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Relating normal vibrational modes to local vibrational modes: benzene and naphthalene

Wenli Zou · Robert Kalescky · Elfi Kraka · Dieter Cremer

Abstract Local vibrational modes can be directly derived from normal vibrational modes using the method of Konkoli and Cremer (Int J Quant Chem 67:29, 1998). This implies the calculation of the harmonic force constant matrix $\mathbf{F}^q$ (expressed in internal coordinates $\mathbf{q}$) from the corresponding Cartesian force constant matrix $\mathbf{f}^x$ with the help of the transformation matrix $\mathbf{U} = \mathbf{WB}^{\dagger}(\mathbf{BWB}^{\dagger})^{-1}$ ($\mathbf{B}$: Wilson's B-matrix). It is proven that the local vibrational modes are independent of the choice of the matrix $\mathbf{W}$. However, the choice $\mathbf{W} = \mathbf{M}^{-1}$ ($\mathbf{M}$: mass matrix) has numerical advantages with regard to the choice $\mathbf{W} = \mathbf{I}$ ($\mathbf{I}$: identity matrix), where the latter is frequently used in spectroscopy. The local vibrational modes can be related to the normal vibrational modes in the form of an adiabatic connection scheme (ACS) after rewriting the Wilson equation with the help of the compliance matrix. The ACSs of benzene and naphthalene based on experimental vibrational frequencies are discussed as nontrivial examples. It is demonstrated that the local-mode stretching force constants provide a quantitative measure for the C–H and C–C bond strength.

Keywords Normal vibrational modes · Local vibrational modes · Adiabatic connection scheme · Local mode analysis · Benzene · Naphthalene

Introduction

Vibrational force constants are nonobservable quantities. They are given by the second derivatives of the molecular energy with regard to the coordinates of a molecule and measure the curvature of the associated potential energy surface (PES).

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Since the PES is a concept based on the Born–Oppenheimer approximation, force constants are conceptual quantities. They relate features of the PES to the vibrational frequencies measured by vibrational spectroscopy [1–4]. However, this relationship is complicated by (i) the dependency of the frequencies on the atomic masses via the kinetic energy of the vibrating molecule and (ii) the description of the PES close to the equilibrium position of a molecule (harmonic, cubic, etc.). The harmonic description of the PES is most commonly used, and the structural features of a molecule are analyzed with the help of its harmonic vibrational force constants.

The force constants depend on the set of coordinates chosen to describe a molecule. These can be Cartesian, internal, or normal coordinates [1–3]. Alternatively, we can use curvilinear coordinates [5–7] such as the deformation and puckering coordinates of Cremer and coworkers [8–10]. The calculation of Cartesian force constants is straightforward and leads to the force constant matrix $\mathbf{f}^x$. The latter can be used as a suitable reference because it depends on neither the choice of internal coordinates nor any coordinate redundancies. However, Cartesian force constants have the disadvantage that chemists can only comprehend molecular structure and chemical bonding in terms of internal coordinates $\mathbf{q}$ rather than Cartesian coordinates $\mathbf{x}$. In the early days of vibrational spectroscopy, it became obvious that internal force constants depend on the internal coordinates chosen to describe a molecule, their redundant or nonredundant character, and the coupling between vibrational modes [1]. It was pointed out that the transformation from a well-defined set of Cartesian force constants to internal coordinate force constants is not unique and can, in principle, lead to an infinite number of different transformations [11–13]. However, this problem could be solved by proving that, independent of the transformation matrix, the same internal coordinate force constant matrix $\mathbf{F}^q$ is obtained. This matrix is independent of mass provided the

geometry of the molecule in question corresponds to a true stationary point (minimum) on the PES [11–13]. Hence, the question of how to derive molecular force constants that do not depend on the choice of internal coordinates for describing the molecular geometry remains.

