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Local mode and normal mode models for molecules with two non equivalent C–H bonds

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For molecules with C–H bonds, a local mode description of the bonds is often adopted to interpret the C–H stretching overtone spectra, although a representation in terms of normal mode is also possible. Equivalence between the two alternative representations demands simple numerical equations between the normal mode anharmonicity constants x_{rs} and the quartic anharmonic coupling constants K_{rstu} , the so-called “ x - K relations”. The relations appropriate to low symmetry molecules with two non-equivalent C–H bonds (ν_1 , ν_2), such as XHC=CHY, are derived in this paper. The consequences of these relations are illustrated with a detailed analysis of the C–H stretching overtone region, where the naive application of the relations obtained for more symmetric molecules could lead to a different interpretation of the overtones $2\nu_1$, $2\nu_2$ and of the combination band $\nu_1 + \nu_2$. The relations are tested with theoretical calculations for difluoro- and chlorofluoro-substituted ethenes, propadiene, and butatrienes.

Keywords: local mode; normal mode; Morse oscillators; quartic anharmonic interactions; Darling-Dennison interactions; C–H overtones

1 Introduction

As discussed in several reviews [1–4] two apparently different models are available for the treatment of C–H stretching (and also N–H, O–H, S–H ...) in polyatomic molecules: the local mode and the normal mode descriptions. In the local mode approach [2–5] the stretching vibrations are described in terms of anharmonic oscillators localized on individual C–H bonds, with harmonic interbond coupling. In the complementary normal mode approach [1,3] the stretching vibrations are represented as harmonic oscillators, the normal modes, coupled by quartic anharmonic interactions.

On the basis of perturbative treatments [1] and numerical computations for several molecules [6], Mills and co-workers suggested that the two treatments should always yield identical results if proper relations are imposed between the parameters of the two model Hamiltonians. The exact mathematical equivalence of the two approaches was soon proved by transforming the operators appearing in the Hamiltonian, first by Lehmann [7] for molecules with two equivalent C–H bonds and later by one of us [8] for any number of equivalent bonds. In this paper we extend the treatment to molecules with non equivalent C–H bonds and discuss in detail the case with two bonds.

2 Local mode and normal mode Hamiltonians

The local mode Hamiltonian for the stretching vibrations [1,3,6] is a sum of single bond contributions H_α plus pair interactions between different bonds $H_{\alpha\beta}$, $H_{\text{local}} = \sum_\alpha H_\alpha + \sum_{\alpha \neq \beta} H_{\alpha\beta}$, where the sums are on all bonds. The single bond Hamiltonians H_α are modeled in terms of Morse oscillators. Their eigenfunctions $|n_\alpha\rangle$, $n_\alpha = 0, 1, 2, \dots$, describe states with n_α vibrational quanta localized on the bond α ,

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and their eigenvalues E_α are given by the Morse expression [1], $E_\alpha = \omega_\alpha n_\alpha + x_\alpha n_\alpha(n_\alpha + 1)$. Here the parameters ω_α and x_α represent the harmonic frequency and anharmonicity of the bond. The matrix elements of the interbond interaction $H_{\alpha\beta}$ are identical to those appropriate to a harmonic model with a quadratic coupling [2, 5], $\langle n_\alpha + 1 | n_\beta - 1 | H | n_\alpha n_\beta \rangle = \lambda_{\alpha\beta} \sqrt{n_\alpha + 1} \sqrt{n_\beta}$, where $\lambda_{\alpha\beta} = \lambda_{\beta\alpha}$ is a non-negative parameter. Due to the form of the matrix elements, all interactions are effectively restricted within stretching overtone manifolds with a constant total vibrational population $n = \sum_\alpha n_\alpha$.

As discussed elsewhere [8], the local mode Hamiltonian is most compactly expressed in terms of operators a_α^\dagger and a_α , defined to add or remove vibrational quanta from the bond α with the same effects as the familiar creation and annihilation operators for the harmonic oscillators:

$$\begin{aligned} a_\alpha^\dagger |n_\alpha\rangle &= \sqrt{n_\alpha + 1} |n_\alpha + 1\rangle \\ a_\alpha |n_\alpha\rangle &= \sqrt{n_\alpha} |n_\alpha - 1\rangle \end{aligned}$$

The other usual properties of the operators follow automatically from their definition. In particular, it may be readily shown that the two operators are mutually adjoint, that they satisfy the boson commutation rules $[a_\alpha, a_\beta^\dagger] = \delta_{\alpha\beta}$, where $\delta_{\alpha\beta}$ is the Kronecker delta, and that the vibrational population n_α may be expressed as the operator $n_\alpha = a_\alpha^\dagger a_\alpha$. The local mode Hamiltonian, designed to yield the same matrix elements as the original H_{local} , is

$$H_{\text{local}} = \sum_\alpha \omega_\alpha a_\alpha^\dagger a_\alpha + \sum_\alpha x_\alpha a_\alpha^\dagger a_\alpha (a_\alpha^\dagger a_\alpha + 1) + \sum_{\alpha \neq \beta} \lambda_{\alpha\beta} a_\alpha^\dagger a_\beta$$

Since the two Hamiltonians have the same matrix elements between all vectors of the basis $|n_\alpha n_\beta \dots\rangle = |n_\alpha\rangle |n_\beta\rangle \dots$, they coincide. The Hamiltonian H_{local} may be expressed more compactly by using the commutation rule $a_\alpha a_\alpha^\dagger = a_\alpha^\dagger a_\alpha + 1$ to reduce the anharmonic term $a_\alpha^\dagger a_\alpha (a_\alpha^\dagger a_\alpha + 1)$ to normal order (all creation operators on the left) and by defining the diagonal coupling $\lambda_{\alpha\alpha}$ as $\lambda_{\alpha\alpha} = \omega_\alpha + 2x_\alpha$, yielding

$$H_{\text{local}} = \sum_{\alpha\beta} \lambda_{\alpha\beta} a_\alpha^\dagger a_\beta + \sum_\alpha x_\alpha a_\alpha^\dagger a_\alpha^\dagger a_\alpha a_\alpha$$

The Hamiltonian contains diagonal and non-diagonal quadratic terms $\lambda_{\alpha\beta} a_\alpha^\dagger a_\beta$, together with purely diagonal quartic terms $x_\alpha a_\alpha^\dagger a_\alpha^\dagger a_\alpha a_\alpha$. Since the matrix $\lambda = (\lambda_{\alpha\beta})$ is Hermitian, we may always find a transformation $\mathbf{D}^\dagger \lambda \mathbf{D}$ which diagonalizes the quadratic part, possibly at the cost of introducing non-diagonal quartic terms. Here \mathbf{D} is a unitary matrix (i.e. its inverse \mathbf{D}^{-1} is identical to its conjugate transpose \mathbf{D}^\dagger) to be determined. We use the matrix $\mathbf{D} = (D_{\alpha r})$ to introduce new operators A_r^\dagger and A_r , implicitly defined by $a_\alpha = \sum_r D_{\alpha r} A_r$ and $a_\alpha^\dagger = \sum_r D_{\alpha r}^* A_r^\dagger$, where the asterisk indicates the complex conjugate. Since \mathbf{D} is unitary, we may directly invert the definitions, obtaining explicit expressions $A_r = \sum_\alpha D_{\alpha r}^* a_\alpha$ and $A_r^\dagger = \sum_\alpha D_{\alpha r} a_\alpha^\dagger$. From these expressions it may be shown that the operators A_r^\dagger and A_r also satisfy boson commutation rules and, as a consequence [9], they behave as creation and annihilation operators. While a_α^\dagger and a_α act on states $|n_\alpha\rangle$ describing excitations localized on single bonds, A_r and A_r^\dagger act on states $|v_r\rangle$ describing vibrations delocalized on all bonds. To avoid ambiguities, we use lower case letters and greek labels for local operators, and upper-case letters and roman labels for non-local operators. Using the definition for a_α and a_α^\dagger in terms of the new non-local operators A_r and A_r^\dagger , we find a transformed Hamiltonian H_{normal} ,

