac{1}{\sqrt{M}} |\Phi_T\rangle + \frac{y_\tau}{\sqrt{I_x}} |\Phi_{Rx}\rangle - \frac{x_\tau}{\sqrt{I_y}} |\Phi_{Ry}\rangle \right] + \sum_{i(\lambda_i \neq \lambda_j)}^{n-3} \frac{\langle \Phi_i | \tau \rangle}{\varepsilon_k - \lambda_i} |\Phi_i\rangle. \tag{13c}$$

Thus isotopomer $\mathbf{B}_\tau$ has weakly singular vibration with the eigenvalue $\varepsilon_k \equiv \lambda_j$ if and only if all amplitudes $\langle \Phi_{jl} | \tau \rangle$ $(l = 1, \ldots, \eta_j)$ vanish (i.e. if the eigenvalue λ_j is passive) and if in addition this eigenvalue satisfies (13b). This is exceptionally rare situation. However if this is the case, the corresponding eigenstate is given by (13c). In addition, in this case each eigenstate $|\Phi_{jl}\rangle$ $(l = 1, \ldots, \eta_j)$ of $\mathbf{A}$ is at the same time a strongly singular eigenstate of $\mathbf{B}_\tau$.

In conclusion, if the eigenvalue $\varepsilon_k \equiv \lambda_j$ is active, isotopomer $\mathbf{B}_\tau$ has $\eta_j - 1$ strongly singular vibrations with this eigenvalue, and no weakly singular vibration with this eigenvalue. In this case introduction of a single isotope in molecule $\mathbf{A}$ decreases degeneracy of the eigenvalue λ_j by one. In particular, if λ_j is nondegenerate ($\eta_j = 1$) isotopomer $\mathbf{B}_\tau$ has no singular solution with this eigenvalue. If however eigenvalue $\varepsilon_k \equiv \lambda_j$ is passive, vibrations $|\Phi_{jl}\rangle$ are not effected by isotopic substitution and isotopomer $\mathbf{B}_\tau$ has η_j strongly singular vibrations with this eigenvalue. Those vibrations coincide with vibrations $|\Phi_{jl}\rangle$ of the parent molecule $\mathbf{A}$. There are additional two possibilities. If λ_j does not satisfy (13b), $|\Phi_{jl}\rangle$ are the only singular vibrations associated with this eigenvalue, and in this case introduction of a single isotope does not change degeneracy of the initial eigenvalue λ_j. However, if λ_j satisfies (13b), isotopomer $\mathbf{B}_\tau$ has in addition to strongly singular vibrations a single weakly singular vibration (13c) that has this eigenvalue. If this is the case, introduction of a single isotope in a parent molecule $\mathbf{A}$ at a position τ increases degeneracy of the eigenvalue λ_j by one. All above possibilities are in accord with the interlacing rule (10b).

Solution of the vibrational isotope effect in the case of the single isotopic substitution demonstrates efficiency of the LRP approach. In a standard approach one has to diagonalize potentially huge eigenvalue equation 3a. In the LRP approach this equation is essentially replaced with the expressions (11) which produce all cardinal solutions. Expressions (12–13) which produce singular solutions are in most cases much less important. It is usually much easier to find roots of the function (11a) (which produces all cardinal frequencies), than to diagonalize potentially huge eigenvalue equation 3a.

3.1 Inversion relations

Since (11a) is satisfied for each cardinal eigenvalue $\varepsilon = \varepsilon_k$, this implies matrix equation [7,8]

$$\mathbf{A}\mathbf{\Sigma} = \mathbf{X}. \tag{14a}$$

where $\mathbf{A}$ is matrix with matrix elements A_{ki} while $\mathbf{X}$ and $\mathbf{\Sigma}$ are column vectors with components X_k and Σ_i, respectively

$$A_{ki} = \frac{1}{\varepsilon_k - \lambda_i}, \quad X_k = -\frac{1}{\varepsilon_k}\left[\frac{1}{M} + \frac{x_\tau^2}{I_y} + \frac{y_\tau^2}{I_x} + \frac{1}{\Delta m_\tau}\right], \tag{14b}$$

$$\Sigma_j = \sum_l^{\eta_j} \langle\tau|\Phi_{jl}\rangle\langle\Phi_{jl}|\tau\rangle. \tag{14c}$$

Usually isotopomer $\mathbf{B}_\tau$ contains no passive eigenvalues. In this case in the above expressions quantities $\varepsilon_k \notin \{\lambda_i\}$ are cardinal eigenvalues of $\mathbf{B}_\tau$, while each eigenvalue λ_i of $\mathbf{A}$ is taken only once (i.e. disregarding possible degeneracies). Accordingly, summation in (14c) is over all degenerate vibrations $|\Phi_{il}\rangle$ associated with the eigenvalue λ_j. If however a particular eigenvalue $\varepsilon_k \equiv \lambda_j$ is passive one has $\Sigma_j = 0$, and in this case the corresponding eigenvalue λ_j should be excluded from the definition of matrix elements A_{ki} in (14b) [8]. In both cases (with and without passive eigenvalues) eigenvalues ε_k and λ_i that define matrix $\mathbf{A}$ are mutually distinct.

From (14) one derives *inversion relation* [7,8]

$$\mathbf{\Sigma} = \mathbf{A}^{-1}\mathbf{X}. \tag{15}$$

For this relation to apply, $\mathbf{A}$ must be an invertible square matrix. One finds that this is almost always the case.

Using inversion relation (15), one can derive squares of the amplitudes $\langle\tau|\Phi_i\rangle$ at the substitution site τ (more precisely, if λ_i is degenerate, sum Σ_i of such squares) from the known eigenvalues λ_i and ε_k which define matrix elements A_{ki}, and from quantities M, $I_x, (x_\tau, y_\tau)$ and Δm_τ. According to (2c) and (3c), eigenvalues λ_i and ε_k are determined by the out-of-plane frequencies of molecules $\mathbf{A}$ and $\mathbf{B}_\tau$, respectively. All remaining quantities are determined by the geometry and atomic masses of molecules $\mathbf{A}$ and $\mathbf{B}_\tau$. In conclusion, using expression (15), one can derive squares of the amplitudes $\langle\tau|\Phi_i\rangle$ at the substitution site τ from well known properties of molecules $\mathbf{A}$ and $\mathbf{B}_\tau$. Those properties can be taken as some reliable theoretical data, and/or as some reliable experimental quantities. Using several substitution sites τ (i.e. several different isotopomers $\mathbf{B}_\tau$), one can reconstruct amplitude squares at all those substitution sites. According to theorems (1a) and (2a), eigenvalues ε_k and corresponding vibrations $|\Psi_k\rangle$ of isotopomer $\mathbf{B}$ which differs from $\mathbf{A}$ by multiple isotopic substitutions are determined by amplitudes $\langle\mu|\Phi_i\rangle$ of the vibrations $|\Phi_i\rangle$ of $\mathbf{A}$ at all those substitution

sites. Expression (15) produces squares of amplitudes $\langle\tau|\Phi_i\rangle$, not those amplitudes. However, since all proper vibrations $|\Phi_i\rangle$ are orthogonal to non-proper vibrations $|\Phi_T\rangle$, $|\Phi_{Rx}\rangle$ and $\left|\Phi_{Ry}\right\rangle$, and since in addition those vibrations are mutually orthogonal, those orthogonality requirements in most cases uniquely determine all relative phases of amplitudes $\langle\tau|\Phi_i\rangle$ [7,8].

In conclusion, if one knows out-of-plane frequencies of planar molecule **A** and out-of-plane frequencies of several mono-substituted isotopomers $\mathbf{B}_{\tau s}$ ($s = 1, 2, \ldots$) involving several substitution sites $\tau_1, \tau_2, \ldots$, one can derive amplitudes $\langle\tau_1|\Phi_i\rangle$, $\langle\tau_2|\Phi_i\rangle$, …, of the vibrations $|\Phi_i\rangle$ of **A** at all those substitution sites. Once those amplitudes and out-of-plane frequencies of a parent molecule **A** are known, one can derive out-of-plane frequencies and corresponding vibrations for all isotopomers **B** that contain substituted isotopes at thus selected substitution sites τ_s. The only additional information which is required in order to obtain frequencies and vibrations of isotopomer **B** is molecular mass M and moments of inertia I_x and I_y of the parent molecule **A**, as well as information about substituted isotopes: coordinate positions $(x_{\tau s}, y_{\tau s})$ and mass changes $\Delta m_{\tau s}$ ($s = 1, 2, \ldots$) of those isotopes. Note in particular that in order to derive frequencies and vibrations of isotopomer **B**, no information about force field either of the parent molecule **A** or of this isotopomer is required.

If a parent molecule **A** has some symmetry (in addition to being planar) amplitudes $\langle\tau|\Phi_i\rangle$ can be partly or completely determined by this symmetry. For example, ethen (C_2H_4) has three out-of-plane vibrations $|\Phi_i\rangle$. Each of those vibrations has six amplitudes, two amplitudes at two carbon atoms and another four at four hydrogen atoms. However, all those amplitudes are completely determined by the symmetry [8]. LRP treatment of ethen is hence extremely simple, and one can derive all out-of-plane frequencies and corresponding vibrations of all ethen isotopomers using only three ethen out-of-plane frequencies [8]. In some other cases, such as various haloeten, this reduction may be only partial [7]. In general, whenever a planar molecule has some symmetry, this symmetry efficiently reduces the dimension of matrix **A** and vectors $\mathbf{\Sigma}$ and **X** that are involved in the construction of the inversion relation (15). Quantities **A**, **X** and $\mathbf{\Sigma}$ obtained in this way are accordingly modified, and they differ from their generic form (14).

4 Out-of-plane vibrations of (H,D)-benzene isotopomers

Benzene is a planar molecule with $n = 12$ atoms. It is shown in Fig. 1. In the literature one finds various data for the benzene equilibrium geometry [3,10,11]. Thus one has $r_{CH} = 1.08880$ Å and $r_{CC} = 1.40307$ Å(B3LYP/DZP calculation [10]), $r_{CH} = 1.08183$ Å and $r_{CC} = 1.39144$ Å (B3LYP/TZ2P calculation [10]), $r_{CH} = 1.0813$ (10) Å and $r_{CC} = 1.3937(10)$ Å, coupled cluster CCSD(T) calculation [11], etc. In this paper equilibrium geometry from Ref. [3] is used

$$r_{CH} = 1.0897\text{Å}, \quad r_{CC} = 1.4000\text{Å}, \tag{16a}$$

while atom masses are taken from Ref. [12]

Fig. 1 Atom numbering and coordinate system of benzene molecule
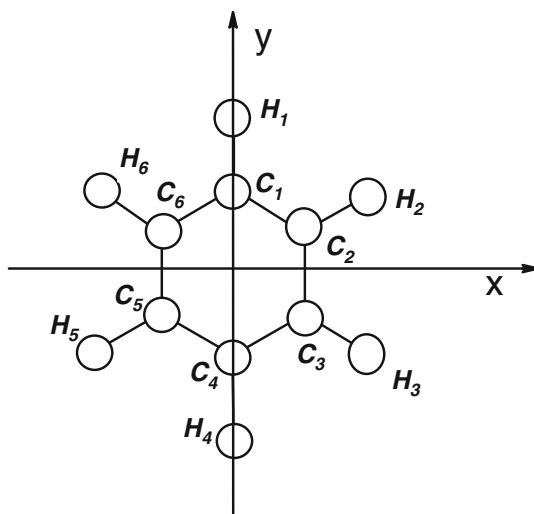
$$m_C = 12.0107u \quad m_H = 1.007825u, \quad m_D = 2.0141018\ u, \tag{16b}$$

Note that m_C is atomic mass of a natural mixture of 98.93% of ^{12}C (atomic mass 12.0000 u) and of 1.07% of ^{13}C (atomic mass 13.00335 u [12]).

Above data imply

$$M = 78.11115u, \quad I_x = I_y = 89.36425\ u\left(\text{Å}\right)^2. \tag{16c}$$

Benzene (H,D)-isotopomers are shown in Fig. 2. There are 13 such isotopomers. Isotopomers connected by an arrow differ from each other by a single isotopic substitution. In the harmonic approximation out-of-plane frequencies of all such isotopomer pairs satisfy interlacing rule (10b). This property can be used in order to test whether a particular model is in accord with a harmonic approximation.

Wu and Cremer [13] derived all vibrational frequencies for all (H,D)-benzene isotopomers using density functional theory (DFT) with the hybrid functional B3LYP [14–16] and Pople's 6-31G(d,p) basis set [17]. This is a rather sophisticated DFT approach which required extensive calculation at the supercomputers of the Nationellt Superdatorcentrum (NSC) Linköping, Sweden [13]. In order to calculate vibrational isotope effect one can use other approaches such as MP2 or HF theory [18,19]. However, vibrational analysis by the DFT method, in particular the B3LYP density functional, is superior to those alternant approaches [20]. Therefore LRP approach will be compared here with DFT approach.