This problem hampers vibrational spectroscopy and the determination of internal coordinate force constants from measured vibrational frequencies, which are, contrary to the force constants, measurable quantities. One has provided arguments and transformation procedures to obtain a reasonable presentation of molecular force constants. One has also tried to use force constants obtained in different ways to describe chemical bonding, angle strain, conformational flexibility and other features of the electronic structure of molecules, often without considering the fact that force constants, when expressed in terms of the internal coordinates of a molecule, are not well-defined quantities. These attempts were driven by the understanding that the properties of molecular vibrations reflect features of molecular structure and stability in a unique way [14, 15]. A vibration causes small displacements of the atomic positions in a molecule and, in this way, probes molecular bonding without significantly changing the electronic structure of a molecule. The properties of the molecular vibrations, such as vibrational frequencies and force constants, are defined for infinitesimal displacements and are therefore ideal for discussing the electronic structure and bonding of a molecule in a dynamic fashion without changing any structural features (e.g., during bond dissociation). Since vibrational frequencies always depend on the masses of the atoms moving, vibrational force constants would be ideal descriptors of molecular bonding provided they could be defined in a unique way in terms of internal coordinates.

In 1963, Decius [16] showed that the inverse of matrix $\mathbf{F}^q$ leads to the compliance matrix $\mathbf{\Gamma}^q = (\mathbf{F}^q)^{-1}$ and, by this, to a set of compliance constants that are the diagonal elements of $\mathbf{\Gamma}^q$, which describe local features of the molecule and do not depend on the choice of internal coordinates [17–19]. Although Decius was able to relate the compliance matrix to an expansion of the PES function in terms of generalized displacement forces, the physical meaning of the compliance constants, especially the relationship between diagonal and off-diagonal elements of the compliance matrix, remained unclear. In this work, we will show that the compliance matrix of Decius provides the missing link between normal-mode force constants and the local force constants of Konkoli and Cremer [20]. We will derive the conditions for the transformation of the Cartesian force constant matrix $\mathbf{f}^x$ via the internal force constant matrix $\mathbf{F}^q$ and compliance matrix $\mathbf{\Gamma}^q$ into a unique set of local-mode force constants, which are ideally suited for the electronic structure analysis of a molecule. This derivation will be suitable for any stationary point on the PES and will be valid for any transformation of $\mathbf{f}^x$ into $\mathbf{F}^q$ and $\mathbf{\Gamma}^q$.

In addition, we will show how local vibrational modes can be related to normal vibrational modes in the form of an adiabatic connection scheme. This will be demonstrated for benzene and naphthalene as two nontrivial examples where we will base the ACSs on experimental frequencies to exclude any discussion of the quantum chemical approach used. The local-mode force constants obtained for benzene and naphthalene will be the basis for a bond order relationship to analyze the electronic structure of the two molecules.

The basic problem of determining the force constant matrix $\mathbf{F}^q$

The dynamics of the N nuclei of a vibrating molecule can be determined by solving the Euler–Lagrange equations. In this way, the basic secular equation of vibrational spectroscopy is obtained [1–4]:

$$\mathbf{f}^x \mathbf{L} = \mathbf{M} \mathbf{L} \mathbf{\Lambda} \tag{1}$$

Here, matrix $\mathbf{M}$ is the mass matrix, the eigenvalue matrix $\mathbf{\Lambda}$ contains on its diagonal the values $4\pi^2 c^2 \omega_\mu^2$, where ω_μ are the vibrational frequencies, and matrix $\mathbf{L}$ contains $3N$ mode vectors $\mathbf{l}_\mu$, among which a subset with Σ mode vectors corresponds to translations and rotations of the molecule, as reflected by values of ω_μ that are equal to zero. For the following, we eliminate the Σ external motions of the molecule so that matrix $\mathbf{L}$ adopts the dimension $3N \times N_{\text{vib}}$ and the diagonal eigenvalue matrix $\mathbf{\Lambda}$ becomes N_{vib}-dimensional ($N_{\text{vib}} = 3N - \Sigma$). Expressing Eq. 1 in internal rather than Cartesian coordinates, the Wilson GF formalism is obtained [1, 2, 4]:

$$\mathbf{F}^q \mathbf{D} = \mathbf{G}^{-1} \mathbf{D} \mathbf{\Lambda}. \tag{2}$$