$$H_{\text{normal}} = \sum_{rs} \nu_{rs} A_r^\dagger A_s + \sum_{rstu} X_{rstu} A_r^\dagger A_s^\dagger A_t A_u$$

where ν_{rs} and X_{rstu} are combinations of $D_{\alpha r}$ coefficients:

$$\begin{aligned}\nu_{rs} &= \sum_{\alpha\beta} \lambda_{\alpha\beta} D_{\alpha r}^* D_{\beta s} \\ X_{rstu} &= \sum_{\alpha} x_{\alpha} D_{\alpha r}^* D_{\alpha s}^* D_{\alpha t} D_{\alpha u}\end{aligned}$$

The number of terms in the unrestricted sums \sum_{rs} and \sum_{rstu} may be reduced by remembering that ν_{rs} has been diagonalized with a suitable choice of the matrix \mathbf{D} and by considering that the quartic term in H_{normal} is symmetric for exchanges of r,s or t,u indexes. By restricting the sums and introducing counting factors one obtains

$$H_{\text{normal}} = \sum_r \nu_{rr} A_r^\dagger A_r + \sum_{r \leq s, t \leq u} (2 - \delta_{rs}) (2 - \delta_{tu}) X_{rstu} A_r^\dagger A_s^\dagger A_t A_u$$

where, to account for the number of possible exchanges, X_{rstu} is multiplied by a factor 1 when $r = s$ and $t = u$, 2 when one of the pairs differs, or 4 when both pairs differ.

The Hamiltonian H_{normal} is most naturally expressed in the normal mode basis $|v_1 v_2 \dots\rangle$ which diagonalizes the quadratic Hamiltonian. With this choice, as described elsewhere [8] and as shown below, the matrix elements of H_{normal} become identical to those of a Hamiltonian describing harmonic normal modes with fundamental transition frequencies $\nu_r = \nu_{rr}$ and with quartic anharmonic interactions.

The “ x - K ” relations between the local mode and the normal mode Hamiltonians may be obtained by matching the coefficients in H_{normal} with those of the standard normal mode expressions from the literature [1, 10, 11]. The diagonal part H'_{normal} of H_{normal} , which involves only paired operators $A_r^\dagger A_r$ and $A_s^\dagger A_s$ and thus contains all quadratic terms and the quartic terms $A_r^\dagger A_r^\dagger A_r A_r$ and $A_r^\dagger A_s^\dagger A_r A_s$, may be written in terms of the number operators $v_r = A_r^\dagger A_r$ as

$$H'_{\text{normal}} = \sum_r \nu_r v_r + \sum_r X_{rrrr} v_r (v_r - 1) + \sum_{r < s} 4X_{rsrs} v_r v_s.$$

The corresponding literature expression [1] for the unperturbed energy of the normal mode state $|v_1 v_2 \dots\rangle$ is

$$E = \sum_r \omega_r \left(v_r + \frac{1}{2} \right) + \sum_r x_{rr} \left(v_r + \frac{1}{2} \right)^2 + \sum_{r < s} x_{rs} \left(v_r + \frac{1}{2} \right) \left(v_s + \frac{1}{2} \right).$$

It may be easily verified that the transition frequency $E - E_{\text{GS}}$ from the ground state (GS) to $|v_1 v_2 \dots\rangle$ becomes identical to H'_{normal} by imposing $x_{rr} = X_{rrrr}$, $x_{rs} = 4X_{rsrs}$ and $\omega_r = \nu_r - \sum_s 2X_{rsrs}$ or, equivalently, $\nu_r = \omega_r + 2x_{rr} + \sum_{s \neq r} x_{rs}/2$.

The off-diagonal part H''_{normal} contains all terms of the quartic Hamiltonian not already included in H'_{normal} . The corresponding interactions in the normal mode literature are described by coupling constants K_{rstu} , which are best defined [10] as coefficients of the quartic term $\sum_{r < s \leq t \leq u} K_{rstu} Q_r Q_s Q_t Q_u$ in the expansion of the Hamiltonian H_{normal} in power series of the normal coordinates Q_r . The coordinates Q_r have matrix elements $\langle n_r - 1 | Q_r | n_r \rangle = \langle n_r | Q_r | n_r - 1 \rangle = \sqrt{n_r/2}$, which correspond to $Q_r = (A_r^\dagger + A_r)/\sqrt{2}$. Matrix elements identical to those of H''_{normal} , within stretching overtone manifolds with constant $n = \sum_r v_r$, are easily obtained by imposing $K_{rstu}/4 = (2 - \delta_{rs})(2 - \delta_{tu}) X_{rstu}$. Five essentially distinct types of off-diagonal terms are thus found. Their matrix elements, mostly reported in Table 1 of Ref. [8], match those found in the normal mode literature [1, 6, 11].

3 Case with two bonds only

We now analyse the case in which there are only two C–H bonds, which may be equivalent or non-equivalent, as it happens for dihalogenoethenes such as FHC=CHF or ClHC=CHF, respectively. The local mode

Hamiltonian, explicitly written in terms of creation and annihilation operators acting on the two bonds α and β , is $H_{\text{local}} = H_{\alpha} + H_{\beta} + H_{\alpha\beta}$, where $H_{\alpha} = \lambda_{\alpha\alpha} a_{\alpha}^{\dagger} a_{\alpha} + x_{\alpha} a_{\alpha}^{\dagger} a_{\alpha}^{\dagger} a_{\alpha} a_{\alpha}$, $H_{\beta} = \lambda_{\beta\beta} a_{\beta}^{\dagger} a_{\beta} + x_{\beta} a_{\beta}^{\dagger} a_{\beta}^{\dagger} a_{\beta} a_{\beta}$ and $H_{\alpha\beta} = \lambda_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta} + \lambda_{\beta\alpha} a_{\beta}^{\dagger} a_{\alpha}$. The coefficients $\lambda_{\alpha\alpha} = \omega_{\alpha} + 2x_{\alpha}$ and $\lambda_{\beta\beta} = \omega_{\beta} + 2x_{\beta}$ are the diagonal coupling for the two bonds, x_{α} and x_{β} represent the anharmonicity of the bonds, and $\lambda_{\alpha\beta} = \lambda_{\beta\alpha}$ is the inter-bond coupling parameter. In this simple 2-dimensional case, the 2×2 unitary matrix \mathbf{D} may be written as a function of a single parameter, the mixing angle ϕ :

$$\mathbf{D} = \begin{pmatrix} \cos \phi & -\sin \phi \\ \sin \phi & \cos \phi \end{pmatrix}$$