Since $n = 12$, each benzene isotopomer has 9 out-of-plane vibrations. In Table 1 are shown DFT out-of-plane frequencies for d_0- and d_1-benzene [13]. Benzene out-of-plane vibrations, arranged in the order of increasing frequency, are shown in Fig. 3. Thus vibration $|\Phi_9\rangle$ in this figure has the largest frequency, while vibrations $|\Phi_1\rangle$ and $|\Phi_2\rangle$ which are mutually degenerate have lowest frequency. In order to simplify presentation of out-of-plane vibrations, notation in this figure differs from the standard
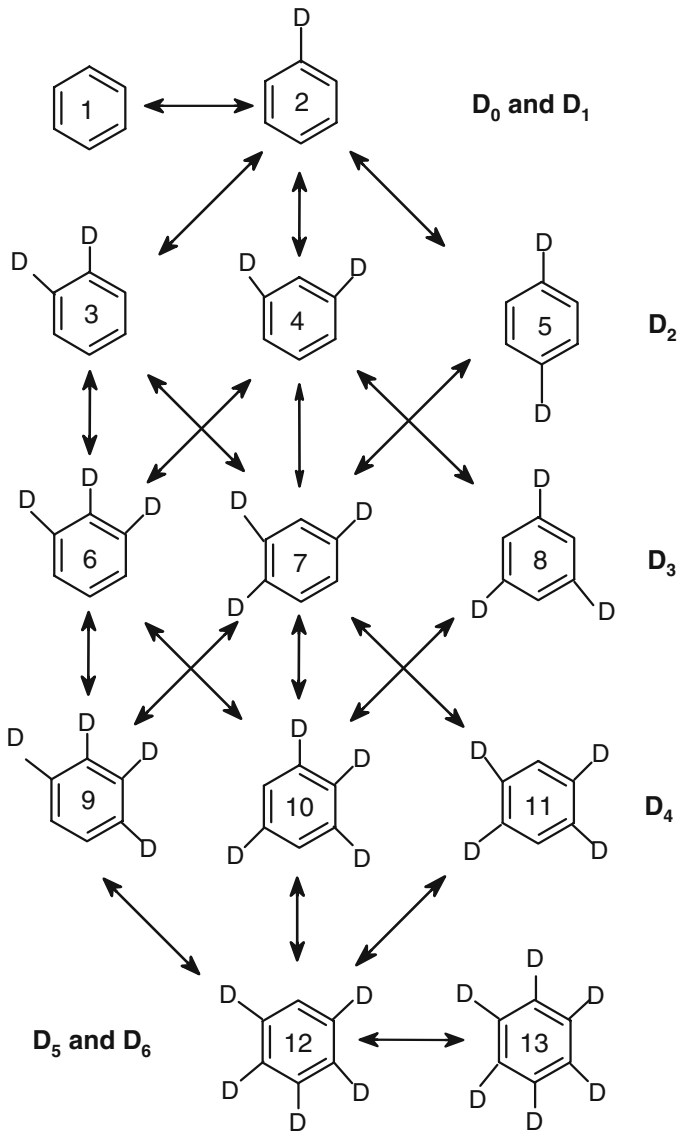
Fig. 2 Benzene (H,D)-isotopomers. In the harmonic approximation out-of-plane frequencies of isotopomer pairs connected by an arrow satisfy interlacing rule (10b)

notation [4]. This standard notation is also shown in Fig. 3. For example, in a standard notation vibration $|\Phi_1\rangle$ is vibration $|\nu_{16b}\rangle$, vibration $|\Phi_2\rangle$ is vibration $|\nu_{16a}\rangle$, etc.

4.1 Amplitudes of out-of-plane benzene vibrations

Symmetry constrains partially or complete determine all benzene out-of-plane vibrations. Vibration $|\Phi_3\rangle \equiv |\nu_{11}\rangle$ is the only vibration of a symmetry type a_{2u}. This

Table 1 DFT out-of-plane frequencies of d_0- and d_1-benzene

		1 C_6H_6 D_{6h}		2 C_6DH_5 C_{2v}	
	1	e_{2u}	414	b_2	393
	2	e_{2u}	414	a_2	414
	3	a_{2u}	694	b_2	622
	4	b_{2g}	718	b_2	714
	5	e_{1g}	865	b_2	792
	6	e_{1g}	865	a_2	865
	7	e_{2u}	974	b_2	934
	8	e_{2u}	974	a_2	974
	9	b_{2g}	1,013	b_2	1,003

B3LYP/6-31G(d,p) calculation [13]. All frequencies in cm^{-1}
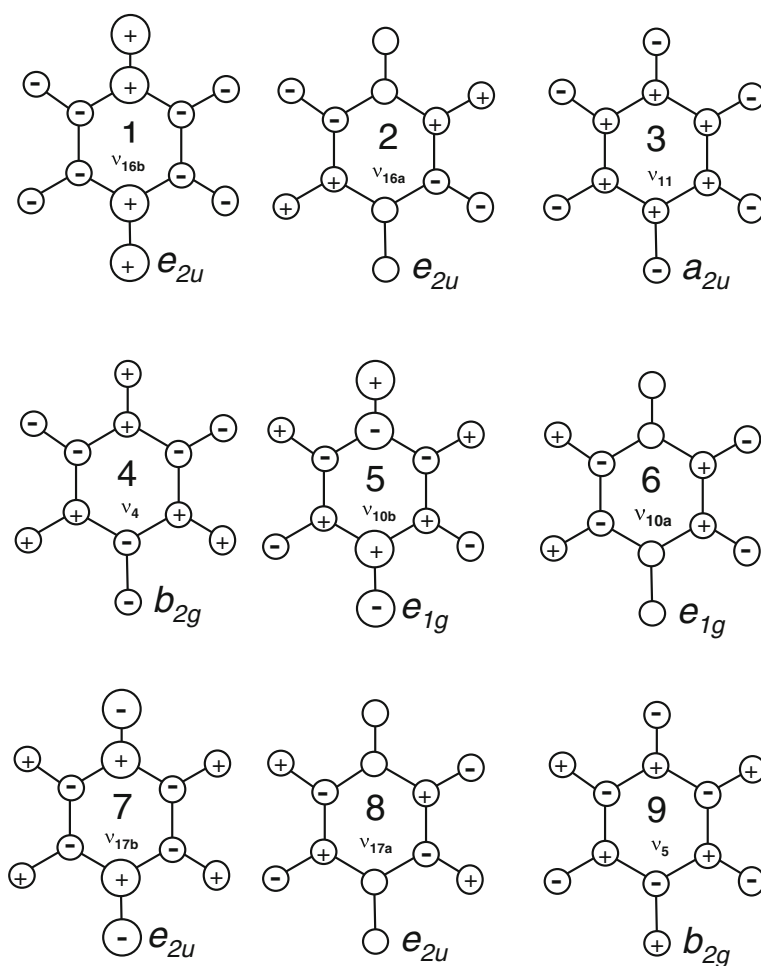
Fig. 3 Benzene out-of-plane normal modes arranged in the order of increasing frequency

vibration is hence completely determined by the symmetry. Orthonormality conditions (2b) imply

$$\langle \Phi_3 | \mathbf{M} | \Phi_3 \rangle \equiv 6m_H \langle H_1 | \Phi_3 \rangle^2 + 6m_C \langle C_1 | \Phi_3 \rangle^2 = 1, \tag{17a}$$

$$\langle \Phi_3 | \mathbf{M} | \Phi_T \rangle \propto m_H \langle H_1 | \Phi_3 \rangle + m_C \langle C_1 | \Phi_3 \rangle = 0. \tag{17b}$$

where $\langle H_1 | \Phi_3 \rangle$ is the amplitude of the vibration $|\Phi_3\rangle$ at the position of the hydrogen atom H_1, while $\langle C_1 | \Phi_3 \rangle$ is the amplitude of this vibration at the position of the carbon atom C_1. Symbol $\propto$ in (17b) denotes proportionality. Expressions (17) imply

$$\langle H_1 | \Phi_3 \rangle = -\sqrt{\frac{m_C}{m_H M}}, \quad \langle C_1 | \Phi_3 \rangle = \sqrt{\frac{m_H}{m_C M}}, \tag{18a}$$

Using (16) one finds

$$\langle H_1 | \Phi_3 \rangle = -0.39060, \quad \langle C_1 | \Phi_3 \rangle = 0.03278. \tag{18b}$$

By symmetry one has $\langle H_\alpha | \Phi_3 \rangle = \langle H_1 | \Phi_3 \rangle$ and $\langle C_\alpha | \Phi_3 \rangle = \langle C_1 | \Phi_3 \rangle$ for each $\alpha = 2, \ldots 6$. This determines all amplitudes of the out-of-plane vibration $|\Phi_3\rangle$. The signs in expressions (18) are chosen in accord with vibration $|\Phi_3\rangle$ as shown in Fig. 3. There is no absolute meaning of a global sign of a particular vibration $|\Phi_i\rangle$. However, for each vibration $|\Phi_i\rangle$ relative signs of various amplitudes $\langle H_\alpha | \Phi_i \rangle$ and $\langle C_\alpha | \Phi_i \rangle$ ($\alpha = 1, \ldots, 6$) are well defined and they should be in accord with amplitudes as shown in Fig. 3.

There are two vibrations of a symmetry type e_{1g} which are mutually degenerate. Those are vibrations $|\Phi_5\rangle$ and $|\Phi_6\rangle$. Concerning vibration $|\Phi_6\rangle$ one has

$$\langle H_1 | \Phi_6 \rangle = 0, \quad \langle C_1 | \Phi_6 \rangle = 0, \tag{19a}$$

$$\langle \Phi_6 | \mathbf{M} | \Phi_6 \rangle \equiv 4m_H \langle H_2 | \Phi_6 \rangle^2 + 4m_C \langle C_2 | \Phi_6 \rangle^2 = 1, \tag{19b}$$

$$\langle \Phi_6 | \mathbf{M} | \Phi_{Ry} \rangle \propto m_H x_{H2} \langle H_2 | \Phi_6 \rangle + m_C x_{C2} \langle C_2 | \Phi_6 \rangle = 0. \tag{19c}$$

Relation (19c) expresses the condition that during the vibration $|\Phi_6\rangle$ there is no rotation around y-axis. Above expressions imply

$$\langle H_2 | \Phi_6 \rangle = -\frac{1}{2\sqrt{m_H \left(1 + \frac{m_H x_{H2}^2}{m_C x_{C2}^2}\right)}}, \quad \langle C_2 | \Phi_6 \rangle = \frac{1}{2\sqrt{m_C \left(1 + \frac{m_C x_{C2}^2}{m_H x_{H2}^2}\right)}}. \tag{20a}$$

Using (16) one finds

$$\langle H_2|\Phi_6\rangle = -0.44276, \quad \langle C_2|\Phi_6\rangle = 0.06607. \tag{20b}$$

By symmetry this fixes all other amplitudes of the vibration $|\Phi_6\rangle$.

Degenerate vibration $|\Phi_5\rangle$ is a linear combination of two Φ_6-type vibrations. One finds $|\Phi_5\rangle = \gamma\left(|\Phi_6(2)\rangle + |\Phi_6(3)\rangle\right)$ where γ is unknown constant, $|\Phi_6(2)\rangle$ is vibration $|\Phi_6\rangle$ rotated in a positive sense by $\pi/3$, while $|\Phi_6(3)\rangle$ is vibration $|\Phi_6\rangle$ rotated in a positive sense by $2\pi/3$. Accordingly, vibration $|\Phi_6(2)\rangle$ has zero amplitudes at atoms H_2, C_2, C_5 and H_5, while vibration $|\Phi_6(3)\rangle$ has zero amplitudes at atoms H_3, C_3, C_6 and H_6 (see Figs. 1 and 3). One finds

$$\begin{aligned}
\langle H_1|\Phi_6(2)\rangle &= -\langle H_2|\Phi_6\rangle, \quad &\langle H_2|\Phi_6(2)\rangle &= 0, \\
\langle C_1|\Phi_6(2)\rangle &= -\langle C_2|\Phi_6\rangle, \quad &\langle C_2|\Phi_6(2)\rangle &= 0, \\
\langle H_1|\Phi_6(3)\rangle &= -\langle H_2|\Phi_6\rangle, \quad &\langle H_2|\Phi_6(3)\rangle &= -\langle H_2|\Phi_6\rangle, \\
\langle C_1|\Phi_6(3)\rangle &= -\langle C_2|\Phi_6\rangle, \quad &\langle C_2|\Phi_6(3)\rangle &= -\langle C_2|\Phi_6\rangle.
\end{aligned} \tag{21}$$

while normalization condition $\langle\Phi_5|\mathbf{M}|\Phi_5\rangle = 1$ reads

$$2m_H\langle H_1|\Phi_5\rangle^2 + 2m_C\langle C_1|\Phi_5\rangle^2 + 4m_H\langle H_2|\Phi_5\rangle^2 + 4m_C\langle C_2|\Phi_5\rangle^2 = 1.$$

Inserting $|\Phi_5\rangle = \gamma\left(|\Phi_6(2)\rangle + |\Phi_6(3)\rangle\right)$ into this expression and using (20a) and (21) one finds

$$\gamma^2 = \frac{1}{12\left(m_H\langle H_2|\Phi_6\rangle^2 + m_C\langle C_2|\Phi_6\rangle^2\right)} = 1/3.$$

Hence

$$|\Phi_5\rangle = \frac{1}{\sqrt{3}}\left(|\Phi_6(2)\rangle + |\Phi_6(3)\rangle\right). \tag{22}$$

Expressions (20) and (21) now determine all amplitude of the vibration $|\Phi_5\rangle$:

$$\begin{aligned}
\langle H_1|\Phi_5\rangle &= -\frac{2}{\sqrt{3}}\langle H_2|\Phi_6\rangle = 0.51126, \quad &\langle H_2|\Phi_5\rangle &= 0.5\langle H_1|\Phi_5\rangle = 0.25563, \\
\langle C_1|\Phi_5\rangle &= -\frac{2}{\sqrt{3}}\langle C_2|\Phi_6\rangle = -0.07629, \quad &\langle C_2|\Phi_5\rangle &= 0.5\langle C_1|\Phi_5\rangle = -0.03815.
\end{aligned} \tag{23}$$

and by symmetry for all remaining amplitudes on H and C atoms.