In Eq. 2, Wilson's $\mathbf{G}$ represents the kinetic energy part, and the eigenvector matrix $\mathbf{D}$ (containing as columns the normal-mode vectors $\mathbf{d}_\mu$, $\mu = 1, ..., N_{\text{vib}}$) is defined by

$$\mathbf{D} = \mathbf{B} \mathbf{L}, \tag{3}$$

where matrix $\mathbf{B}$ is a rectangular ($N_{\text{vib}} \times 3N$) matrix containing the first derivatives of the internal coordinates with regard to the Cartesian coordinates. Matrix $\mathbf{F}^q$ is calculated according to

$$\mathbf{F}^q = \mathbf{U}^\dagger \mathbf{f}^x \mathbf{U}, \tag{4}$$

where the ($3N \times N_{\text{vib}}$)-dimensional rectangular matrix $\mathbf{U}$ is the pseudoinverse matrix of $\mathbf{B}$,

$$\mathbf{B} \mathbf{U} = \mathbf{I}. \tag{5}$$

The unit matrix $\mathbf{I}$ is of dimension $N_{\text{vib}} \times N_{\text{vib}}$, and can be written

$$\begin{pmatrix} \mathbf{B} \\ \mathbf{B_0} \end{pmatrix} (\mathbf{U} \quad \mathbf{U}_0) = \begin{pmatrix} \mathbf{BU} & \mathbf{BU_0} \\ \mathbf{B_0U} & \mathbf{B_0U_0} \end{pmatrix},$$
$$= \begin{pmatrix} \mathbf{I}_{N\text{vib}} & \mathbf{0}_{N\text{vib},\Sigma} \\ \mathbf{0}_{\Sigma,N\text{vib}} & \mathbf{I}_{\Sigma} \end{pmatrix} \quad (6)$$

where $\mathbf{B_0}$ represents the $\mathbf{B}$ matrix of the Σ rotation and translation modes, which was introduced by Woodward [2].

Since $\mathbf{B}$ is a rectangular matrix, the solution of Eq. 5 is not unique. (We note that a unique solution for a square, invertible matrix $\mathbf{R}$ implies the existence of a matrix $\mathbf{S}$ that fulfills $\mathbf{RS}=\mathbf{SR}=\mathbf{I}$.) The general solution is [11–13]

$$\mathbf{U} = \mathbf{WB}^{\dagger} \left(\mathbf{BWB}^{\dagger} \right)^{-1} \quad (7)$$

where $\mathbf{W}$ is an arbitrary nonsingular $3N \times 3N$ square matrix. Although Eq. 5 is fulfilled by any matrix $\mathbf{W}$, reverse multiplication does not lead in general to a unit matrix of dimension $3N \times 3N$ because

$$(\mathbf{U} \quad \mathbf{U}_0) \begin{pmatrix} \mathbf{B} \\ \mathbf{B_0} \end{pmatrix} = \mathbf{UB} + \mathbf{U_0B_0} = \mathbf{I_{3N}}. \quad (8)$$

By deriving under the conditions through which Eq. 1 can be transformed into Eq. 2, we can determine the transformation matrix $\mathbf{U}$ in Eq. 4:

$$\mathbf{U}^{\dagger} \mathbf{f}^x \mathbf{I}_{3N} \mathbf{L} = \mathbf{U}^{\dagger} \mathbf{M} \mathbf{I}_{3N} \mathbf{L\Lambda}$$
$$\mathbf{U}^{\dagger} \mathbf{f}^x (\mathbf{UB} + \mathbf{U_0B_0}) \mathbf{L} = \mathbf{U}^{\dagger} \mathbf{M} (\mathbf{UB} + \mathbf{U_0B_0}) \mathbf{L\Lambda} \quad ,$$
$$\mathbf{F}^q \mathbf{D} + \mathbf{U}^{\dagger} \mathbf{f}^x \mathbf{U_0B_0L} = \mathbf{U}^{\dagger} \mathbf{MUD\Lambda} + \mathbf{U}^{\dagger} \mathbf{MU_0B_0L\Lambda}$$
$$(9)$$