After substitution, the off-diagonal harmonic normal mode coupling $\nu_{12} = \nu_{21}$ becomes

$$\begin{aligned} \nu_{12} &= \cos^2 \phi \lambda_{\alpha\beta} - \sin^2 \phi \lambda_{\beta\alpha} - \cos \phi \sin \phi \lambda_{\alpha\alpha} + \cos \phi \sin \phi \lambda_{\beta\beta} \\ &= \cos 2\phi \lambda_{\alpha\beta} - \frac{1}{2} \sin 2\phi (\lambda_{\alpha\alpha} - \lambda_{\beta\beta}) \end{aligned}$$

where we have used the trigonometric identities $\cos^2 \phi - \sin^2 \phi = \cos 2\phi$ and $\cos \phi \sin \phi = \frac{1}{2} \sin 2\phi$. The off-diagonal harmonic coupling ν_{12} may be canceled with a suitable choice of ϕ . This is achieved by requiring $\tan 2\phi = 2\lambda_{\alpha\beta}/(\lambda_{\alpha\alpha} - \lambda_{\beta\beta})$, where ϕ may be chosen as non-negative by imposing $\lambda_{\alpha\alpha} \geq \lambda_{\beta\beta}$. Once determined ϕ , substitution back in the quadratic Hamiltonian yields the fundamental frequencies ν_1 and ν_2 , reported in Table 1. When ν_1 and ν_2 are already known, as it often happens, it may be useful to use the inverse relations, obtaining the harmonic couplings as $\lambda_{\alpha\alpha} = \bar{\nu} + \Delta\nu \cos 2\phi$, $\lambda_{\beta\beta} = \bar{\nu} - \Delta\nu \cos 2\phi$ and $\lambda_{\alpha\beta} = \Delta\nu \sin 2\phi$, where $\bar{\nu} = (\nu_1 + \nu_2)/2$ and $\Delta\nu = (\nu_1 - \nu_2)/2$.

Substitution in the quartic Hamiltonian yields five distinct X_{rstu} coefficient, namely X_{1111} , X_{2222} , $X_{1212} = X_{1122} = X_{2211}$, $X_{1112} = X_{1211}$ and $X_{1222} = X_{2212}$, all reported in Table 1 as a function of the mixing angle ϕ . In the Table we also list all terms of the normal mode Hamiltonian H_{normal} , along with their non-zero matrix elements in the normal mode basis $|v_1 v_2\rangle$. The Hamiltonian has two quadratic terms, both diagonal, and nine quartic terms, three of which diagonal.

For symmetric molecules with two equivalent C–H bonds, having $\omega_{\alpha} = \omega_{\beta} = \omega$ and $x_{\alpha} = x_{\beta} = x$, we find $\tan 2\phi = +\infty$ and thus $\phi = \pi/4$. For low symmetry molecules with non equivalent bonds, the mixing angle ϕ may assume any value and the lowered symmetry does no longer requires $x_{\alpha} = x_{\beta}$. To simplify the discussion, we temporarily assume that the two bonds have the same anharmonicity, $x_{\alpha} = x_{\beta} = x$. In Fig. 1 we display, as a function of ϕ , the essentially distinct coupling coefficients $X_{1111} = X_{2222} = x(\cos^4 \phi + \sin^4 \phi)$, $X_{1212} = 2x \cos^2 \phi \sin^2 \phi$, $X_{1112} = x \cos \phi \sin \phi (\sin^2 \phi - \cos^2 \phi)$, and $X_{1222} = x \cos \phi \sin \phi (\cos^2 \phi - \sin^2 \phi)$. As shown by Fig. 1 and as easily verified, $X_{1111} = x_{11}$ and $X_{1212} = x_{12}/4$ are inversely correlated, since their sum is constant: $X_{1111} + X_{1212} = x$. The same holds for $X_{1112} = K_{1112}/8$ and $X_{1222} = K_{1222}/8$, since $X_{1112} + X_{1222} = 0$.

By examining Fig. 1 and by inspection of the ν_r and X_{rstu} coefficients listed in Table 1, we can identify three limit cases, with $\phi = 0$, $\pi/4$ and $\pi/8$:

$\phi = 0$: In this case the interbond coupling $\lambda_{\alpha\beta}$ is zero and all off-diagonal quartic matrix elements also vanish.

We have independent vibrations on the two bonds, corresponding to a pure local mode model.

$\phi = \pi/4$: This is the previously mentioned case of two equivalent C–H bonds, with $\lambda_{\alpha\alpha} = \lambda_{\beta\beta} = \lambda = \omega + 2x$. The two normal modes describe symmetric and antisymmetric combinations of the two C–H bond stretchings, with the two usual eigenvalues $\nu_1 = \lambda + \lambda_{\alpha\beta}$ and $\nu_2 = \lambda - \lambda_{\alpha\beta}$. We also obtain $X_{1111} = X_{2222} = X_{1212} = X_{1122} = x/2$, which correspond to the usual “ x - K ” relations [1] $x_{11} = x_{22} = x_{12}/4 = K_{1122}/4 = x/2$. Finally, we find $X_{1112} = X_{2212} = 0$, which is to be expected. In fact, since the two normal modes ν_1 and ν_2 belong to different irreducible representations, Hamiltonian terms involving odd numbers of operators acting on either modes vanish.

$\phi = \pi/8$: In this limit case, with $\lambda_{\alpha\beta} = (\lambda_{\alpha\alpha} - \lambda_{\beta\beta})/2$, the off-diagonal matrix elements of the form $\langle v_1 \pm 1 v_2 \mp 1 | H | v_1 v_2 \rangle$ assume their extremal values. These matrix elements, which are non-zero for molecules with non equivalent C–H bonds, connect states in which a single vibrational quantum is transferred from one mode to the other one.

The ω_r , x_{rs} and K_{rstu} coefficients as a function of the Morse parameters ω and x for the three limit cases with mixing angle $\phi = 0$, $\pi/8$, and $\pi/4$ radians are reported in Table 2. The coefficients for the generic case may be obtained by combining the relations in the first column of Table 2 with the expressions in Table 1. It should be emphasized that the coefficients may vary quite rapidly with ϕ , as shown in Fig. 1. For ϕ close to $\pi/8$, for example, even small changes of ϕ will result in large K_{1111} and K_{1212} changes, with little effects on K_{1112} and K_{1222} . The opposite happens with ϕ close to $\pi/4$.

To illustrate the relations developed in this paper, we now investigate how the mixing angle ϕ affects the C–H stretching overtone and combination spectra. All the Hamiltonian matrix elements between states $|v_1 v_2\rangle$ with $n = v_1 + v_2$ up to 4 are shown in Table 3. Since, as previously discussed, only states within the same overtone manifold actually interact, the Hamiltonian matrix factorizes into a single block for each value of n . For molecules with equivalent C–H bonds ($\phi = \pi/4$), these blocks factorize even further, since only states with the same even/odd parity of v_2 or, equivalently, the same parity of v_1 , may interact. Finally, complete factorization to a purely diagonal Hamiltonian matrix occurs for non interacting bonds ($\phi = 0$). It may also be noticed that since each state $|v_1 v_2\rangle$ couples only with itself and with the states $|v_1 \pm 1 v_2 \mp 1\rangle$ and $|v_1 \pm 2 v_2 \mp 2\rangle$, the Hamiltonian matrices with $n > 2$ exhibit a band diagonal structure.