In accord with (2b), vibrations $|\Phi_5\rangle$ and $|\Phi_6\rangle$ defined by amplitudes (20) and (23) are normalized and mutually orthogonal:

$$\langle\Phi_5|\mathbf{M}|\Phi_5\rangle = \langle\Phi_6|\mathbf{M}|\Phi_6\rangle = 1, \quad \langle\Phi_5|\mathbf{M}|\Phi_6\rangle = 0.$$

Consider next vibrations $|\Phi_4\rangle$ and $|\Phi_9\rangle$ which are of a symmetry type b_{2g}. Requirements (2b) imply

$$\langle\Phi_4|\mathbf{M}|\Phi_4\rangle \equiv 6m_H \langle H_1|\Phi_4\rangle^2 + 6m_C \langle C_1|\Phi_4\rangle^2 = 1, \tag{24a}$$

$$\langle\Phi_9|\mathbf{M}|\Phi_9\rangle \equiv 6m_H \langle H_1|\Phi_9\rangle^2 + 6m_C \langle C_1|\Phi_9\rangle^2 = 1, \tag{24b}$$

$$\langle\Phi_4|\mathbf{M}|\Phi_9\rangle \propto m_H \langle H_1|\Phi_4\rangle \langle H_1|\Phi_9\rangle + m_C \langle C_1|\Phi_4\rangle \langle C_1|\Phi_9\rangle = 0. \tag{24c}$$

Those are three conditions in four unknowns. One can choose one amplitude and express remaining three amplitudes in terms of this amplitude. As a particular choice use amplitude $\langle H_1|\Phi_4\rangle$. With this choice one has

$$\langle C_1|\Phi_4\rangle = \sqrt{\frac{1 - 6m_H \langle H_1|\Phi_4\rangle^2}{6m_C}}, \quad \langle H_1|\Phi_9\rangle = -\sqrt{\frac{1 - 6m_H \langle H_1|\Phi_4\rangle^2}{6m_H}},$$

$$\langle C_1|\Phi_9\rangle = \sqrt{\frac{m_H}{m_C}} \langle H_1|\Phi_4\rangle. \tag{25}$$

Symmetry determines all remaining amplitudes of the out-of-plane vibrations $|\Phi_4\rangle$ and $|\Phi_9\rangle$. Each of those amplitudes can be expressed in terms of the above three amplitudes, and hence ultimately in terms of the amplitude $\langle H_1|\Phi_4\rangle$. For example one has $\langle H_2|\Phi_4\rangle = -\langle H_1|\Phi_4\rangle$, $\langle C_2|\Phi_4\rangle = -\langle C_1|\Phi_4\rangle$, $\langle H_2|\Phi_9\rangle = -\langle H_1|\Phi_9\rangle$, etc.

Vibrations $|\Phi_1\rangle$, $|\Phi_2\rangle$, $|\Phi_7\rangle$ and $|\Phi_8\rangle$ are of a symmetry type e_{2u}. Since $|\Phi_1\rangle$ and $|\Phi_2\rangle$ are mutually degenerate, vibration $|\Phi_1\rangle$ is a linear combination of two $|\Phi_2\rangle$-type vibrations. Similarly, since $|\Phi_7\rangle$ and $|\Phi_8\rangle$ are mutually degenerate, vibration $|\Phi_7\rangle$ is a linear combination of two $|\Phi_8\rangle$-type vibrations. In analogy to (22) one finds

$$|\Phi_1\rangle = \frac{1}{\sqrt{3}} (|\Phi_2(3)\rangle - |\Phi_2(2)\rangle). \tag{26a}$$

$$|\Phi_7\rangle = \frac{1}{\sqrt{3}} (|\Phi_8(3)\rangle - |\Phi_8(2)\rangle). \tag{26b}$$

where $|\Phi_2(2)\rangle$ is a vibration $|\Phi_2\rangle$ rotated in a positive sense by $\pi/3$, while $|\Phi_2(3)\rangle$ is a vibration $|\Phi_2\rangle$ rotated in a positive sense by $2\pi/3$, and analogously for vibrations $|\Phi_8(2)\rangle$ and $|\Phi_8(3)\rangle$. Hence

$$\begin{aligned}
\langle H_1|\Phi_2(2)\rangle &= -\langle H_1|\Phi_2(3)\rangle = \langle H_2|\Phi_2(3)\rangle = -\langle H_2|\Phi_2\rangle, \quad \langle H_2|\Phi_2(2)\rangle = 0, \\
\langle H_1|\Phi_8(2)\rangle &= -\langle H_1|\Phi_8(3)\rangle = \langle H_2|\Phi_8(3)\rangle = -\langle H_2|\Phi_8\rangle, \quad \langle H_2|\Phi_8(2)\rangle = 0,
\end{aligned} \tag{27a}$$

$$\langle C_1|\Phi_2(2)\rangle = -\langle C_1|\Phi_2(3)\rangle = \langle C_2|\Phi_2(3)\rangle = -\langle C_2|\Phi_2\rangle, \quad \langle C_2|\Phi_2(2)\rangle = 0,$$
$$\langle C_1|\Phi_8(2)\rangle = -\langle C_1|\Phi_8(3)\rangle = \langle C_2|\Phi_8(3)\rangle = -\langle C_2|\Phi_8\rangle, \quad \langle C_2|\Phi_8(2)\rangle = 0,$$
$$\tag{27b}$$

Further, orthonormality conditions (2b) imply

$$4m_H \langle H_2|\Phi_2\rangle^2 + 4m_C \langle C_2|\Phi_2\rangle^2 = 1,$$
$$4m_H \langle H_2|\Phi_8\rangle^2 + 4m_C \langle C_2|\Phi_8\rangle^2 = 1,$$
$$m_H \langle H_2|\Phi_8\rangle \langle H_2|\Phi_2\rangle + m_C \langle C_2|\Phi_8\rangle \langle C_2|\Phi_2\rangle = 0.$$

and similarly for the vibrations $|\Phi_1\rangle$ and $|\Phi_7\rangle$. Using above relations one can express all amplitudes of vibrations $|\Phi_1\rangle$, $|\Phi_2\rangle$, $|\Phi_7\rangle$ and $|\Phi_8\rangle$ in terms of only one amplitude. With the choice of the amplitude $\langle H_1|\Phi_1\rangle$ one finds

$$\langle C_1|\Phi_1\rangle = \sqrt{\frac{1 - 3m_H \langle H_1|\Phi_1\rangle^2}{3m_C}}, \quad \langle H_2|\Phi_1\rangle = -0.5 \langle H_1|\Phi_1\rangle,$$
$$\langle C_2|\Phi_1\rangle = -0.5 \langle C_1|\Phi_1\rangle, \quad \langle H_1|\Phi_2\rangle = \langle C_1|\Phi_2\rangle = 0,$$
$$\langle H_2|\Phi_2\rangle = \frac{\sqrt{3}}{2} \langle H_1|\Phi_1\rangle, \quad \langle C_2|\Phi_2\rangle = \frac{\sqrt{3}}{2} \langle C_1|\Phi_1\rangle, \tag{28a}$$

$$\langle H_1|\Phi_7\rangle = -\sqrt{\frac{1 - 3m_H \langle H_1|\Phi_1\rangle^2}{3m_H}}, \quad \langle H_2|\Phi_7\rangle = -0.5 \langle H_1|\Phi_7\rangle,$$
$$\langle C_1|\Phi_7\rangle = \sqrt{\frac{m_H}{m_C}} \langle H_1|\Phi_1\rangle, \quad \langle C_2|\Phi_7\rangle = -0.5 \langle C_1|\Phi_7\rangle, \tag{28b}$$

$$\langle H_1|\Phi_8\rangle = \langle C_1|\Phi_8\rangle = 0, \quad \langle H_2|\Phi_8\rangle = -\sqrt{\frac{1 - 3m_H \langle H_1|\Phi_1\rangle^2}{4m_H}},$$
$$\langle C_2|\Phi_8\rangle = \sqrt{\frac{3m_H}{4m_C}} \langle H_1|\Phi_1\rangle. \tag{28c}$$

By symmetry, expressions (28) determine all remaining amplitudes of those vibrations. For example, one has $\langle H_3|\Phi_1\rangle = \langle H_2|\Phi_1\rangle$, $\langle C_3|\Phi_1\rangle = \langle C_2|\Phi_1\rangle$, $\langle H_3|\Phi_2\rangle = -\langle H_2|\Phi_2\rangle$ etc. (see Fig. 3).

This completes determination of benzene out-of-plane vibrations. Expressions (18), (20) and (23) uniquely fix vibrations $|\Phi_3\rangle$, $|\Phi_6\rangle$ and $|\Phi_5\rangle$. Expressions (25) and (28) express all amplitudes of the remaining 6 vibrations in terms of only two amplitudes, $\langle H_1|\Phi_4\rangle$ and $\langle H_1|\Phi_1\rangle$.

4.2 d_0-Benzene vibrations and d_1-benzene frequencies

According to (12), since d_0-benzene frequencies $\nu_1 = \nu_2$, $\nu_5 = \nu_6$ and $\nu_7 = \nu_8$ are doubly degenerate, d_1-benzene has three strongly singular vibrations with those frequencies. Without loss of generality one can place deuterium at the benzene H_1 position. Since $\langle H_1|\Phi_2\rangle = \langle H_1|\Phi_6\rangle = \langle H_1|\Phi_8\rangle = 0$, with this choice d_0-benzene vibrations $|\Phi_2\rangle$, $|\Phi_6\rangle$ and $|\Phi_8\rangle$ are at the same time d_1-benzene strongly singular vibrations. There are no weakly singular vibrations, and remaining six out-of-plane d_1-benzene vibrations are hence cardinal. Corresponding eigenvalues are roots of the expression (11a) which reads

$$f(\varepsilon) \equiv \frac{\langle H_1|\Phi_1\rangle^2}{\varepsilon - \lambda_1} + \frac{\langle H_1|\Phi_3\rangle^2}{\varepsilon - \lambda_3} + \frac{\langle H_1|\Phi_4\rangle^2}{\varepsilon - \lambda_4} + \frac{\langle H_1|\Phi_5\rangle^2}{\varepsilon - \lambda_5} + \frac{\langle H_1|\Phi_7\rangle^2}{\varepsilon - \lambda_7} + \frac{\langle H_1|\Phi_9\rangle^2}{\varepsilon - \lambda_9}$$
$$+ \frac{1}{\varepsilon}\left[\frac{1}{M} + \frac{y_{H1}^2}{I_x} + \frac{1}{\Delta m}\right] = 0 \tag{29}$$

Using (25) and (28b) one can eliminate amplitudes $\langle H_1|\Phi_9\rangle$ and $\langle H_1|\Phi_7\rangle$ from this expression to obtain

$$\left[\frac{1}{\varepsilon - \lambda_1} - \frac{1}{\varepsilon - \lambda_7}\right]\langle H_1|\Phi_1\rangle^2 + \left[\frac{1}{\varepsilon - \lambda_4} - \frac{1}{\varepsilon - \lambda_9}\right]\langle H_1|\Phi_4\rangle^2 = g(\varepsilon), \tag{30a}$$

where

$$g(\varepsilon) = -\frac{1}{\varepsilon}\left[\frac{1}{M} + \frac{y_{H1}^2}{I_x} + \frac{1}{\Delta m}\right] - \frac{\langle H_1|\Phi_3\rangle^2}{\varepsilon - \lambda_3} - \frac{\langle H_1|\Phi_5\rangle^2}{\varepsilon - \lambda_5}$$
$$- \frac{1}{3m_H(\varepsilon - \lambda_7)} - \frac{1}{6m_H(\varepsilon - \lambda_9)}. \tag{30b}$$

Amplitudes $\langle H_1|\Phi_3\rangle$ and $\langle H_1|\Phi_5\rangle$ are given by (18) and (23), respectively. Function $g(\varepsilon)$ hence depends only on a parameter ε, since all other quantities in the expression (30b) are known (y-coordinate y_{H1} of the hydrogen atom H_1, isotope mass change $\Delta m \equiv m_D - m_H$, etc.).

Expression (30a) should be satisfied for each cardinal eigenvalue $\varepsilon_k = 4\pi^2\omega_k^2$ of d_1-benzene. There are six such eigenvalues. One can choose any two of those six eigenvalues to fix unknowns $\langle H_1|\Phi_1\rangle$ and $\langle H_1|\Phi_4\rangle$. Once $\langle H_1|\Phi_1\rangle$ and $\langle H_1|\Phi_4\rangle$ are known, one can derive remaining four cardinal eigenvalues as (remaining) roots of (30a).

Let $x_1 = \varepsilon_{k1}$ and $x_2 = \varepsilon_{k2}$ be a particular choice of two cardinal eigenvalues ε_k. According to (30), those eigenvalues satisfy matrix equation $\mathbf{A\Sigma} = \mathbf{X}$ where $\mathbf{A}$ is a 2×2 matrix while $\mathbf{\Sigma}$ and $\mathbf{X}$ are two-component column vectors:

$$A_{i,1} = \frac{1}{x_i - \lambda_1} - \frac{1}{x_i - \lambda_7}, \quad A_{i,2} = \frac{1}{x_i - \lambda_4} - \frac{1}{x_i - \lambda_9},$$
$$\Sigma_1 = \langle H_1|\Phi_1\rangle^2, \quad \Sigma_2 = \langle H_1|\Phi_4\rangle^2, \quad X_i = g(x_i), \quad i = 1, 2. \tag{31}$$

Above quantities satisfy a 2×2 inversion relation (15). Original 6×6 inversion relation that involves 6 cardinal out-of-plane vibrations of d_1-benzene is thus reduced to a much simpler 2×2 inversion relation. Using this relation, each choice $(\omega_{k1}, \omega_{k2})$ of two d_1-benzene cardinal out-of-plane frequencies determines amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$. With a choice $\omega_1 = 393 \, \text{cm}^{-1}$ and $\omega_3 = 622 \, \text{cm}^{-1}$ of d_1-frequencies one obtains

$$\langle H_1 | \Phi_1 \rangle = 0.30583, \quad \langle H_1 | \Phi_4 \rangle = 0.17971, \tag{32a}$$

Amplitudes of benzene vibrations $|\Phi_3\rangle$, $|\Phi_5\rangle$ and $|\Phi_6\rangle$ are fixed by symmetry and those amplitudes are given by expressions (18), (20) and (23). Once amplitudes (32a) are known, expressions (25) and (28) determine all remaining benzene amplitudes of vibrations $|\Phi_1\rangle$, $|\Phi_2\rangle$, $|\Phi_4\rangle$, $|\Phi_7\rangle$, $|\Phi_8\rangle$ and $|\Phi_9\rangle$:

$$
\begin{aligned}
\langle H_2 | \Phi_1 \rangle &= -0.15291, \quad \langle C_1 | \Phi_1 \rangle = 0.14108, \quad \langle C_2 | \Phi_1 \rangle = -0.07054, \\
\langle H_2 | \Phi_2 \rangle &= 0.26485, \quad \langle C_2 | \Phi_2 \rangle = 0.12218, \quad \langle C_1 | \Phi_4 \rangle = 0.10567, \\
\langle H_1 | \Phi_7 \rangle &= -0.48705, \quad \langle H_2 | \Phi_7 \rangle = 0.24352, \quad \langle C_1 | \Phi_7 \rangle = 0.08859, \\
\langle C_2 | \Phi_7 \rangle &= -0.04429, \quad \langle H_2 | \Phi_8 \rangle = -0.42180, \quad \langle C_2 | \Phi_8 \rangle = 0.07672 \\
\langle H_1 | \Phi_9 \rangle &= -0.36480, \quad \langle C_1 | \Phi_9 \rangle = 0.05206.
\end{aligned}
\tag{32b}
$$

Remaining amplitudes of those vibrations are determined by symmetry (see Fig. 3). According to theorems 1a and 1b, once above amplitudes are known, this determines all frequencies and vibrations of all benzene isotopomers. Amplitudes (32) are obtained from a particular choice $\omega_1 = 393 \, \text{cm}^{-1}$ and $\omega_3 = 622 \, \text{cm}^{-1}$ of two DFT d_1-frequencies. Each such choice produces slightly different result.