where Eq. 3 is used. Winnewisser and Watson [13] proved that the following equation is fulfilled:

$$\mathbf{f}^x \mathbf{U_0} = \mathbf{0}_{3N,\Sigma}, \quad (10)$$

which implies that the second term on the l.h.s. of Eq. 12 vanishes. Woodward [2] showed that

$$\mathbf{U}^{\dagger} \mathbf{MU} = \mathbf{G}^{-1} \quad (11)$$

provided

$$\mathbf{U}^{\dagger} \mathbf{MU_0} = \mathbf{0}_{N\text{vib},\Sigma}. \quad (12)$$

Hence, Eq. 12 becomes identical to Eq. 2. However, Eq. 15 is not fulfilled in general by an arbitrary $\mathbf{U}$ defined by Eq. 10. One group of solutions of Eq. 10 is given by $\mathbf{W}=s\mathbf{M}^{-1}$, where s is an arbitrary nonzero scalar value. For reasons of simplicity, we set $s=1$ and obtain $\mathbf{W}=\mathbf{M}^{-1}$. This implies that

$$\mathbf{U} = \mathbf{C} = \mathbf{M}^{-1} \mathbf{B}^{\dagger} \mathbf{G}^{-1}, \quad (13)$$

which is also obtained when applying the Eckart conditions [21]. Since $\mathbf{G}=\mathbf{BM}^{-1}\mathbf{B}^{\dagger}$, it holds that $\mathbf{BC}=\mathbf{I}$.

Another frequently used choice is $\mathbf{W}=\mathbf{I}_{3N}$ [11–13], leading to

$$\mathbf{U} = \mathbf{Z} = \mathbf{B}^{\dagger} \left(\mathbf{BB}^{\dagger} \right)^{-1}. \quad (14)$$

It has been proven that both choices of $\mathbf{W}$ ($\mathbf{W}=\mathbf{M}^{-1}$ and $\mathbf{W}=\mathbf{I}$) lead to identical matrices $\mathbf{F}^q$ (i.e., the transformation from matrix $\mathbf{f}^x$ to matrix $\mathbf{F}^q$ is independent of $\mathbf{W}$), and that the elements of matrix $\mathbf{F}^q$ are independent of the atomic masses [13]. This implies that, for a given set of $3N-\Sigma=N_{\text{para}}$ internal coordinates describing the molecule in question, there is only one matrix $\mathbf{F}^q$ and one compliance matrix $\mathbf{\Gamma}^q$.

Setting $\mathbf{U}=\mathbf{C}$ fulfills Eq. 12 because

$$\mathbf{C}^{\dagger} \mathbf{MU_0} = \mathbf{G}^{-1} \mathbf{BM}^{-1} \mathbf{MU_0},$$
$$= \mathbf{G}^{-1} \mathbf{BU_0} = \mathbf{0}_{N\text{vib},\Sigma} \quad (15)$$

where $\mathbf{BU_0} = \mathbf{0}_{N\text{vib},\Sigma}$ from Eq. 6 is used. However, $\mathbf{U}=\mathbf{Z}$ does not satisfy Eq. 15. Although the same matrix $\mathbf{F}^q$ is obtained, the kinetic energy part is not described correctly, and the frequency calculation is erroneous. Of course, we can circumvent this dilemma by using $\mathbf{U}=\mathbf{C}$ for the potential energy part and $\mathbf{U}=\mathbf{Z}$ for the kinetic energy part only. Note that this is, strictly speaking, not justified, so $\mathbf{U}=\mathbf{C}$ is the only proper pseudoinverse of $\mathbf{B}$, which can transform Eq. 1 into Eq. 2. This is of relevance when relating normal-mode to local-mode force constants, as we will see in the next section. For this purpose, we derive an important relationship between matrix $\mathbf{C}$ and matrix $\mathbf{D}$.