In Fig. 2 we display the transition frequencies as a function of ϕ , for all overtone and combination states up to $n = 4$, computed by numerical diagonalization of the Hamiltonian matrices. For all angles, we assume that the two stretching fundamental [12] transitions occur at wavenumbers $\nu_1 = 3114 \text{ cm}^{-1}$ and $\nu_2 = 3102 \text{ cm}^{-1}$. The Morse's anharmonicity constant is assumed to be $x_1 = x_2 = x = -60 \text{ cm}^{-1}$ [13].

For the local mode case $\phi = 0$ the Hamiltonian matrices (Table 3) are purely diagonal. The first overtones and the combination band, for example, are thus simply calculated as $(2\nu_1) = 2\nu_1 + 2x_{11} = 6108 \text{ cm}^{-1}$, $(2\nu_2) = 2\nu_2 + 2x_{22} = 6084 \text{ cm}^{-1}$ and $(\nu_1 + \nu_2) = \nu_1 + \nu_2 = 6216 \text{ cm}^{-1}$, respectively.

For the $\phi = \pi/4$ limit case we have (from Table 2): $x_{11} = x_{22} = -30 \text{ cm}^{-1}$, $x_{12} = K_{1122} = -120 \text{ cm}^{-1}$. Both $2\nu_1$ and $2\nu_2$ belong to the same symmetry species (the total-symmetric irreducible representation) and therefore interact through a Darling-Dennison resonance term $K_{1122}/2$, giving a block diagonal Hamiltonian matrix (from Table 3):

$$\begin{pmatrix} 2\nu_1 + x & 0 & x \\ 0 & \nu_1 + \nu_2 + 2x & 0 \\ x & 0 & 2\nu_2 + x \end{pmatrix} = \begin{pmatrix} 6168 & 0 & -60 \\ 0 & 6096 & 0 \\ -60 & 0 & 6144 \end{pmatrix}$$

The combination band is calculated as $(\nu_1 + \nu_2) = \nu_1 + \nu_2 + x_{12} = 6096 \text{ cm}^{-1}$. The overtone frequencies, obtained by matrix diagonalization, have the final perturbed values $(2\nu_1) = 6217.19 \text{ cm}^{-1}$ and $(2\nu_2) = 6094.81 \text{ cm}^{-1}$.

For the $\phi = \pi/8$ case, the states $|2 0\rangle$, $|0 2\rangle$ and $|1 1\rangle$, corresponding to the $2\nu_1$, $2\nu_2$ overtones and to the $\nu_1 + \nu_2$ combination band, all belong to the total-symmetric symmetry species and may therefore interact. While the fundamental values of ν_1 , ν_2 and the Morse's anharmonicity x do not change, the other parameters from Table 2 now are: $x_{11} = x_{22} = -45 \text{ cm}^{-1}$, $x_{12} = K_{1122} = -60 \text{ cm}^{-1}$, and in addition, $K_{1112} = 120 \text{ cm}^{-1}$ and $K_{1222} = -120 \text{ cm}^{-1}$. The Hamiltonian matrix is non diagonal:

$$\begin{pmatrix} 2\nu_1 + 3x/2 & -\sqrt{2}x/2 & x/2 \\ -\sqrt{2}x/2 & \nu_1 + \nu_2 + x & \sqrt{2}x/2 \\ x/2 & \sqrt{2}x/2 & 2\nu_2 + 3x/2 \end{pmatrix} = \begin{pmatrix} 6138 & 42.43 & -30 \\ 42.43 & 6156 & -42.43 \\ -30 & -42.43 & 6114 \end{pmatrix}$$

After diagonalization, the perturbed values are found to be $(2\nu_1) = 6104.17 \text{ cm}^{-1}$, $(2\nu_2) = 6087.23 \text{ cm}^{-1}$ and $(\nu_1 + \nu_2) = 6216.60 \text{ cm}^{-1}$.

In Fig. 2 the wavenumbers of the overtones and combination modes displayed as a function of the mixing angle ϕ appear to move evenly from $\phi = 0$ up to $\phi = \pi/4$. However, if we consider the eigenvectors and therefore the approximate descriptions of the vibrational modes, we have at $\phi = 0$ that all modes are completely pure vibrations — all the out of diagonal matrix elements of Table 3 are zeros — with the assignments reported in the left side of Fig. 2, whereas when $\phi = \pi/4$ we get the assignments displayed in the right part of Fig. 2. For intermediate values of the mixing angle ϕ , the overtones and combination

bands are mingled in great extent and it is difficult to describe the vibrations in terms of only one mode.

Although other interactions have to be considered in actual cases, it appears evident from these results that the naive use of the symmetric “ x - K ” relations would lead, for non-symmetric molecules, to misassignment of C–H overtone and combination bands.

To complete this investigation, we now illustrate how the mixing angle ϕ behaves for actual molecules with two non equivalent C–H bonds. In order to determine the spectroscopic parameters described previously, namely ω_1 , ω_2 , x_{11} , x_{22} , x_{12} , ν_1 , ν_2 , K_{1122} , K_{1112} , K_{1222} , $2\nu_1$, $2\nu_2$ and $\nu_1 + \nu_2$, the anharmonic force fields of two series of molecules have been computed from density functional theory (DFT) quantum mechanical calculations.

The DFT calculations have been carried out by using Dunning correlation consistent polarized triple zeta (cc-pVTZ) basis set [14] and the Becke [15] three parameter exchange functional (B3) in combination with the Lee, Yang, and Parr [16] (LYP) correlation functional. All B3LYP/cc-pVTZ computations have been performed with the G03 system of programs [17]. Details about the calculations of the anharmonic force field are given elsewhere [18]. Here, we recall that following the approach first proposed by Schneider and Thiel [19], a full cubic and a semidiagonal quartic force field is obtained by central numerical differentiation of analytical second derivatives, performed in dimensionless normal coordinates around the equilibrium geometry.

The molecules investigated with two equivalent C–H bonds were 1,1-difluoroethene ($\text{F}_2\text{C}=\text{CH}_2$), *cis*- and *trans*-1,2-difluoroethene ($\text{FHC}=\text{CHF}$), 1,3-difluoropropadiene ($\text{FHC}=\text{C}=\text{CHF}$), *cis*- and *trans*-1,4-difluorobutatriene ($\text{FHC}=\text{C}=\text{C}=\text{CHF}$). By substitution of one F atom with a Cl atom in each molecule, we get the corresponding cases with two non-equivalent C–H bonds: $\text{ClFC}=\text{CH}_2$, *cis*- and *trans*- $\text{ClHC}=\text{CHF}$, $\text{ClHC}=\text{C}=\text{CHF}$, *cis*- and *trans*- $\text{ClHC}=\text{C}=\text{C}=\text{CHF}$.