In conclusion, given six d_0-benzene out-of-plane frequencies ν_i and a choice $(\omega_{k1}, \omega_{k2})$ of any two d_1-benzene out-of-plane cardinal frequencies, this determines all out-of-plane frequencies and vibrations of all benzene isotopomers. From those frequencies one first obtains d_0-benzene amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$ using the inversion relation (15) with quantities $\mathbf{A}$, $\mathbf{X}$ and $\mathbf{\Sigma}$ as defined by (31). Once those amplitudes are known, one obtains remaining four cardinal out-of-plane frequencies of d_1–benzene from the roots ε_k of (30). Due to small uncertainties in input frequencies ν_i and $(\omega_{k1}, \omega_{k2})$, d_0-benzene amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$ as well as d_1-benzene frequencies obtained in this way slightly differ for various choices of d_1-frequencies $(\omega_{k1}, \omega_{k2})$. Amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$ obtained in this way for all possible choices of $(\omega_{k1}, \omega_{k2})$ are shown in Table 2. Variations of those amplitudes are relatively small with average amplitudes $\langle H_1 | \Phi_1 \rangle_{avr} = 0.30667 \pm 0.0016$ and $\langle H_1 | \Phi_4 \rangle = 0.17896 \pm 0.0037$. The corresponding d_1–benzene frequencies are shown in Table 3. In the first column of this table are DFT d_1-frequencies [13], and in the remaining columns are LRP frequencies. DFT d_1-frequencies $(\omega_{k1}, \omega_{k2})$ which are used as input data are emphasized with bold figures. For example, in the second column DFT frequencies $\omega_1 = 393 \, \text{cm}^{-1}$ and $\omega_3 = 622 \, \text{cm}^{-1}$ of d_1-benzene are used in order to obtain LRP frequencies for the remaining four cardinal vibrations of d_1-benzene. Standard deviation of thus obtained cardinal frequencies from the "exact" DFT frequencies is also shown and in this case it equals $\Delta = 0.26 \, \text{cm}^{-1}$. This

Table 2 LRP amplitudes $\langle H_1|\Phi_1\rangle$ and $\langle H_1|\Phi_4\rangle$ of benzene vibrations $|\Phi_1\rangle$ and $|\Phi_4\rangle$ for various choices of two d_1-benzene frequencies

Comb.[a]	1–3	1–4	1–5	1–7	1–9	3–4	3–5	3–7
$\langle H_1|\Phi_1\rangle$	0.30583	0.30575	0.30593	0.30572	0.30590	0.30838	0.30347	0.30717
$\langle H_1|\Phi_4\rangle$	0.17971	0.18404	0.17355	0.18582	0.17490	0.18487	0.17553	0.18206

Comb.[a]	3–9	4–5	4–7	4–9	5–7	5–9	7–9	Average
$\langle H_1|\Phi_1\rangle$	0.30189	0.29322	0.30640	0.32423	0.31214	0.30492	0.30917	0.30667 ± 0.0016
$\langle H_1|\Phi_4\rangle$	0.17270	0.18342	0.18407	0.18500	0.16835	0.17436	0.17670	0.17896 ± 0.0037

[a] Particular choice of two DFT d_1-benzene cardinal frequencies

Table 3 LRP cardinal frequencies of out-of-plane vibrations of d_1-benzene

C_6DH_5 ω_k	1–3 $\Delta = 0.26$	1–4 $\Delta = 0.43$	1–5 $\Delta = 0.30$	1–7 $\Delta = 0.51$	1–9 $\Delta = 0.26$	3–4 $\Delta = 0.51$	3–5 $\Delta = 0.30$
1	393[a]	**393.00[a]**	**393.00[a]**	**393.00[a]**	**393.00[a]**	**393.00[a]**	392.68	393.29
3	622[a]	**622.00[a]**	621.74	622.36	621.63	622.28	**622.00[a]**	**622.00[a]**
4	714[a]	714.16	**714.00[a]**	714.37	713.94	714.33	**714.00[a]**	714.30
5	792[a]	792.46	792.78	**792.00[a]**	792.92	792.10	792.95	**792.00[a]**
7	934[a]	933.84	933.95	933.68	**934.00[a]**	933.72	934.15	933.56
9	1,003[a]	1,003.11	1,003.21	1,002.97	1,003.25	**1,003.00[a]**	1,003.18	1,003.04

	3–7 $\Delta = 0.38$	3–9 $\Delta = 0.47$	4–5 $\Delta = 1.16$	4–7 $\Delta = 0.44$	4–9 $\Delta = 1.83$	5–7 $\Delta = 0.80$	5–9 $\Delta = 0.28$	7–9 $\Delta = 0.41$
1	392.83	393.49	394.49	392.92	390.74	392.26	393.12	392.60
3	**622.00[a]**	**622.00[a]**	620.52	621.80	623.57	623.27	622.21	622.51
4	714.07	714.40	**714.00[a]**	**714.00[a]**	714.57	714.57	714.34	714.27
5	792.72	791.69	**792.00[a]**	792.82	793.99	**792.00[a]**	**792.00[a]**	792.43
7	**934.00[a]**	933.37	933.06	**934.00[a]**	935.37	**934.00[a]**	933.63	**934.00[a]**
9	1,003.15	**1,003.00[a]**	1,003.34	1,003.20	**1,003.00[a]**	1,002.78	**1,003.00[a]**	**1,003.00[a]**

Two such frequencies are treated as input (emphasized in bold). Other four frequencies are then calculated. Input frequencies are DFT frequencies [13]. All frequencies in cm^{-1}
[a] DFT frequencies. B3LYP/6-31G(d,p) calculation [13]

standard deviation is normalized to four quantities, i.e. it excludes three strongly singular frequencies $\omega_2 = \nu_2 = 414\,cm^{-1}$, $\omega_6 = \nu_6 = 865\,cm^{-1}$ and $\omega_8 = \nu_8 = 974\,cm^{-1}$ which are exact and the two cardinal frequencies which are used in order to derive remaining four cardinal frequencies (in this case frequencies $\omega_1 = 393\,cm^{-1}$ and $\omega_3 = 622\,cm^{-1}$). Other columns contain other possible combinations. In all cases LRP reproduces DFT frequencies with high precision. On average, standard deviations between two sets of data is of the order $\Delta \approx 0.59\,cm^{-1}$. The agreement is not exact, since DFT frequencies in ref. [13] are reported only up to $1\,cm^{-1}$, and hence those frequencies are reliable up to $\pm 0.5\,cm^{-1}$. Since LRP uses six d_0-benzene and two d_1-benzene DFT frequencies as input data, this error propagates and it is reflected as slight discrepancy between four remaining DFT d_1- and LRP d_1-frequencies. In addition, there is a possible difference in input quantities (16) which are not reported in reference [13]. In an exact calculation and in the harmonic approximation LRP should

produce identical results as DFT. Small discrepancies of the order $\Delta \approx 0.59\,\mathrm{cm}^{-1}$ are due to the above mentioned small differences and uncertainties of input data.

4.3 Comparison of the DFT and LRP out-of-plane frequencies of (H,D)-benzene isotopomers

Once benzene out-of-plane frequencies and vibrational amplitudes are known, this uniquely determines out-of-plane frequencies and vibrations of all benzene isotopomers. If one considers all possible (H,D) and (^{12}C, ^{13}C) combinations, there are few hundreds of such isotopomers. If in addition one includes isotopomers that may contain ^{3}H and ^{14}C isotopes, one finds almost one hundred thousands of such isotopomers. LRP produces with a single stroke vibrational frequencies and normal modes for all those isotopomers. In this paper are considered only (H, D)-isotopomers shown in Fig. 2. In Table 4 are compared LRP out-of-plane frequencies for 11 poly-deuterated (H,D)-isotopomers with the DFT out-of-plane frequencies of those isotopomers. Benzene vibrations as obtained with the choice $\omega_1 = 393\,\mathrm{cm}^{-1}$ and $\omega_3 = 622\,\mathrm{cm}^{-1}$ for d_1-frequencies were used (see expressions 32). Once those vibrations are known, expressions (4–6) determine all cardinal out-of-plane vibrations while expressions (8) and (9) determine remaining strongly and weakly singular vibrations for all benzene isotopomers. Concerning (H,D)-benzene isotopomers considered in Table 4, there are only three strongly singular vibrations described by expressions (8), and no weakly singular vibration. Those strongly singular vibrations correspond to frequencies ω_2, ω_6 and ω_8 of d_2-benzene 1,4-$C_6D_2H_4$. This isotopomer has two deuterium atoms at positions H_1 and H_4. At those positions d_0-benzene vibrations $|\Phi_2\rangle$, $|\Phi_6\rangle$ and $|\Phi_8\rangle$ have no amplitude (see Fig. 3). Accordingly, those vibrations are not effected by the isotopic substitutions at positions H_1 and H_4. Therefore those d_0-benzene vibrations are strongly singular vibrations of d_2-isotopomer 1,4-$C_6D_2H_4$. As explained in the previous section, those d_0-benzene vibrations are also strongly singular d_1-benzene vibrations.

As shown in Table 4, LRP calculation practically reproduces much more sophisticated DFT calculation. Standard deviation between two sets of data is on average $\approx 0.38\,\mathrm{cm}^{-1}$. The largest standard deviation ($\Delta = 0.62\,\mathrm{cm}^{-1}$) is obtained in the case of d_4-benzene 1,2,4,5-$C_6D_4H_2$. Since in the reference [13] DFT frequencies are reported to within $\pm 0.5\,\mathrm{cm}^{-1}$, this error can be entirely attributed to the uncertainties of input d_0-and d_1-frequencies, and to the small uncertainties in bond lengths (16a). In conclusion, frequencies as obtained by the highly sophisticated DFT calculation can be obtained much more efficiently and much easier within the LRP approach.

LRP frequencies of (H,D)-benzene isotopomers shown in Table 4, were derived using amplitudes $\langle H_1|\Phi_1\rangle = 0.30583$ and $\langle H_1|\Phi_4\rangle = 0.17971$. Those amplitudes were obtained from six DFT out-of-plane d_0-frequencies and two DFT d_1-frequencies $\omega_1 = 393\,\mathrm{cm}^{-1}$ and $\omega_3 = 622\,\mathrm{cm}^{-1}$. One could equally well use other possible amplitude choices shown in Table 2. All such choices produce more or less similar results. A more systematic approach would be to derive amplitudes $\langle H_1|\Phi_1\rangle$ and $\langle H_1|\Phi_4\rangle$ not from a particular choice (ε_{k1}, ε_{k2}) of two d_1-benzene out-of-plane cardinal frequencies, but rather from the condition that those amplitudes should minimize deviation of LRP d_1-frequencies from DFT d_1-frequencies.

Table 4 DFT[a] and LRP[b] frequencies of out-of-plane vibrations of d_2-, d_3-, d_4-, d_5- and d_6-benzenes

	3 1,2-$C_6D_2H_4$ $\Delta = 0.34$			4 1,3-$C_6D_2H_4$ $\Delta = 0.23$			5 1,4-$C_6D_2H_4$ $\Delta = 0.40$			6 1,2,3-$C_6D_3H_3$ $\Delta = 0.28$		
	C_{2v}	DFT[a]	LRP[b]	C_{2v}	DFT[a]	LRP[b]	D_{2h}	DFT[a]	LRP[b]	C_{2v}	DFT[a]	LRP[b]
1	a_2	384	383.89	a_2	386	386.02	b_{1u}	374	373.30	b_2	383	383.05
2	b_2	403	402.87	b_2	402	401.83	a_u	414	414.00	a_2	386	386.02
3	b_2	591	590.81	b_2	582	581.71	b_{1u}	611	611.31	b_2	558	558.10
4	a_2	676	675.96	b_2	714	714.12	b_{3g}	648	647.61	b_2	670	669.72
5	a_2	782	782.58	a_2	719	719.48	b_{3g}	750	749.99	a_2	719	719.48
6	b_2	797	797.12	b_2	830	830.19	b_{2g}	865	865.00	b_2	790	790.16
7	a_2	900	900.25	a_2	934	933.73	b_{1u}	879	878.57	b_2	840	840.53
8	b_2	960	959.57	b_2	934	934.07	a_u	974	974.00	a_2	934	933.73
9	a_2	998	998.61	b_2	991	990.90	b_{3g}	978	978.16	b_2	991	990.88

	7 1,2,4-$C_6D_3H_3$ $\Delta = 0.53$			8 1,3,5-$C_6D_3H_3$ $\Delta = 0.36$			9 1,2,3,4-$C_6D_4H_2$ $\Delta = 0.36$			10 1,2,3,5-$C_6D_4H_2$ $\Delta = 0.38$		
	C_s	DFT[a]	LRP[b]	D_{3h}	DFT[a]	LRP[b]	C_{2h}	DFT[a]	LRP[b]	C_{2v}	DFT[a]	LRP[b]
1	a''	370	369.24	e''	386	386.02	b_2	368	367.78	b_2	368	367.23
2	a''	400	399.16	e''	386	386.02	a_2	384	383.70	a_2	386	386.02
3	a''	573	573.13	a_2''	545	545.16	b_2	544	544.23	b_2	537	537.14
4	a'	647	646.16	a_2''	714	714.11	a_2	640	639.65	b_2	646	645.81
5	a''	718	718.07	e''	719	719.48	a_2	698	698.13	b_2	718	717.73
6	a''	782	782.61	e''	719	719.48	b_2	746	745.73	a_2	719	719.48
7	a''	873	873.41	e''	934	933.73	a_2	822	822.60	b_2	810	810.33
8	a''	934	934.06	e''	934	933.73	b_2	873	873.61	a_2	934	933.73
9	a'	976	976.13	a_2''	934	934.74	a_2	976	976.07	b_2	934	934.44