Starting from $\mathbf{F}^q\mathbf{D}=\mathbf{U}^{\dagger}\mathbf{f}^x\mathbf{L}$, as given by Eq. 12, we obtain

$$\mathbf{B}^{\dagger} \mathbf{F}^q \mathbf{D} = \mathbf{B}^{\dagger} \mathbf{U}^{\dagger} \mathbf{f}^x \mathbf{L} = (\mathbf{I_{3N}} - \mathbf{B_0}^{\dagger} \mathbf{U_0}^{\dagger}) \mathbf{f}^x \mathbf{L}$$
$$= \mathbf{f}^x \mathbf{L} - \mathbf{B_0}^{\dagger} \mathbf{U_0}^{\dagger} \mathbf{f}^x \mathbf{L} \quad (16)$$

The last term on the r.h.s. of Eq. 19 vanishes because of Eq. 13. By combining Eqs. 1 and 2 with Eq. 19, we can write

$$\mathbf{f}^x \mathbf{L} = \mathbf{B}^{\dagger} (\mathbf{F}^q \mathbf{D})$$
$$\mathbf{ML\Lambda} = \mathbf{B}^{\dagger} (\mathbf{G}^{-1} \mathbf{D\Lambda}) \quad . \quad (17)$$
$$\mathbf{L} = \mathbf{M}^{-1} \mathbf{B}^{\dagger} \mathbf{G}^{-1} \mathbf{D} = \mathbf{CD}$$

The relationship $\mathbf{L}=\mathbf{CD}$ is needed in the following.

Obtaining local vibrational modes

We could assume that the local-mode vectors $\mathbf{d}_{\mu}$ are unit vectors, each of which depend on just one internal coordinate, and that the force constant matrix $\mathbf{F}^q$ is diagonal, thus indicating that there is no electronic coupling between the vibrational modes. Nevertheless, there would still be mass coupling between the vibrational eigenvectors because the $\mathbf{G}$ matrix is nondiagonal. This shows that local vibrational

modes can only be obtained by suppressing mass coupling [20].

The local vibrational mode associated with the internal coordinate q_n describing the molecular fragment ϕ_n is obtained by setting all masses except those of the atoms of fragment ϕ_n equal to zero, which is straightforward when expressing the vibrational problem in terms of Cartesian coordinates. In this way, the Euler–Lagrange equations lead to a local vibration of ϕ_n. However, this solution is not useful because chemists analyze molecular structure and dynamics in terms of internal rather than Cartesian coordinates. The assumption $m_i = 0$ ($i \in \phi_m$) implies that the generalized momentum p_m is also equal to zero (the subscript i refers to Cartesian coordinates, and subscripts m and n refer to internal coordinates). Hence, the Euler–Lagrange equations for a local mode of ϕ_n expressed in internal coordinates read [20]

$$p_n = \frac{\partial L(\mathbf{q}, \overline{\mathbf{q}})}{\partial \overline{q}_n} \neq 0 \tag{18}$$

$$p_m = \frac{\partial L(\mathbf{q}, \overline{\mathbf{q}})}{\partial \overline{q}_m} = 0 \tag{19}$$

$$\frac{d}{dt} p_n = \frac{\partial V(\mathbf{q})}{\partial q_n} \neq 0 \tag{20}$$

$$\frac{d}{dt} p_m = \frac{\partial V(\mathbf{q})}{\partial q_m} = 0$$
$$\text{for} \quad m \neq n \tag{21}$$

where $L = T - V$ is the Lagrangian (T and V are the kinetic and potential energy, respectively). It has been shown that the mass constraints correspond to carrying out a local vibration triggered by a displacement of internal coordinate q_n (i.e., the mode is led by q_n; this is the *leading parameter principle* [20]) under the requirement that all internal coordinates q_m are relaxed. This led to the term "adibatic (relaxed) internal coordinate modes" (AICoMs), which will be replaced here with the simpler term "local vibrational modes." The local modes obtained in this way take the form [20]