The spectroscopic normal mode terms were evaluated from the quantum mechanical anharmonic force fields using second-order perturbation theory [20]. In addition, the cubic and quartic semidiagonal force constants, expressed in terms of dimensionless normal coordinates, were used to compute the Darling-Dennison constants K_{rstu} [11, 21]. These data are collected in Tables 4 and 5 for equivalent and non-equivalent C–H bonds, respectively. The calculated x_{rs} and K_{rstu} parameters are also shown in Fig. 1.

For molecules with equivalent C–H bonds, it can be seen that the parameters reported in Table 4 accurately follow the usual x - K relations [6] expected for $\phi = \pi/4$: $x_{11} \approx x_{22} \approx x_{12}/4 \approx K_{1122}/4$. In this case the vibrational normal modes 1 and 2 belong to different symmetry species and consequently $\nu_1 + \nu_2$ cannot interact with $2\nu_1$ and/or $2\nu_2$. For the same reason, the Darling-Dennison constants K_{1112} and K_{1222} involving an odd number of identical modes are zero (see also the last column of Table 2).

In the molecules with two non-equivalent C–H bonds, the spectroscopic terms reported in Table 5 correspond to a wide range of mixing angles ϕ . The angle ϕ , also indicated in Table 5, has been obtained by inverting the relations of Tables 1 and 2, as mentioned in the caption of Fig. 1. For all molecules we find $K_{1112} \approx -K_{1222}$, which implies $x_\alpha \approx x_\beta$ (Tables 1 and 2), $x_{11} \approx x_{22}$ and $x_{12} \approx K_{1122}$, as expected in this case. In $\text{ClFC}=\text{CH}_2$ ϕ approaches the $\pi/4$ limit, showing that the two strongly coupled C–H bonds actually behave as almost equivalent stretchings, whereas *cis*- $\text{ClHC}=\text{CHF}$ has $\phi \simeq \pi/8$. Going to the longer molecules of *cis*- or *trans*-1-chloro-4-fluorobutatriene ($\text{ClHC}=\text{C}=\text{C}=\text{CHF}$), the interaction between the two distant C–H bonds further decreases and the mixing angle ϕ approaches 0. The two C–H bonds may be considered as two isolated pure local modes.

For all molecules, the theoretically computed spectroscopic parameters x_{rs} and K_{rstu} are in good agreement with expected behaviour, depicted in Fig. 1. The six anharmonic constants x_{11} , x_{22} , x_{12} , K_{1122} , K_{1112} and K_{1222} , which appear as independent parameters in a normal mode treatment, can be accurately described in terms of a reduced set of three local mode parameters, namely the mixing angle ϕ and the bond anharmonicities x_α and x_β (with $x_\alpha \approx x_\beta$). The residual deviations from the ideal behaviour are due to coupling to other modes and to anharmonic interactions between the bonds, which restore the independence of the parameters.

4 Conclusions

For molecules with C–H bonds it is often believed that a normal mode model is not accurate and that a local mode description of the bonds is preferable. However, as previously shown for specific cases [1,6–8] and now proved in general, a local mode problem may be mapped onto a normal mode problem with exactly identical matrix elements, and therefore exactly identical energies. Thus, there is no fundamental difference between the local mode and normal mode descriptions, since normal modes are exactly as good, or as bad, as local modes. The choice between the two models is mainly one of mathematical convenience for the problem at hand.

The operator method [8] has been used to derive a normal mode model, including quartic anharmonicity, corresponding to the local mode model for low-symmetry molecules containing two non-equivalent C–H bonds. For this non-symmetric case, quartic anharmonic constants of the type K_{rrrs} are no longer zero as for symmetric molecules, and should be taken into account. These constants may be calculated by second order perturbation theory using the cubic and quartic anharmonic force field obtained from *ab initio* calculations [11,21].

DFT quantum chemical calculations for a number of molecules with non-equivalent C–H bonds show that the mixing between the two stretchings decreases with their distance, rapidly approaching the limit of two non-interacting local modes. Complete mixing, regardless of the distance, is instead invariably found in molecules with equivalent C–H bonds, which would have degenerate energy levels in absence of interaction.

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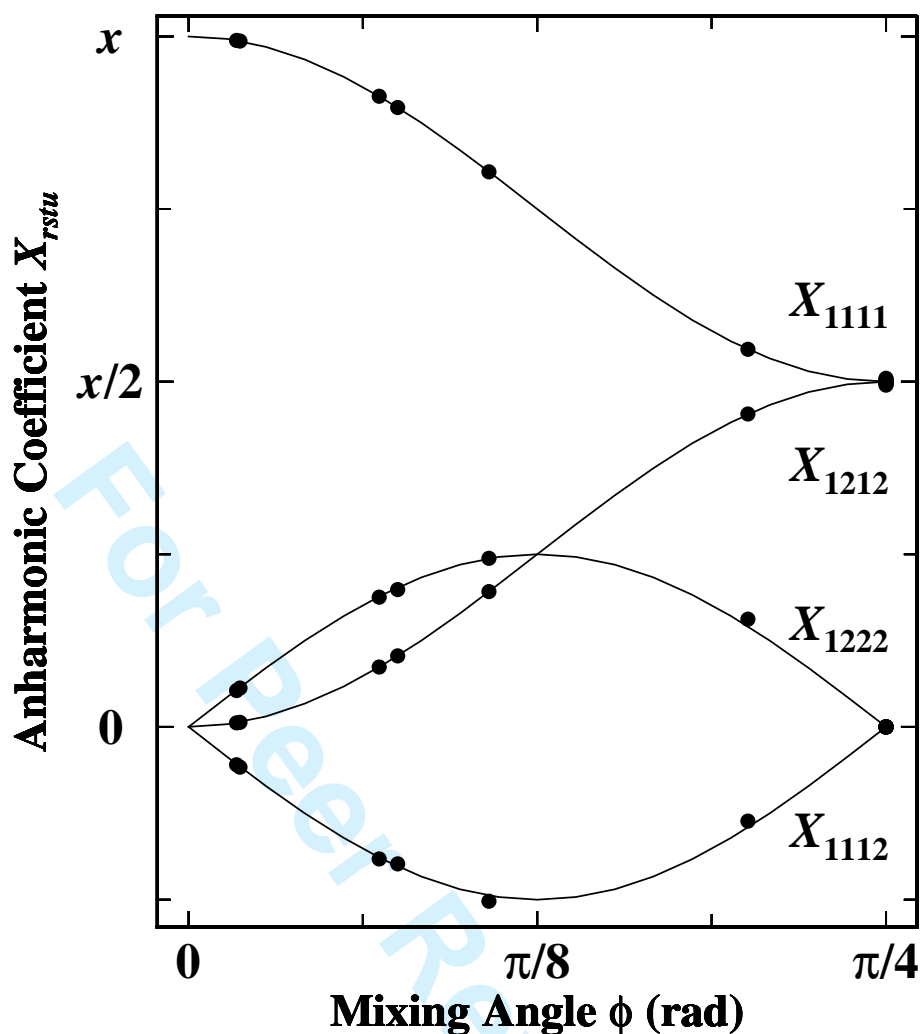


Figure 1. Curves: distinct anharmonic couplings $X_{1111} = x_{11} = x_{22}$, $X_{1212} = x_{12}/4 = K_{1122}/4$, $X_{1112} = K_{1112}/8$ and $X_{1222} = K_{1222}/8$ as a function of the mixing angle ϕ , for the case in which $x_\alpha = x_\beta = x$. Points: *ab initio* estimates of $X_{1111} = \frac{1}{2}(x_{11} + x_{22})$, $X_{1212} = \frac{1}{2}(x_{12}/4 + K_{1122}/4)$, $X_{1112} = K_{1112}/8$ and $X_{1222} = K_{1222}/8$ for the various molecules reported in Tables 4 and 5, with $x = X_{1111} + X_{1212}$ and ϕ obtained from $\sin 2\phi = \sqrt{2X_{1212}/x}$.