	11 1,2,4,5-$C_6D_4H_2$ $\Delta = 0.62$			12 C_6D_5H $\Delta = 0.34$			13 C_6D_6 $\Delta = 0.41$		
	D_{2h}	DFT[a]	LRP[b]	C_{2v}	DFT[a]	LRP[b]	D_{6h}	DFT[a]	LRP[b]
1	a_u	361	360.54	a_2	361	360.54	e_{2u}	361	360.54
2	b_{1u}	390	389.45	b_2	376	375.41	e_{2u}	361	360.54
3	b_{1u}	560	559.63	b_2	526	525.69	a_{2u}	509	509.54
4	b_{3g}	631	629.99	b_2	628	627.43	b_{2g}	615	614.31
5	b_{2g}	673	672.90	a_2	673	672.90	e_{1g}	673	672.90
6	b_{3g}	779	779.90	b_2	719	718.90	e_{1g}	673	672.90
7	a_u	791	791.16	a_2	791	791.16	e_{2u}	791	791.16
8	b_{1u}	931	931.37	b_2	825	825.14	e_{2u}	791	791.16
9	b_{3g}	936	936.87	b_2	934	934.11	b_{2g}	837	837.53

All frequencies in cm^{-1}

[a] DFT frequencies. B3LYP/6-31G(d,p) calculation [13]

[b] LRP frequencies using six d_0-benzene DFT cardinal frequencies (Table 1) and (cardinal) d_1-benzene DFT frequencies $\omega_1 = 393\,cm^{-1}$ and $\omega_3 = 622\,cm^{-1}$

4.4 Comparison of LRP frequencies with scaled DFT frequencies

Though vibrational analyze by the DFT method is quite sophisticated, it still produces unsatisfactory agreement with experimental frequencies [13,20]. A general strategy designed in order to improve DFT frequencies is scaling technique [13,20]. Key idea

in this approach is to use several individual mode scaling factors which optimally reproduce frequencies of the parent molecule **A** [13,20]. Since those scaling factors improve frequencies of **A**, it is assumed that those same factors should improve frequencies of all isotopomers **B** of **A**. Depending on the number of such scaling factors, the agreement with experimental frequencies can be more or less improved [20]. In general one can use two different scaling techniques; one can either scale theoretical force field [20], or one can directly scale theoretical frequencies [13].

Wu and Cremer in addition to the (H,D)-benzene DFT frequencies reported also scaled frequencies for those isotopomers [13]. They apply scaling technique to theoretical DFT benzene frequencies, and not to theoretical benzene force field. Those scaled frequencies are obtained using individual scaling factors which accurately reproduce all vibrational frequencies of benzene [13]. Since benzene has six mutually distinct out-of-plane frequencies, six scaling factors are required in order to reproduce exactly out-of-plane benzene frequencies. Of course, additional scaling factors are needed in order to reproduce exactly remaining in-plane benzene frequencies [13].

Scaled benzene out-of-plane frequencies which exactly reproduce experimental benzene frequencies are shown in Table 5. DFT out-of-plane scaled frequencies for remaining 12 (H,D)-benzene isotopomers are compared with the corresponding LRP frequencies in Table 6. Those LRP frequencies are derived in the following way: as input frequencies of the system **A**, d_0-benzene frequencies from Table 5, i.e. experimental out-of-plane benzene frequencies are used. Concerning benzene amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$, the same amplitudes as in the Table 4 were used. This is a hybrid approach where DFT theoretical d_0-frequencies from Table 1 are replaced with experimental d_0-frequencies, while amplitudes $\langle H_1 | \Phi_1 \rangle = 0.30583$ and $\langle H_1 | \Phi_4 \rangle = 0.17971$ as derived using six DFT d_0-frequencies and two DFT d_1-frequencies $\omega_1 = 393 \, \text{cm}^{-1}$ and $\omega_3 = 622 \, \text{cm}^{-1}$ are retained. Accordingly, those amplitudes should agree with DFT benzene amplitudes. In a more consistent approach, in order to derive amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$ one should use six experimental d_0-frequencies and a choice of any two experimental d_1-frequencies. Still better approach is to use all available experimental (cardinal) d_1-frequencies instead of only two such frequencies, and to chose amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$ subject to the condition that standard error of those input d_1-frequencies is minimized. It is not correct instead of experimental d_1-frequencies to use scaled d_1-frequencies. Scaling technique based on the scaling of theoretical frequencies may lead to the violation of the interlacing rule (10b), which rule is strictly satisfied in the LRP approach. For example, if one compares scaled frequencies of (H,D)-benzene isotopomers 7 and 11 in Figure 2 (isotopomers 1,2,4-$C_6D_3H_3$ and 1,2,4,5-$C_6D_4H_2$) one finds (see Table 6)

$$347(11)_1 < 356(7)_1 < 375(11)_2 < 385(7)_2 < 582(11)_3?556(7)_3 <$$
$$621(11)_4 < 637(7)_4 < 658(11)_5 < 702(7)_5 < 762(11)_6 < 765(7)_6 <$$
$$785(11)_7 < 867(7)_7 < 915(11)_8 < 927(7)_8?924(11)_9 < 954(7)_9. \qquad (33)$$

There are two violations of the interlacing rule (10b) which are indicated with a question mark. Particularly serious is the violation $582(11)_3 ?556(7)_3$ which amounts to $26 \, \text{cm}^{-1}$. It is highly unlikely that violation as large as $26 \, \text{cm}^{-1}$ is due to the

Table 5 Scaled out-of-plane benzene frequencies [13]

	C_6H_6 D_{6h}	
1	e_{2u}	398
2	e_{2u}	398
3	a_{2u}	673
4	b_{2g}	707
5	e_{1g}	846
6	e_{1g}	846
7	e_{2u}	967
8	e_{2u}	967
9	b_{2g}	990

Those frequencies equal experimental frequencies [13,21]. All frequencies in cm^{-1}

anharmonicity effects. Both violations demonstrate that those scaled frequencies are not consistent with harmonic approximation. Though anharmonicity effects can in principle violate interlacing rule, each such violation, especially if it is large, is highly suspicious and it very likely indicates erroneous frequencies which do not agree with experiment [9]. Above example demonstrates that scaling technique which is based on scaling of theoretical frequencies may be contaminated with implicit strong anharmonicity assumptions. Since LRP is based on the harmonic approximation, it is not correct to use such scaled DFT frequencies as input in the LRP calculations. On the other hand, scaled technique based on the force field scaling does not violate interlacing rule. Modified problem involving modified force field is still within a harmonic approximation, and hence resulting frequencies should satisfy interlacing rule. Accordingly, on theoretical grounds force field scaling is preferable to frequency scaling. Unfortunately, only (H,D)-benzene isotopomers scaled frequencies based on frequency scaling were available [13]. Note finally that experimental frequencies can also violate the interlacing rule. If this is the case, it indicated inadequacy of the LRP approach for the particular problem. However, for this to happen anharmonicity effects must be quite strong.

In conclusion, by its very nature scaling technique based on frequency scaling violates harmonic approximation which is an essential part of the LRP approach. Therefore, in the absence of the reliable experimental d_1-frequencies and in the absence of force field scaled frequencies, it is better to use amplitudes as obtained from DFT d_1-frequencies, which are by construction guaranteed to satisfy the interlacing rule. Accordingly, in the derivation of LRP frequencies in Table 6 were used experimental d_0-frequencies and d_0-amplitudes $\langle H_1 | \Phi_1 \rangle$ and $\langle H_1 | \Phi_4 \rangle$ as obtained from the DFT (unscaled) six d_0- and two d_1-frequencies.

In Table 6 are also shown standard deviations of those LRP frequencies from DFT scaled frequencies. On average those standard deviations are of the order $\Delta \approx 4.41$ cm^{-1} which is substantially higher from standard deviations ($\Delta \approx 0.38$ cm^{-1}) of LRP frequencies from original DFT frequencies (Table 4). This illustrates qualitative difference between original DFT frequencies which are in accord with harmonic approximation and scaled DFT frequencies which violate this approximation.

In comparing LRP and scaled DFT frequencies an additional point should be emphasized. With the exception of C_6D_6, all remaining (H,D)-benzene isotopomers have lower symmetry then benzene. Hence in order to obtain scaled frequencies of those isotopomers one has to solve a nontrivial problem of pairing (H,D)-isotopomer

Table 6 DFT[a] scaled frequencies and LRP[b] frequencies of out-of-plane vibrations of deuterated benzene

	2 C_6DH_5 $\Delta = 2.65$			3 1,2-$C_6D_2H_4$ $\Delta = 3.90$			4 1,3-$C_6D_2H_4$ $\Delta = 3.98$			5 1,4-$C_6D_2H_4$ $\Delta = 2.06$		
	C_{2v}	DFT[a]	LRP[b]	C_{2v}	DFT[a]	LRP[b]	C_{2v}	DFT[a]	LRP[b]	D_{2h}	DFT[a]	LRP[b]
1	b_2	378	378.02	a_2	369	369.32	a_2	371	371.33	b_{1u}	360	359.21
2	a_2	398	398.00	b_2	387	387.43	b_2	386	386.46	a_u	398	398.00
3	b_2	603	605.28	b_2	573	574.01	b_2	564	565.75	b_{1u}	592	593.77
4	b_2	703	701.73	a_2	666	665.11	b_2	703	701.68	b_{3g}	638	635.23
5	b_2	775	775.45	a_2	765	768.95	a_2	703	705.81	b_{3g}	734	736.26
6	a_2	846	846.00	b_2	780	778.69	b_2	812	811.97	b_{2g}	846	846.00
7	b_2	927	922.08	a_2	894	885.07	a_2	927	919.31	b_{1u}	873	870.02
8	a_2	967	967.00	b_2	953	951.70	b_2	927	923.65	b_{3g}	956	956.07
9	b_2	980	983.32	a_2	975	980.98	b_2	968	975.72	a_u	967	967.00

	6 1,2,3-$C_6D_3H_3$ $\Delta = 8.22$			7 1,2,4-$C_6D_3H_3$ $\Delta = 4.65$			8 1,3,5-$C_6D_3H_3$ $\Delta = 2.22$			9 1,2,3,4-$C_6D_4H_2$ $\Delta = 3.98$		
	C_{2v}	DFT[a]	LRP[b]	C_s	DFT[a]	LRP[b]	D_{3h}	DFT[a]	LRP[b]	C_{2v}	DFT[a]	LRP[b]
1	b_2	379	368.54	a''	356	355.31	e''	371	371.33	b_2	354	353.91
2	a_2	382	371.33	a''	385	383.91	e''	371	371.33	a_2	369	369.15
3	b_2	541	542.06	a''	556	556.62	a_2''	528	530.01	b_2	528	528.21
4	b_2	656	658.98	a'	637	633.86	a_2''	703	701.67	a_2	630	628.18
5	a_2	706	705.81	a''	702	704.63	e''	703	705.81	a_2	683	684.52
6	b_2	775	774.40	a''	765	769.00	e''	703	705.81	b_2	730	732.74
7	b_2	841	825.48	a''	867	861.11	a_2''	913	913.15	a_2	816	809.52
8	a_2	935	923.65	a''	927	919.32	e''	927	923.65	b_2	867	861.76
9	b_2	973	975.32	a'	954	962.13	e''	927	923.65	a_2	954	961.74

	10 1,2,3,5-$C_6D_4H_2$ $\Delta = 2.56$			11 1,2,4,5-$C_6D_4H_2$ $\Delta = 13.07$			12 C_6D_5H $\Delta = 4.48$			13 C_6D_6 $\Delta = 1.09$		
	C_{2v}	DFT[a]	LRP[b]	D_{2h}	DFT[a]	LRP[b]	C_{2v}	DFT[a]	LRP[b]	D_{6h}	DFT[a]	LRP[b]
1	b_2	354	353.39	a_u	347	346.97	a_2	347	346.97	e_{2u}	347	346.97
2	a_2	371	371.33	b_{1u}	375	374.69	b_2	363	361.22	e_{2u}	347	346.97
3	b_2	521	521.66	b_{1u}	582	542.97	b_2	510	510.06	a_{2u}	494	494.12
4	b_2	636	633.49	b_{3g}	621	618.60	b_2	618	616.21	b_{2g}	606	603.64
5	b_2	702	704.34	b_{2g}	658	658.12	a_2	658	658.12	e_{1g}	658	658.12
6	a_2	703	705.81	b_{3g}	762	764.65	b_2	703	705.31	e_{1g}	658	658.12
7	b_2	804	800.07	a_u	785	784.63	a_2	785	784.63	e_{2u}	785	784.63
8	b_2	913	916.40	b_{3g}	915	915.92	b_2	819	811.39	e_{2u}	785	784.63
9	a_2	927	923.65	b_{1u}	924	923.52	b_2	913	923.52	b_{2g}	818	820.21

All frequencies in cm^{-1}

[a] Scaled DFT frequencies. B3LYP/6-31G(d,p) calculation [13]

[b] LRP frequencies obtained using six d_0-benzene experimental frequencies and amplitudes $\langle H_1|\Phi_1\rangle = 0.30583$ and $\langle H_1|\Phi_4\rangle = 0.17971$

frequencies with frequencies of the parent benzene molecule. This pairing requires a rather sophisticated method involving stepwise mass increments which in many small steps transform parent benzene molecule into the corresponding benzene isotopomer [13]. This procedure might work in the particular case of benzene, but it is

not general and there is always a possibility of serious problems due to mass reaction paths crossings. In any case, this is a highly artificial procedure, and computationally quite demanding, since the calculation should be repeated in many points along the mass reaction path [13]. In comparison, LRP has no such problem. Each cardinal out-of-plane vibration of the particular (H,D)-isotopomer is obtained using expressions (4–9), and the only deference is that in those expressions DFT d_0-frequencies from Table 1 are replaced with experimental d_0-frequencies from Table 5. There is no need for pairing (H,D)-benzene isotopomer frequencies with frequencies of a parent benzene molecule, since all cardinal frequencies of those isotopomers are obtained directly from the roots of the expression (5c). It remains to find out how well LRP frequencies agree with experimental frequencies.

4.5 Comparison of LRP and scaled DFT frequencies with experimental frequencies

LRP and scaled DFT frequencies are compared with experimental frequencies in Table 7. Standard deviations of LRP as well as of scaled DFT frequencies from experimental frequencies are also shown. There are no experimental frequencies for all (H,D)-benzene isotopomers. In Ref. [13], in addition to d_0-benzene frequencies shown in Table 5, the authors report only experimental frequencies for $C_6(HD)_3$ and C_6D_6 benzene isotopomers [13,21]. As shown in Table 7, in the case of the isotopomer $C_6(HD)_3$, standard deviation of LRP out-of-plane frequencies from experimental frequencies is $\Delta_{LRP} = 2.78 \, \text{cm}^{-1}$, while standard deviation of scaled DFT out-of-plane frequencies from experimental frequencies is $\Delta_{DFT} = 4.04 \, \text{cm}^{-1}$. In the case of benzene isotopomer C_6D_6 one finds $\Delta_{LRP} = 3.78 \, \text{cm}^{-1}$ and $\Delta_{DFT} = 4.69 \, \text{cm}^{-1}$. In both cases LRP frequencies are in much better agreement with experimental frequencies then DFT scaled frequencies. Note that original (non-scaled) DFT frequencies shown in Table 4 have substantially bigger error then scaled DFT frequencies. In the case of isotopomer $C_6(HD)_3$, this error is $\Delta_{DFT} = 14.39 \, \text{cm}^{-1}$, while in the case of benzene isotopomer C_6D_6 this error is $\Delta_{DFT} = 12.34 \, \text{cm}^{-1}$. In both cases scaling technique substantially reduces experimental error: in the former case from $\Delta_{DFT} = 14.39 \, \text{cm}^{-1}$ to $\Delta_{DFT} = 4.04 \, \text{cm}^{-1}$ and in the latter case from $\Delta_{DFT} = 12.34 \, \text{cm}^{-1}$ to $\Delta_{DFT} = 4.69 \, cm^{-1}$. However, in both cases resulting errors are still bigger then the corresponding LRP errors.

In Table 7 are also compared LRP and scaled DFT out-of-plane frequencies with experimental frequencies for C_6DH_5, $1,4$-$C_6D_2H_4$ and $1,2,4,5$-$C_6D_4H_2$ benzene isotopomers. Those experimental frequencies are taken from ref. [3]. In all cases considered, except in the case of $1,4$-$C_6D_2H_4$ isotopomer, LRP frequencies are in better agreement with experimental frequencies from scaled DFT frequencies. In the case of $1,4$-$C_6D_2H_4$ isotopomer one finds $\Delta_{LRP} = 5.72 \, \text{cm}^{-1}$ and $\Delta_{DFT} = 5.69 \, \text{cm}^{-1}$. Scaled DFT out-of-plane frequencies are in this case only marginally better then LRP frequencies. It is very likely that this is not due to presumably better performance of DFT, but rather to relatively unreliable experimental frequencies in this particular case. On average, considering all five (H,D)-benzene isotopomers shown in Table 7, one has $\Delta_{LRP} \approx 4.74 \, \text{cm}^{-1}$ and $\Delta_{DFT} \approx 6.79 \, \text{cm}^{-1}$. This shows that, as far as avai-

Table 7 Comparison of DFT scaled frequencies[a] and LRP frequencies[b] with experimental frequencies[c,d]

	2 C6DH5			5 1,4-C6D2H4			8 C6(DH)3			11 1,2,4,5-C6D4H2			13 C6D6		
	DFT[a] $\Delta=6.42$	LRP[b] $\Delta=5.04$	Exp.[d]	DFT[a] $\Delta=5.69$	LRP[b] $\Delta=5.72$	Exp.[d]	DFT[a] $\Delta=4.04$	LRP[b] $\Delta=2.78$	Exp.[c]	DFT[a] $\Delta=13.09$	LRP[b] $\Delta=6.39$	Exp.[d]	DFT[a] $\Delta=4.69$	LRP[b] $\Delta=3.78$	Exp.[c]
1	378	378.02	380	360	359.21	367	371	371.33	368	347	346.97	352	347	346.97	345
2	398	398.00	405	398	398.00	405	371	371.33	368	375	374.69	383	347	346.97	345
3	603	605.28	608	592	593.77	597	528	530.01	531	528	542.97	548	494	494.12	496
4	703	701.73	698	638	635.23	634	703	701.67	697	621	618.60	615	606	603.64	599
5	775	775.43	775	734	736.26	736	703	705.81	708	658	658.12	664	658	658.12	660
6	846	846.00	849	846	846.00	849	703	705.81	708	762	764.65	767	658	658.12	660
7	927	922.08	922	873	870.02	876	913	913.15	917	785	784.63	793	785	784.63	787
8	967	967.00	970	956	956.07	967	927	923.65	924	915	915.92	925	785	784.63	787
9	980	983.32	995	967	967.00	970	927	923.65	924	924	923.52	930	818	820.21	829

All frequencies in cm^{-1}

[a] DFT scaled frequencies. B3LYP/6-31G(d,p) calculation [13]

[b] LRP frequencies obtained using six d_0-benzene experimental frequencies and amplitudes $\langle H_1|\Phi_1\rangle = 0.30583$ and $\langle H_1|\Phi_4\rangle = 0.17971$

[c] Experimental frequencies [13,21]

[d] Experimental frequencies [3]

lable experimental frequencies are considered, LRP frequencies are superior to the scaled DFT frequencies.

5 Conclusions

Vibrational isotope effect was analyzed by the Low rank perturbation (LRP) method. LRP treatment of this effect is based on the harmonic approximation and on the assumption (consistent with the Born-Oppenheimer approximation) that if the parent molecule **A** is replaced by an isotopomer **B**, force field does not change. Within those approximations LRP is exact.

In a present paper out-of-plane vibrations of benzene (H,D)-isotopomers were considered. One finds that LRP reproduces DFT frequencies with high precision. Virtual equality of DFT and LRP results is due to the fact that DFT approach (which was used in those calculations [13]) is also consistent with the above approximations. Small discrepancies in calculated vibrational frequencies of the order $\approx 0.38\,\mathrm{cm}^{-1}$ are entirely due to the uncertainties ($\approx 0.5\,\mathrm{cm}^{-1}$) of the reported DFT frequencies [13], and to possible small differences in input benzene geometry and atomic masses of carbon, hydrogen and deuterium atoms. A standard method used to improve DFT frequencies is a scaling technique [13,20]. There are two ways how one can apply this technique: one can scale either theoretical force field [20] or on can scale theoretical frequencies [13]. Applying six scaling factors to DFT theoretical frequencies one can exactly reproduce benzene out-of-plane frequencies, and those same scaling factors are expected to improve out-of-plane frequencies of all benzene (H,D)-isotopomers [13]. One finds that LRP out-of-plane frequencies (obtained using experimental d_0-frequencies as input data) differ from such DFT scaling frequencies [13] on average with a standard deviation $\Delta \approx 4.41\,\mathrm{cm}^{-1}$. This is significant and it is due to the fact that scaled DFT frequencies based on frequency scaling may violate harmonic approximation. On the other hand, harmonic approximation is strictly obeyed by the LRP approach. Within this approach is derived interlacing rule [7–9] which generalizes well known order rule [3]. Each violation of the interlacing rule indicated violation of the harmonic approximation. Though anharmonicity effects may in principle violate this rule, those effects are usually small and hence violation of this rule should be also small. However, in the case of benzene (H,D)-isotopomers some violations of the harmonic approximation by the DFT scaled frequencies are as large as $\approx 26\,\mathrm{cm}^{-1}$ [8]. This almost certainly indicated scaled frequencies which are in error [8].

Concerning comparison with experiment, one finds that standard deviation of LRP frequencies from available experimental frequencies is on average $\Delta_{LRP} \approx 4.74\,\mathrm{cm}^{-1}$, while standard deviation of DFT scaled frequencies from the same experimental frequencies is on average $\Delta_{DFT} \approx 6.79\,\mathrm{cm}^{-1}$. This shows that DFT scaled frequencies based on frequency scaling are less reliable from LRP frequencies. Since DFT scaled frequencies based on force field scaling do not violate interlacing rule, such scaled frequencies are expected to have a better agreement with experimental frequencies. Unfortunately, those scaled frequencies were not available [13].

In the present paper vibrational isotope effect of out-of-plane vibrations of planar molecules was considered and illustrated with a particular example of benzene (H,D)-

isotopomers. However, LRP equally well applies to in plane vibrations of planar molecules as well as to vibrational isotope effect of arbitrary (non-planar) molecules. This includes not only (H,D)-, but all other possible isotopomers [7,8]. In all those cases LRP is computationally much simpler than DFT. For example, in the case of out-of-plane vibrations, LRP essentially involves solution of the $\rho \times \rho$ matrix Eq. 5a (where ρ is the number of isotope substitutions), while DFT involves solution of the $n \times n$ matrix Eq. 3a (where n is the number of all atoms in the isotopomer **B**). In addition, if one wants to improve DFT frequencies with scaling technique, one has to introduce one or several adjustable parameters (scaling factors). Of course, if one increases the number of such parameters one can improve agreement with experimental frequencies. However, such a technique is in principle not very clean, since those parameters have no clear theoretical basis. On the other hand, without any introduction of such or similar adjustable parameters, LRP frequencies agree with experimental frequencies (at least in the case considered) better than scaled DFT frequencies.

LRP provides a new conceptual insight into the regularities of the vibrational isotope effect in the harmonic approximation. Within the LRP formalism one can show that frequencies ω_k and vibrations $|\Psi_k\rangle$ of isotopomer **B** depend mainly on local properties involving region subject to the isotopic substitution. The only global properties needed to obtain frequencies and normal modes of the isotopomer **B** are frequencies ν_i of the parent molecule **A**. All remaining quantities refer to the region subject to the isotopic substitution: amplitudes $\langle \tau s | \Phi_i \rangle$ of the vibrations $|\Phi_i\rangle$ of the parent molecule **A** at the positions of isotopic substitutions and information about substituted isotopes τ, their coordinate positions (x_τ, y_τ, z_τ) and mass changes Δm_τ. There are also four apparently global quantities, molecular mass M and moments of inertia I_x, I_y and I_z of a parent molecule **A**. However, those quantities can be expressed in terms of the local properties: amplitudes $\langle \tau s | \Phi_{Tp} \rangle$ and $\langle \tau s | \Phi_{Rp} \rangle$ of non-proper vibrations $|\Phi_{Tp}\rangle$ and $|\Phi_{Rp}\rangle$ at any position subject to the isotopic substitution. Therefore frequencies ν_i of the parent molecule **A** remain as the only global properties required. No information about amplitudes $\langle \alpha s | \Phi_i \rangle$ of the vibrations $|\Phi_i\rangle$ at atoms α that are not substituted by an isotope is needed. Also no information about force field is needed. This shows that frequencies and vibrations of the isotopomer **B** do not depend on any fine details of molecular structure outside the region affected by the isotopic substitution. Huge amount of data which is usually needed in order to calculate vibrational isotope effect in a standard way, such as force field constants for the entire molecule, is hence redundant.

It is not important how frequencies ν_i and amplitudes $\langle \tau s | \Phi_i \rangle$ of the parent molecule **A** are obtained in the LRP approach. Those quantities can be obtained from some reliable independent theoretical calculation. But also, and more important, those quantities can be obtained from the experimental data alone. In the case of out-of-plane vibrations it is sufficient to know experimental frequencies of the parent molecule **A**, and few selected experimental frequencies of mono-substituted isotopomers $\mathbf{B}_\tau$. Those quantities are sufficient to reconstruct required vibrational amplitudes of the parent molecule **A**. In particular, in the case of vibrational isotope effect of out-of-plane vibrations of benzene isotopomers, it is sufficient to know six experimental out-of-plane d_0-benzene frequencies and only two experimental out of plane d_1-benzene frequencies. Those experimental quantities, in conjuncture with benzene geometry

and masses and positions of various possible isotopes, uniquely determine out-of-plane frequencies and corresponding vibrations of all benzene isotopomers. If one considers all possible isotopomers containing ^1H, ^2H, ^3H, ^{12}C, ^{13}C and ^{14}C isotopes, there are almost one hundred thousands of such benzene isotopomers. It is remarkable that frequencies and normal modes of all those isotopomers are completely determined (within the harmonic approximation) by so few experimental data.

In conclusion, LRP approach provides a new insight in the nature of the vibrational isotope effect in the harmonic approximation, it is conceptually and computationally simple, and in addition it produces (at least in the examples considered) better agreement with experimental frequencies then DFT improved with scaling technique.

Appendices

A Vibrational isotope effect in the harmonic approximation

In the harmonic approximation vibrations of a molecule **A** consisting of n atoms connected by harmonic forces can be described by the generalized eigenvalue equation 2a where **F** and **M** are force field and mass operators, respectively. If in the original molecule **A** some or all atoms are replaced by an isotope, to a very high degree of accuracy force field is not effected by those replacements [1,3,4]. In this approximation vibrations of the isotopomer **B** are described by the eigenvalue equation 3a where $\Delta\mathbf{M}$ represents isotope mass changes.