Table 1. Terms of the normal mode Hamiltonian, together with their coefficients ν_r and X_{rstu} as a function of the mixing angle ϕ . The non zero matrix elements of each term are also listed.

Hamiltonian term	ν_r or X_{rstu} coefficient	Non zero matrix element
$\nu_1 A_1^\dagger A_1$	$\nu_1 = \cos^2 \phi \lambda_{\alpha\alpha} + \sin^2 \phi \lambda_{\beta\beta} + 2 \cos \phi \sin \phi \lambda_{\alpha\beta}$	$\langle v_1 v_2 H v_1 v_2 \rangle = \nu_1 v_1$
$\nu_2 A_2^\dagger A_2$	$\nu_2 = \sin^2 \phi \lambda_{\alpha\alpha} + \cos^2 \phi \lambda_{\beta\beta} - 2 \cos \phi \sin \phi \lambda_{\alpha\beta}$	$\langle v_1 v_2 H v_1 v_2 \rangle = \nu_2 v_2$
$X_{1111} A_1^\dagger A_1^\dagger A_1 A_1$	$X_{1111} = \cos^4 \phi x_\alpha + \sin^4 \phi x_\beta$	$\langle v_1 v_2 H v_1 v_2 \rangle = X_{1111} (v_1^2 - v_1)$
$X_{2222} A_2^\dagger A_2^\dagger A_2 A_2$	$X_{2222} = \sin^4 \phi x_\alpha + \cos^4 \phi x_\beta$	$\langle v_1 v_2 H v_1 v_2 \rangle = X_{2222} (v_2^2 - v_2)$
$4 X_{1212} A_1^\dagger A_2^\dagger A_1 A_2$	$X_{1212} = \cos^2 \phi \sin^2 \phi (x_\alpha + x_\beta)$	$\langle v_1 v_2 H v_1 v_2 \rangle = 4 X_{1212} v_1 v_2$
$X_{1122} A_1^\dagger A_1^\dagger A_2 A_2$	$X_{1122} = X_{1212}$	$\langle v_1 + 2 v_2 - 2 H v_1 v_2 \rangle = X_{1122} \sqrt{(v_1 + 2)(v_1 + 1)(v_2 - 1)v_2}$
$X_{2211} A_2^\dagger A_2^\dagger A_1 A_1$	$X_{2211} = X_{1212}$	$\langle v_1 - 2 v_2 + 2 H v_1 v_2 \rangle = X_{2211} \sqrt{(v_2 + 2)(v_2 + 1)(v_1 - 1)v_1}$
$2 X_{1112} A_1^\dagger A_1^\dagger A_1 A_2$	$X_{1112} = \cos \phi \sin \phi (\sin^2 \phi x_\beta - \cos^2 \phi x_\alpha)$	$\langle v_1 + 1 v_2 - 1 H v_1 v_2 \rangle = 2 X_{1112} \sqrt{(v_1 + 1)v_1^2 v_2}$
$2 X_{1211} A_1^\dagger A_2^\dagger A_1 A_1$	$X_{1211} = X_{1112}$	$\langle v_1 - 1 v_2 + 1 H v_1 v_2 \rangle = 2 X_{1211} \sqrt{(v_2 + 1)(v_1 - 1)^2 v_1}$
$2 X_{1222} A_1^\dagger A_2^\dagger A_2 A_2$	$X_{1222} = \cos \phi \sin \phi (\cos^2 \phi x_\beta - \sin^2 \phi x_\alpha)$	$\langle v_1 + 1 v_2 - 1 H v_1 v_2 \rangle = 2 X_{1222} \sqrt{(v_1 + 1)(v_2 - 1)^2 v_2}$
$2 X_{2212} A_2^\dagger A_2^\dagger A_1 A_2$	$X_{2212} = X_{1222}$	$\langle v_1 - 1 v_2 + 1 H v_1 v_2 \rangle = 2 X_{2212} \sqrt{(v_2 + 1)v_2^2 v_1}$

Table 2. Spectroscopic normal mode terms ω_r , x_{rs} and K_{rstu} , expressed as multiples or combinations of the corresponding ν_r and X_{rstu} coefficients (listed in the same order of Table 1) for the limit cases (see text) with mixing angle $\phi = 0$, $\pi/8$, and $\pi/4$.

	$\phi = 0$	$\phi = \pi/8$	$\phi = \pi/4$
	$\lambda_{\alpha\beta} = 0$	$\lambda_{\alpha\beta} = (\omega_\alpha - \omega_\beta)/2$	$\lambda_{\alpha\beta} \neq 0$
	$\omega_\alpha \neq \omega_\beta$	$\omega_\alpha \neq \omega_\beta$	$\omega_\alpha = \omega_\beta = \omega$
	$x_\alpha \neq x_\beta$	$x_\alpha = x_\beta = x$	$x_\alpha = x_\beta = x$
$\omega_1 = \nu_1 - 2X_{1111} - 2X_{1212}$	ω_α	$\frac{1}{2}(\omega_\alpha + \omega_\beta) + \sqrt{2}\lambda_{\alpha\beta}$	$\omega + \lambda_{\alpha\beta}$
$\omega_2 = \nu_2 - 2X_{2222} - 2X_{1212}$	ω_β	$\frac{1}{2}(\omega_\alpha + \omega_\beta) - \sqrt{2}\lambda_{\alpha\beta}$	$\omega - \lambda_{\alpha\beta}$
$x_{11} = X_{1111}$	x_α	$\frac{3}{4}x$	$\frac{1}{2}x$
$x_{22} = X_{2222}$	x_β	$\frac{3}{4}x$	$\frac{1}{2}x$
$x_{12} = K_{1122} = K_{2211} = 4X_{1212}$	0	x	$2x$
$K_{1112} = K_{1211} = 8X_{1112}$	0	$-2x$	0
$K_{1222} = K_{2212} = 8X_{1222}$	0	$2x$	0

Table 3. Matrix elements of the normal mode Hamiltonian H_{normal} between states $|v_1 v_2\rangle$ with $n = v_1 + v_2$ up to 4. The Hamiltonian matrix factorizes into a block for each value of n . The states listed on the right hand side refer to the rows, and also apply to the corresponding columns.