We will use Greek letters α and β in order to label different atoms, and indices s and p in order to denote x-, y- and z-coordinate directions. Using this convention operators **F** and **M** can be written in the form

$$\mathbf{F} = \sum_{\alpha\beta}^{n} \sum_{sp}^{3} f_{\alpha s,\beta p} \, |\alpha s\rangle \, \langle\beta p|, \quad \mathbf{M} = \sum_{\alpha}^{n} m_{\alpha} \sum_{s}^{3} |\alpha s\rangle \, \langle\alpha s|, \tag{A1a}$$

where $f_{\alpha s,\beta p}$ are force constants and where $|\alpha s\rangle$ are ket vectors which denote a unit displacement of α-th atom in the s-th coordinate direction. Those unit displacements are orthonormalized and complete in the molecular vibrational space X_{3n}

$$\langle\alpha s|\beta p\rangle = \delta_{\alpha\beta}\delta_{sp}, \quad \sum_{\alpha s} |\alpha s\rangle \, \langle\alpha s| = \mathbf{I}, \tag{A1b}$$

We will label atoms that are affected by isotope substitution with Greek letters μ and τ. If there are ρ such atoms, mass change operator $\Delta\mathbf{M}$ can be written in the form

$$\Delta\mathbf{M} = \sum_{\mu}^{\rho} \Delta m_{\mu} \sum_{s}^{3} |\mu s\rangle \, \langle\mu s|. \tag{A1c}$$

where Δm_μ is isotope mass change of atom μ. Accordingly, in a base $\{|\alpha s\rangle\}$ operator $\Delta \mathbf{M}$ effects only 3ρ base vectors $|\mu s\rangle$. Those vectors span a 3ρ dimensional isotope substitution space $X_{3\rho}^b$, subspace of a vibrational space X_{3n}. If $\rho < n$, which is usually the case, the space $X_{3\rho}^b$ can be substantially smaller than the space X_{3n}.

B LRP treatment of the vibrational isotope effect

Vibrational isotope effect can be efficiently treated within the formalism of the low rank perturbation (LRP) approach [5–7]. This is a general mathematical method which gives a solution of a system **B** in terms of a known solution to a "reference" system **A**. In general, the system **A** is described by the generalized eigenvalue equation

$$\mathbf{A}\,|\Phi_i\rangle = \lambda_i \mathbf{S}\,|\Phi_i\rangle , \tag{B1a}$$

while the system **B** is described by the generalized eigenvalue equation

$$\mathbf{B}\,|\Psi_k\rangle = \varepsilon_k \mathbf{C}\,|\Psi_k\rangle . \tag{B1b}$$

One can consider system **B** as "modified" system **A** where $\mathbf{B} = \mathbf{A} + \mathbf{V}$ and $\mathbf{C} = \mathbf{S} + \mathbf{P}$. The system **B** differs from the system **A** by the operators (**V**, **P**). Quantities **A**, **S**, **V** and **P** can be any operators. In particular, those operators are not necessarily Hermitian [5] and they can be also infinite dimensional [6]. The only restriction to the generality of the LRP approach is that the ranks of operators **V** and **P** which represent modification of the system **A** should be finite and preferably small. Hence the name "Low rank perturbation" (LRP) [5,6].

In the LRP approach the solution (eigenvalues ε_k and eigenstates $|\Psi_k\rangle$) of the system **B** are expressed in terms of the solution (eigenvalues λ_i and eigenstates $|\Phi_i\rangle$) of the system **A** [5–7]. In this respect LRP is similar to a standard perturbation expansion approach which also expresses each perturbed solution in terms of the (presumably known) unperturbed eigenstates and eigenvalues. However, unlike the standard perturbation approach, LRP does not rely on a power series expansion, and it produces correct results, however strong the "perturbation" (**V**, **P**). Numerical complexity of the LRP solution does not depend on the magnitude of this "perturbation", but rather on the ranks of the operators **V** and **P**. In particular, this numerical complexity is essentially independent on the dimension of the systems **A** and **B**. Hence one can with the LRP approach treat even infinite-dimensional [6] systems, as long as rank of the operator **V** as well as rank of the operator **P** is finite.

Expressions (2a) and (3a) describing vibrational isotope effect in the harmonic approximation are a special case of a general type of problems that can be treated by the LRP method. LRP solution of the perturbed system **B** described by eigenvalue equation 3a is given elsewhere [7,8] and only main results will be presented here.

Define $3\rho \times 3\rho$ Hermitian matrices $\mathbf{\Omega}(\varepsilon)$ and $\Delta \mathbf{M}$. Matrix $\mathbf{\Omega}(\varepsilon)$ depends on a real parameter ε and it has matrix elements

$$\mathbf{\Omega}_{\mu s, \tau p}(\varepsilon) = \sum_{i(\lambda_i \neq \varepsilon)}^{3n} \frac{\langle \mu s | \Phi_i \rangle \langle \Phi_i | \tau p \rangle}{\varepsilon - \lambda_i}, \quad \mu, \tau = 1, \ldots, \rho, \quad s, p = 1, 2, 3.$$

(B2a)

In this expression λ_i are eigenvalues of the eigenvalue equation 2a, while $|\Phi_i\rangle$ are the corresponding eigenstates orthonormalized according to (2b). The summation is performed over all i such that $\lambda_i \neq \varepsilon$. In particular, if $\varepsilon \notin \{\lambda_i\}$ this summation is performed over all $3n$ terms.

Matrix $\Delta \mathbf{M}$ is a representation of the mass change operator (A1c) in the base $\{|\mu s\rangle\}$ of the isotope substitution space $X_{3\rho}^b$. It has matrix elements

$$\Delta \mathbf{M}_{\mu s, \tau p} = \delta_{\mu \tau} \delta_{sp} \Delta m_\tau, \quad \mu, \tau = 1, \ldots, \rho, \quad s, p = 1, 2, 3. \quad \text{(B2b)}$$

Above we have used the same symbol $\Delta \mathbf{M}$ for the operator (A1c) as well as for the representation of this operator in the base $\{|\mu s\rangle\}$. Strictly, this is not allowed and one should use two different symbols for the operator $\Delta \mathbf{M}$ and for its representation in some basis. However, from the context it is usually always clear whether $\Delta \mathbf{M}$ refers to the operator or to its representation. Hence, with a due caution, one can use such slightly inaccurate notation.

In the LRP approach one distinguishes *cardinal* ($\varepsilon_k \notin \{\lambda_i\}$) and *singular* ($\varepsilon_k \in \{\lambda_i\}$) eigenvalues and eigenstates of the system **B** [6–8]. Concerning cardinal solutions one finds [7,8].

Theorem 1 (cardinal frequencies and vibrations) *Let (2a) be eigenvalue equation describing harmonic vibrations of a parent molecule* **A**. *Let further the corresponding vibrations* $|\Phi_i\rangle$ *be orthonormalized according to (2b). Then:*

(a) $\varepsilon_k \notin \{\lambda_j\}$ is (cardinal) eigenvalue of the isotope eigenvalue equation 3a describing isotopomer **B** if and only if $\varepsilon = \varepsilon_k$ satisfies matrix equation

$$\mathbf{H}(\varepsilon_k) \mathbf{C}^{(k)} = 0, \quad \text{(B3a)}$$

where $\mathbf{H}(\varepsilon)$ is a Hermitian matrix

$$\mathbf{H}(\varepsilon) \equiv \mathbf{\Omega}(\varepsilon) + \frac{\Delta \mathbf{M}^{-1}}{\varepsilon}, \quad \text{(B3b)}$$

In this expression $\Delta \mathbf{M}^{-1}$ is a $3\rho \times 3\rho$ diagonal matrix, inverse of a matrix $\Delta \mathbf{M}$. It has matrix elements

$$\Delta \mathbf{M}_{\mu s, \tau p}^{-1} = \frac{\delta_{\mu \tau} \delta_{sp}}{\Delta m_\tau}, \quad \mu, \tau = 1, \ldots, \rho, \quad s, p = 1, 2, 3. \quad \text{(B3c)}$$

Expression (B3a) has a nontrivial solution ($\mathbf{C}^{(k)} \neq 0$) if and only if determinant of the system vanishes. All cardinal eigenvalues $\varepsilon_k \notin \{\lambda_i\}$ of $\mathbf{B}$ are hence roots of a function $f(\varepsilon)$:

$$f(\varepsilon) \equiv |\mathbf{H}(\varepsilon)| = 0. \tag{B4}$$

where $|\mathbf{H}(\varepsilon)|$ is determinant of $\mathbf{H}(\varepsilon)$.

(b) Each vibration $|\Psi_k\rangle$ that corresponds to the eigenvalue $\varepsilon_k \notin \{\lambda_i\}$ of $\mathbf{B}$ is a linear combination

$$|\Psi_k\rangle = \sum_i^{3n} \frac{\sum_\tau^\rho \sum_p^3 \langle \Phi_i | \tau p \rangle C_{\tau p}^{(k)}}{\varepsilon_k - \lambda_i} |\Phi_i\rangle, \tag{B5a}$$

where the coefficients $C_{\tau p}^{(k)}$ are the components of a 3ρ-dimensional column vector $\mathbf{C}^{(k)}$, eigenvector of the matrix Eq. B3a.

(c) Coefficients $C_{\tau p}^{(k)}$ that determine vibration $|\Psi_k\rangle$ according to (B5a) satisfy [7,8]

$$C_{\tau p}^{(k)} = -\varepsilon_k \langle \tau p | \Delta \mathbf{M} | \Psi_k \rangle = -\varepsilon_k \Delta m_\tau \langle \tau p | \Psi_k \rangle,$$
$$\tau = 1, \ldots, \rho, \quad p = 1, 2, 3. \tag{B5b}$$

(d) Degeneracy of the eigenvalue $\varepsilon_k \notin \{\lambda_j\}$ of $\mathbf{B}$ equals the number of the linearly independent eigenvectors $\mathbf{C}^{(k)}$ of the matrix Eq. B3a. In other words, this degeneracy equals nullity of the matrix $\mathbf{H}(\varepsilon_k)$.

As far as cardinal eigenvalues and eigenstates are considered, LRP replaces eigenvalue equation 3a acting in the $3n$-dimensional vibration space X_{3n} with the (usually much simpler) matrix equation (B3) acting in the 3ρ-dimensional isotope substitution space $X_{3\rho}^b$.

Concerning singular solutions of the eigenvalue equation 3a one has the following

Theorem 2 (singular frequencies and vibrations) *Let λ_j be a η_j-degenerate eigenvalue of the parent molecule $\mathbf{A}$ and let $|\Phi_{jl}\rangle$ ($l = 1, \ldots, \eta_j$) be the corresponding vibrations orthonormalized according to (2b). Then*

(a) Eigenvalue $\varepsilon_k \equiv \lambda_j \in \{\lambda_i\}$ is (singular) eigenvalue of the isotopomer $\mathbf{B}$ if and only if it satisfies

$$\begin{bmatrix} \mathbf{H}(\lambda_j) & \mathbf{W}^{(j)}/\lambda_j \\ \mathbf{W}^{(j)^T}/\lambda_j & \mathbf{0} \end{bmatrix} \begin{pmatrix} \mathbf{C}^{(j)} \\ \mathbf{D}^{(j)} \end{pmatrix} = 0, \tag{B6a}$$

where $\mathbf{H}(\varepsilon)$ is a $3\rho \times 3\rho$ Hermitian matrix (B3b), $\mathbf{W}^{(j)}$ is a $3\rho \times \eta_j$ matrix with matrix elements

$$\mathbf{W}_{\tau s,l}^j = -\left\langle \tau s | \Delta \mathbf{M}^{-1} | \Phi_{jl} \right\rangle = -\frac{1}{\Delta m_\tau} \langle \tau s | \Phi_{jl} \rangle,$$
$$\tau = 1, \ldots, \rho, \quad s = 1, 2, 3, \quad l = 1, \ldots, \eta_j. \tag{B6b}$$

while $\mathbf{0}$ is a $\eta_j \times \eta_j$ null matrix. Further, $\mathbf{W}^{(j)T}$ is a transpose of $\mathbf{W}^{(j)}$. Equation B6a is hence Hermitian.

Since (B6a) has a nontrivial solution (either $\mathbf{C}^{(j)} \neq 0$ and/or $\mathbf{D}^{(j)} \neq 0$) if and only if determinant of this system vanishes, $\varepsilon_k \equiv \lambda_j$ is a singular eigenvalue of the eigenvalue equation 3a if and only if it satisfies $f(\lambda_j) = 0$ where

$$f(\lambda_j) \equiv \begin{vmatrix} \mathbf{H}(\lambda_j) & \mathbf{W}^{(j)}/\lambda_j \\ \mathbf{W}^{(j)T}/\lambda_j & 0 \end{vmatrix}. \tag{B7}$$

(b) Each vibration $|\Psi_k\rangle$ corresponding to the singular eigenvalue $\varepsilon_k \equiv \lambda_j$ is a linear combination

$$|\Psi_k\rangle = \sum_{i(\lambda_i \neq \lambda_j)}^{3n} \frac{\sum_\tau^\rho \sum_s^3 \langle \Phi_i | \tau s \rangle C_{\tau s}^{(j)}}{\varepsilon_k - \lambda_i} |\Phi_i\rangle + \sum_l^{\eta_j} D_l^{(j)} |\Phi_{jl}\rangle, \tag{B8a}$$

where the coefficients $C_{\tau s}^{(j)}$ are components of a 3ρ column vector $\mathbf{C}^{(j)}$, where coefficients $D_l^{(j)}$ are components of a η_j column vector $\mathbf{D}^{(j)}$, and where those vectors satisfy (B6a).

(c) Coefficients $C_{\tau s}^{(j)}$ and $D_l^{(j)}$ that determine singular vibration $|\Psi_k\rangle$ according to (B8a) satisfy

$$C_{\tau s}^{(j)} = -\varepsilon_k \langle \tau s | \Delta \mathbf{M} | \Psi_k \rangle = -\varepsilon_k \Delta m_\tau \langle \tau s | \Psi_k \rangle, \qquad D_l^{(j)} = \langle \Phi_{jl} | \mathbf{M} | \Psi_k \rangle,$$
$$\tau = 1, \ldots, \rho, \quad s = 1, 2, 3, \quad l = 1, \ldots, \eta_j. \tag{B8b}$$

In the original LRP treatment of the vibrational isotope effect two kinds of singular eigenvalues were considered, *active* and *passive* [8]. By definition, singular eigenvalue $\varepsilon_k \equiv \lambda_j$ is *passive* if all amplitudes $\langle \tau s | \Phi_{jl} \rangle$ ($l = 1, \ldots, \eta_j$) vanish on all sites τ subject to the isotopic substitution. Otherwise it is *active*. In other words, $\varepsilon_k \equiv \lambda_j$ is passive if and only if no vibration $|\Phi_{jl}\rangle$ ($l = 1, \ldots, \eta_j$) has a component in the isotope substitution space $X_{3\rho}^b$. Accordingly, all those vibrations are in the nullspace of the operator $\Delta \mathbf{M}$:

$$\Delta \mathbf{M} |\Phi_{jl}\rangle = 0, \quad l = 1, \ldots, \eta_j. \tag{B9}$$

Passive eigenvalue is an exotic theoretical possibility which is extremely unlikely. More in line with a general LRP approach and more convenient is to distinguish *strongly singular* and *weakly singular* vibrations [7,8]. By definition, vibration $|\Psi_k\rangle$ is *strongly singular* if $\mathbf{C}^{(j)} = 0$, otherwise it is weakly singular. Expressions (B8b) imply that strongly singular vibrations have no component in the vibrational isotope space $X_{3\rho}^b$, while each weakly singular vibration has at least one nonzero component in this space.

According to Theorem 2, each strongly singular vibration $|\Psi_k\rangle$ associated with the eigenvalue $\varepsilon_k \equiv \lambda_j$ is a linear combination

$$|\Psi_k\rangle = \sum_{l}^{\eta_j} D_l^{(j)} |\Phi_{jl}\rangle, \qquad \text{(B10a)}$$

where the coefficients $D_l^{(j)}$ are components of a vector $\mathbf{D}^{(j)}$, nontrivial solution of the matrix equation

$$\mathbf{W}^{(j)}\mathbf{D}^{(j)} = 0, \qquad \text{(B10b)}$$

This equation is much simpler than the original Eq. B6a. Using (B6b) this equation can be written in the explicit form

$$\sum_{l}^{\eta_j} \langle \mu s | \Phi_{jl} \rangle D_l^{(j)} = 0, \quad \mu = 1, \ldots, \rho, \quad s = 1, 2, 3. \qquad \text{(B10c)}$$

This is a set of 3ρ homogenous linear equations in η_j unknowns $D_l^{(j)}$. Hence if $\eta_j > 3\rho$, isotopomer **B** has at least $\eta_j - 3\rho$ strongly singular vibrations with the eigenvalue $\varepsilon_k \equiv \lambda_j$. An extreme case is the case when $\varepsilon_k = \lambda_j$ is passive. In this case all matrix elements $\langle \mu s | \Phi_{jl} \rangle$ in (B10c) vanish and one has maximum number of η_j strongly singular eigenstates. However, this is a very unlikely possibility, and unless isotopomer **B** has some appropriate symmetry, if $\eta_j \leq 3\rho$ this isotopomer has usually no strongly singular vibration with the eigenvalue $\varepsilon_k = \lambda_j$.

As emphasized above, each strongly singular vibration $|\Psi_k\rangle$ satisfies $\langle \tau s | \Psi_k \rangle = 0$ for each $|\tau s\rangle \in X_{3\rho}^b$. Hence no atom subject to the isotopic substitution participates in the strongly singular vibration.

According to (B10a), each strongly singular vibration of the isotopomer **B** is a linear combination of those vibrations $|\Phi_{jl}\rangle$ of the parent molecule **A** that correspond to the same (usually degenerate) frequency ν_j.

Consider now weakly singular vibrations that satisfy $\mathbf{C}^{(j)} \neq 0$. According to theorem 2, each such vibration is a linear combination (B8a) where vectors $\mathbf{C}^{(j)}$ and $\mathbf{D}^{(j)}$ satisfy:

$$\mathbf{W}^{(j)T}\mathbf{C}^{(j)} = 0, \quad \mathbf{H}(\lambda_j)\mathbf{C}^{(j)} + \frac{\mathbf{W}^{(j)}}{\lambda_j}\mathbf{D}^{(j)} = 0, \quad \mathbf{C}^{(j)} \neq 0. \qquad \text{(B11)}$$

First expression in (B11) is a set of η_j homogenous linear equations in 3ρ unknowns $C_{\tau p}^{(j)}$, while second expression in (B11) is a set of 3ρ homogenous linear equations in $(3\rho + \eta_j)$ unknowns; 3ρ coefficients $C_{\tau p}^{(j)}$ and η_j coefficients $D_l^{(j)}$. Accordingly, one has $3\rho + \eta_j$ unknowns and $3\rho + \eta_j$ homogenous linear equations. There are additional two conditions on those unknowns: First, there is a condition $\mathbf{C}^{(j)} \neq 0$ which excludes trivial solutions to $\mathbf{W}^{(j)T}\mathbf{C}^{(j)} = 0$. Second, each weakly singular vibration should

be orthogonal to all strongly singular vibrations. Those orthogonality requirements result in additional constrains on the coefficients $D_l^{(j)}$. In view of so many conditions on the linear expressions (B11), it is highly unlikely for those expressions to have any nontrivial solution. Only exceptionally isotopomer **B** can have a weakly singular vibration. This is also evident from a physical point of view. Since $\mathbf{C}^{(j)} \neq 0$ and due to (B8b), each weakly singular vibration has a non-vanishing component on at least one atom involved in the isotopic substitution. It is highly unlikely that the presence of this atom which participates in the vibration of isotopomer **B** will effect the frequency of this vibration exactly in such a way that modified frequency ε_k coincides with some frequency λ_i of a parent molecule **A**.

According to the expressions (B5a) and (B8a), each vibration $|\Psi_k\rangle$ of isotopomer **B** is expressed as a linear combination of vibrations $|\Phi_i\rangle$ of the parent molecule **A**. Note further that the original Eq. 3a is a $3n \times 3n$ eigenvalue equation, while LRP Eq. B3a that produces cardinal vibrations of (3a) is a $3\rho \times 3\rho$ eigenvalue equation. Concerning singular vibrations, most important are strongly singular vibrations which are obtained according to expressions (B10). In particular, expression (B10c) is a set of η_j homogenous linear equations where η_j is degeneracy of the unperturbed eigenvalue λ_j. This is trivial to solve, especially if η_j is relatively small, which is usually the case. Since in most cases $\rho \ll n$, LRP approach presents a substantial reduction in the computational load.

C Non-proper vibrations

Theorems 1 and 2 are valid provided vibrations $|\Phi_i\rangle$ of the parent molecule **A** are orthonormalized according to (2b). If two such vibrations have different frequencies, they are automatically orthogonal to each other, and one has only to normalize these vibrations, which is trivial. The problem is more complex if some of those vibrations are degenerate, since degenerate vibrations are not automatically orthogonal to each other. In this case one has to choose such linear combinations of degenerate vibrations, which satisfy orthogonality relations (2b). In general, it is not known in advance which vibrations will be degenerate, and this depends on a particular problem. However, there are always six (in the case of nonlinear molecules) or five (in the case of linear molecules) non-proper vibrations which are degenerate and which correspond to the eigenvalue $\lambda_0 = 0$ and frequency $\nu_0 = 0$. These non-proper vibrations describe three translation and three (two) rotations.

Denote the three non-proper vibrations which describe translations in the x-, y- and z-direction with $|\Phi_{Ts}\rangle$ ($s = 1, 2, 3$) and the three non-proper vibrations which describe rotations around x-, y- and z-axis with $|\Phi_{Rs}\rangle$ ($s = 1, 2, 3$). Normalized non-proper vibrations $|\Phi_{Ts}\rangle$ (translations) are [7]:

$$|\Phi_{Ts}\rangle = \frac{1}{\sqrt{M}} \sum_{\alpha}^{n} |\alpha s\rangle, \quad s = 1, 2, 3, \tag{C1a}$$

while normalized non-proper vibration $|\Phi_{R3}\rangle \equiv |\Phi_{Rz}\rangle$ (rotation around z-axis) is

$$|\Phi_{Rz}\rangle = \frac{1}{\sqrt{I_z}} \sum_\alpha^n [x_\alpha |\alpha y\rangle - y_\alpha |\alpha x\rangle], \tag{C1b}$$

and cyclically for the remaining two non-proper vibrations $|\Phi_{R1}\rangle \equiv |\Phi_{Rx}\rangle$ and $|\Phi_{R2}\rangle \equiv |\Phi_{Ry}\rangle$. In the above expressions $M = \sum_\alpha m_\alpha$ is a molecular mass of molecule **A**, I_z is a moment of inertia of this molecule around z-th coordinate axis, while x_α and y_α are x- and y-coordinates of atom α, respectively.

Non-proper vibrations (C1) are normalized. However, those vibrations are in general not mutually orthogonal. Concerning mutual orthogonality of those vibrations one has [7].

Lemma 1 *Let the origin of the coordinate system be in the centre of mass of a molecule* **A***, and let coordinate axis coincide with the principal axis of this molecule. In this case non-proper vibrations (C1) satisfy orthonormality relations (2b):*

$$\begin{aligned}
\langle\Phi_{Ts}|\mathbf{M}\,|\Phi_{Tp}\rangle &= \langle\Phi_{Rs}|\mathbf{M}\,|\Phi_{Rp}\rangle = \delta_{sp}, \\
\langle\Phi_{Ts}|\mathbf{M}\,|\Phi_{Rp}\rangle &= 0, \quad s, p = 1, 2, 3.
\end{aligned} \tag{C2a}$$

In this paper we assume that besides translations and rotations there are no other non-proper vibrations. In other words, there are no such modes as free rotation around some molecular axis, etc. If this is the case and if the molecule is nonlinear (most important case) it has exactly $3n - 6$ proper vibrations $|\Phi_i\rangle$ and six non-proper vibrations $|\Phi_{Ts}\rangle$ and $|\Phi_{Rs}\rangle$ ($s = 1, 2, 3$). Since all proper vibrations $|\Phi_i\rangle$ have nonzero frequency, they are automatically orthogonal to all non-proper vibrations:

$$\langle\Phi_{Ts}|\mathbf{M}\,|\Phi_i\rangle = \langle\Phi_{Rs}|\mathbf{M}\,|\Phi_i\rangle = 0, \quad i = 1, \ldots, 3n - 6, \quad s = 1, 2, 3. \tag{C2b}$$

Using (C1), expression (B5a) for the cardinal vibration $|\Psi_k\rangle$ can be written in a more explicit form

$$\begin{aligned}
|\Psi_k\rangle = \frac{1}{\varepsilon_k} &\left[\sum_s^3 T_s^{(k)} |\Phi_{Ts}\rangle + \sum_s^3 R_s^{(k)} |\Phi_{Rs}\rangle \right] \\
&+ \sum_i^{3n-6} \frac{\sum_\tau^\rho \sum_s^3 \langle\Phi_i|\tau s\rangle\, C_{\tau s}^{(k)}}{\varepsilon_k - \lambda_i} |\Phi_i\rangle,
\end{aligned} \tag{C3a}$$

where the coefficients $T_s^{(k)}$ and $R_x^{(k)}$ are

$$T_s^{(k)} = \frac{1}{\sqrt{M}} \sum_\tau^\rho C_{\tau s}^{(k)}, \quad R_x^{(k)} = \frac{1}{\sqrt{I_x}} \sum_\tau^\rho \left[y_\tau C_{\tau z}^{(k)} - z_\tau C_{\tau y}^{(k)} \right]. \tag{C3b}$$

Remaining two coefficients $R_y^{(k)}$ and $R_z^{(k)}$ are obtained cyclically from the coefficient $R_x^{(k)}$.

In the same way matrix elements (B2a) can be written in the explicit form

$$\mathbf{\Omega}_{\mu x, \tau x}(\varepsilon) = \frac{1}{\varepsilon}\left[\frac{1}{M} + \frac{y_\mu y_\tau}{I_z} + \frac{z_\mu z_\tau}{I_y}\right] + \sum_{i(\lambda_i \neq \varepsilon)}^{3n-6} \frac{\langle \mu x | \Phi_i \rangle \langle \Phi_i | \tau x \rangle}{\varepsilon - \lambda_i}, \quad \text{(C4a)}$$

$$\mathbf{\Omega}_{\mu x, \tau y}(\varepsilon) = -\frac{x_\tau y_\mu}{\varepsilon I_z} + \sum_{i(\lambda_i \neq \varepsilon)}^{3n-6} \frac{\langle \mu x | \Phi_i \rangle \langle \Phi_i | \tau y \rangle}{\varepsilon - \lambda_i}. \quad \text{(C4b)}$$

Remaining matrix elements $\mathbf{\Omega}_{\mu y, \tau y}$, $\mathbf{\Omega}_{\mu z, \tau z}$, $\mathbf{\Omega}_{\mu y, \tau z}$ and $\mathbf{\Omega}_{\mu z, \tau x}$ are obtained by a cyclic substitution in expressions (C4).

Note that vibrations (C3) are not normalized. This can be easily done using orthonormality (2b) and matrix elements

$$\langle \Phi_i | \Delta \mathbf{M} | \Phi_j \rangle = \sum_\mu^\rho \Delta m_\mu \sum_s^3 \langle \Phi_i | \mu s \rangle \langle \mu s | \Phi_j \rangle. \quad \text{(C5)}$$

All quantities in this expression refer to the region subject to the isotopic substitution. Accordingly, in order to normalize vibrations (C3) no specific information about molecules **A** and **B** outside the region subject to the isotopic substitution is needed.

Concerning singular solutions, as emphasized above most important are strongly singular vibrations. Each such vibration is a linear combination (B10a) which contains no non-proper vibration (C1). This also follows from physical reasons. Since strongly singular vibration has no component in the isotope substitution space $X_{3\rho}^b$, there is no need to compensate for the introduction of isotopes in the parent molecule **A** by inclusion of non-proper vibrations. Strongly singular vibration $|\Psi_k\rangle$ of isotopomer **B** is hence at the same time vibration of the parent molecule **A**. Since each strongly singular vibration has no component on the isotopic substitution space $X_{3\rho}^b$, normalization of those vibrations is trivial.

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