$$\begin{aligned}
& \begin{pmatrix} \nu_1 & 0 \\ 0 & \nu_2 \end{pmatrix} \begin{matrix} |10\rangle \\ |01\rangle \end{matrix} \\
& \begin{pmatrix} 2\nu_1 + 2x_{11} & \frac{\sqrt{2}}{4}K_{1112} & \frac{1}{2}K_{1122} \\ \frac{\sqrt{2}}{4}K_{1211} & \nu_1 + \nu_2 + x_{12} & \frac{\sqrt{2}}{4}K_{1222} \\ \frac{1}{2}K_{2211} & \frac{\sqrt{2}}{4}K_{2212} & 2\nu_2 + 2x_{22} \end{pmatrix} \begin{matrix} |20\rangle \\ |11\rangle \\ |02\rangle \end{matrix} \\
& \begin{pmatrix} 3\nu_1 + 6x_{11} & \frac{\sqrt{3}}{2}K_{1112} & \frac{\sqrt{3}}{2}K_{1122} & 0 \\ \frac{\sqrt{3}}{2}K_{1211} & 2\nu_1 + \nu_2 + 2x_{11} + 2x_{12} & \frac{1}{2}K_{1112} + \frac{1}{2}K_{1222} & \frac{\sqrt{3}}{2}K_{1122} \\ \frac{\sqrt{3}}{2}K_{2211} & \frac{1}{2}K_{1211} + \frac{1}{2}K_{2212} & \nu_1 + 2\nu_2 + 2x_{22} + 2x_{12} & \frac{\sqrt{3}}{2}K_{1222} \\ 0 & \frac{\sqrt{3}}{2}K_{2211} & \frac{\sqrt{3}}{2}K_{2212} & 3\nu_2 + 6x_{22} \end{pmatrix} \begin{matrix} |30\rangle \\ |21\rangle \\ |12\rangle \\ |03\rangle \end{matrix} \\
& \begin{pmatrix} 4\nu_1 + 12x_{11} & \frac{3}{2}K_{1112} & \frac{\sqrt{6}}{2}K_{1122} & 0 & 0 \\ \frac{3}{2}K_{1211} & 3\nu_1 + \nu_2 + 6x_{11} + 3x_{12} & \frac{\sqrt{6}}{2}K_{1112} + \frac{\sqrt{6}}{4}K_{1222} & \frac{3}{2}K_{1122} & 0 \\ \frac{\sqrt{6}}{2}K_{2211} & \frac{\sqrt{6}}{2}K_{1211} + \frac{\sqrt{6}}{4}K_{2212} & 2\nu_1 + 2\nu_2 + 2x_{11} + 2x_{22} + 4x_{12} & \frac{\sqrt{6}}{4}K_{1112} + \frac{\sqrt{6}}{2}K_{1222} & \frac{\sqrt{6}}{2}K_{1122} \\ 0 & \frac{3}{2}K_{2211} & \frac{\sqrt{6}}{4}K_{1211} + \frac{\sqrt{6}}{2}K_{2212} & \nu_1 + 3\nu_2 + 6x_{22} + 3x_{12} & \frac{3}{2}K_{1222} \\ 0 & 0 & \frac{\sqrt{6}}{2}K_{2211} & \frac{3}{2}K_{2212} & 4\nu_2 + 12x_{22} \end{pmatrix} \begin{matrix} |40\rangle \\ |31\rangle \\ |22\rangle \\ |13\rangle \\ |04\rangle \end{matrix}
\end{aligned}$$

Table 4. Spectroscopic normal mode terms (cm^{-1}), from B3LYP/cc-pVTZ anharmonic force field (see text), for the case of two equivalent C–H stretchings in difluoro-substituted ethenes, propadiene, and butatrienes. Unperturbed values, no resonances have been taken into account. The *cis* and *trans* diastereomers are indicated by *c* and *t*, respectively.

	$\text{F}_2\text{C}=\text{CH}_2$	<i>c</i> -FHC=CHF	<i>t</i> -FHC=CHF	FHC=C=CHF	<i>c</i> -FHC=C=C=CHF	<i>t</i> -FHC=C=C=CHF
ω_1	3293	3231	3219	3181	3200	3202
ω_2	3194	3208	3213	3180	3199	3201
x_{11}	−29.77	−27.39	−28.20	−29.04	−28.86	−28.65
x_{22}	−25.47	−27.69	−27.74	−29.09	−28.96	−28.74
x_{12}	−105.65	−111.66	−110.89	−116.40	−115.64	−114.77
K_{1122}	−117.13	−113.01	−109.55	−116.47	−115.88	−114.70
ν_1	3154	3101	3088	3053	3065	3068
ν_2	3066	3073	3077	3050	3069	3072
$2\nu_1$	6249	6147	6119	6047	6072	6079
$2\nu_2$	6081	6090	6098	6042	6081	6087
$\nu_1 + \nu_2$	6115	6062	6054	5986	6018	6026

Table 5. Spectroscopic normal mode terms (cm^{-1}) and mixing angle ϕ (rad), from B3LYP/cc-pVTZ anharmonic force field (see text), for the case of two non equivalent C–H stretchings in chlorofluoro-substituted ethenes, propadiene, and butatrienes. Unperturbed values, no resonances have been taken into account. The *cis* and *trans* diastereomers are indicated by *c* and *t*, respectively.

	CIFC=CH ₂	<i>c</i> -ClHC=CHF	<i>t</i> -ClHC=CHF	ClHC=C=CHF	<i>c</i> -ClHC=C=C=CHF	<i>t</i> -ClHC=C=C=CHF
ω_1	3281	3234	3223	3187	3203	3204
ω_2	3179	3199	3214	3185	3197	3197
x_{11}	−32.36	−45.50	−50.94	−54.34	−58.84	−58.40
x_{22}	−28.50	−44.67	−49.90	−53.55	−57.89	−57.20
x_{12}	−95.24	−43.31	−23.89	−20.47	−1.61	−1.38
K_{1122}	−106.50	−44.63	−22.38	−20.49	−1.52	−1.33
K_{1112}	60.69	113.21	89.20	90.31	27.42	25.45
K_{1222}	−69.44	−109.53	−89.49	−88.82	−26.51	−24.52
ν_1	3144	3103	3091	3055	3072	3076
ν_2	3049	3063	3088	3051	3067	3072
$2\nu_1$	6224	6114	6080	6002	6026	6035
$2\nu_2$	6041	6036	6077	5996	6019	6029
$\nu_1 + \nu_2$	6098	6122	6156	6086	6138	6146
ϕ	0.2005π	0.1077π	0.0749π	0.0683π	0.0184π	0.0172π

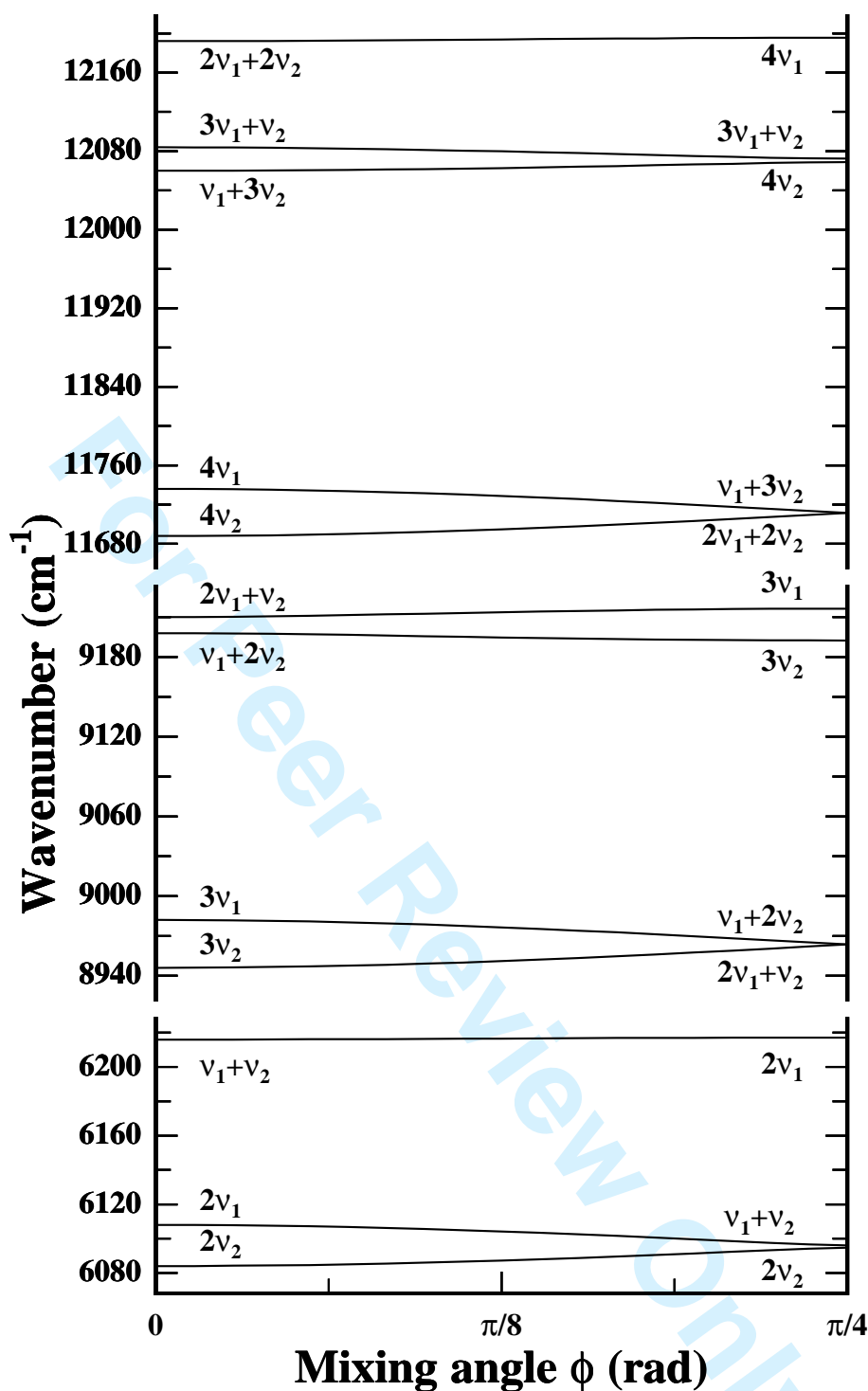
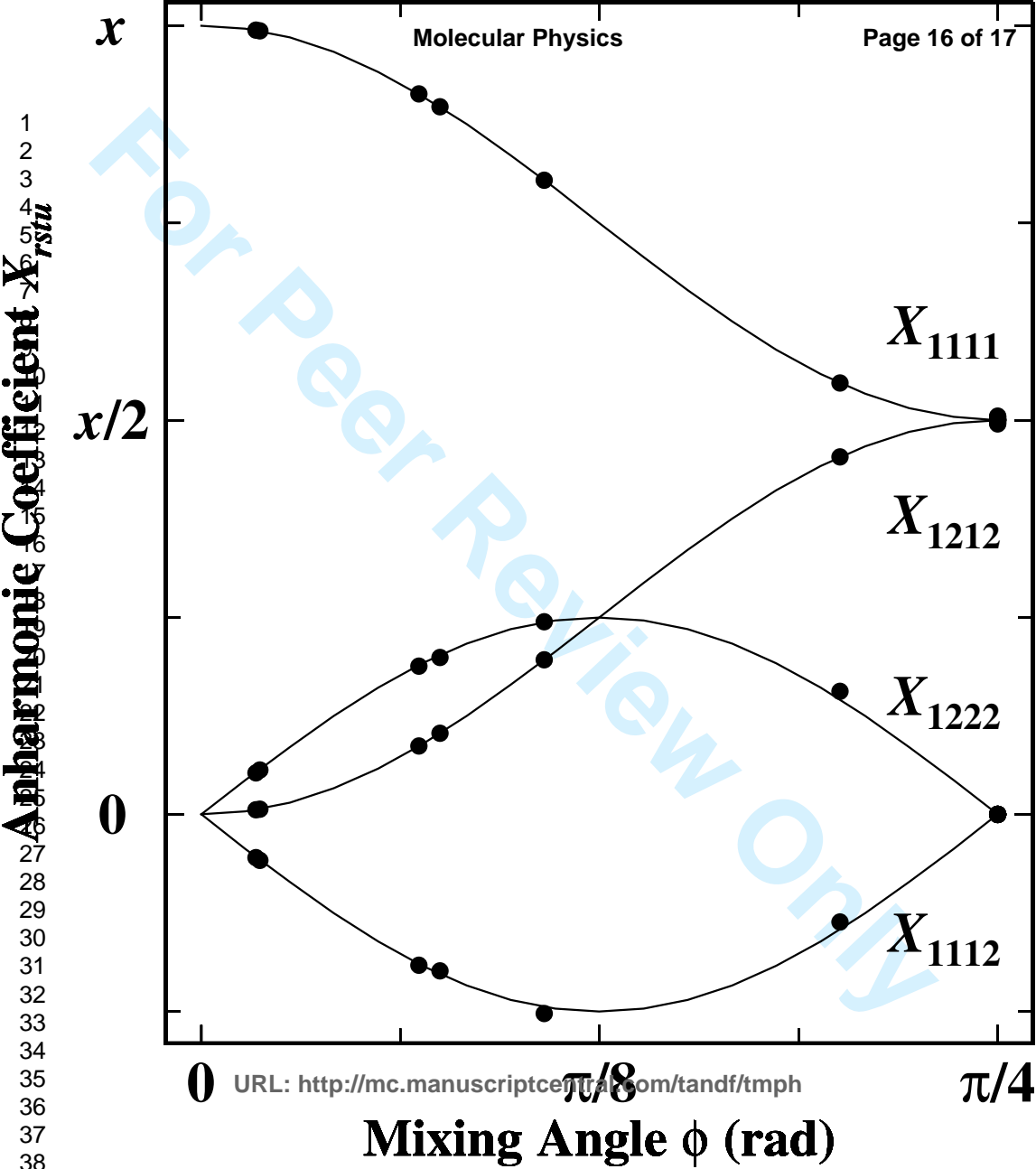


Figure 2. Wavenumbers as a function of the mixing angle ϕ for the overtone and combination modes with $n = v_1 + v_2$ up to 4, with fixed values of the fundamentals.



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