$$\mathbf{a}_n = \frac{\mathbf{K}^{-1} \mathbf{d_n^\dagger}}{\mathbf{d}_n \mathbf{K}^{-1} \mathbf{d_n^\dagger}}, \tag{22}$$

where $\mathbf{a}_n$ is the local-mode vector associated with internal coordinate q_n, and $\mathbf{d}_n$, contrary to $\mathbf{d}_\mu$, is a row vector of matrix $\mathbf{D}$. Matrix $\mathbf{K}$ is the diagonal matrix of force constants k_Q, expressed in normal coordinates Q_μ

$$\mathbf{F}^Q = \mathbf{K} = \mathbf{L}^\dagger \mathbf{f}^\mathbf{x} \mathbf{L}. \tag{23}$$

The local modes are characterized by force constants $k_{\mathrm{a},n}$ (the subscript "a" refers to adiabatic) [20], where

$$k_{\mathrm{a,n}} = \mathbf{a_n^\dagger} \mathbf{K} \mathbf{a_n} = \left(\mathbf{d_n} \mathbf{K}^{-1} \mathbf{d_n^\dagger} \right)^{-1}, \tag{24}$$

and vibrational frequencies $\omega_{\mathrm{a},n}$, where

$$4\pi^2 c^2 (\omega_{\mathrm{a,n}})^2 = k_{\mathrm{a,n}} G_{nn}, \tag{25}$$

in which G_{nn} is a diagonal element of the $\mathbf{G}$ matrix and corresponds to the reduced mass of the local mode $\mathbf{a}_n$ [20]. The local modes of Konkoli and Cremer lead to vibrational frequencies that are close to the frequencies measured in the few cases where, because of the experimental situation, normal-mode properties could be measured that approximate those of local modes [15, 22–24].

The internal constant matrix $\mathbf{F}^q$ can be related to the local-mode force constant matrix $\mathbf{k}_\mathrm{a}$ (with the elements $\mathbf{k}_{\mathrm{a},n}$ on the diagonal and $n = 1, \cdots, N_{\mathrm{para}} = N_{\mathrm{vib}}$), where we consider the two choices of the pseudoinverse matrix $\mathbf{U}$ discussed in the previous section: (i) $\mathbf{U}=\mathbf{C}$ and (ii) $\mathbf{U}=\mathbf{Z}$. In the first case, we obtain

$$\mathbf{F^q} = \mathbf{C}^\dagger \mathbf{f^x} \mathbf{C} \tag{26}$$

and

$$\mathbf{C} = \mathbf{L} \mathbf{D}^{-1} \tag{27}$$

as a consequence of $\mathbf{L}=\mathbf{C}\mathbf{D}$ (the inverse of $\mathbf{D}$ exists because of $N_{\mathrm{para}} = N_{\mathrm{vib}}$), which makes it possible to write

$$\mathbf{F}^q = \left(\mathbf{D}^{-1} \right)^\dagger \mathbf{L}^\dagger \mathbf{f}^x \mathbf{L} \mathbf{D}^{-1} \tag{28a}$$

$$= \left(\mathbf{D}^{-1} \right)^\dagger \mathbf{K} \mathbf{D}^{-1}, \tag{28b}$$

where matrix $\mathbf{K}$ is defined in Eq. 26. The inverse of matrix $\mathbf{F}^q$ is the compliance matrix of Decius [16]:

$$(\mathbf{F^q})^{-1} = \mathbf{\Gamma}^q = \mathbf{D} \mathbf{K}^{-1} \mathbf{D}^\dagger. \tag{29}$$

Hence, the compliance constants are given by

$$(\mathbf{\Gamma}^q)_{nn} = \mathbf{d}_n \mathbf{K}^{-1} \mathbf{d}_n^\dagger, \tag{30}$$

which, if compared with Eq. 27, leads to

$$k_{\mathrm{a,n}}(\mathbf{U} = \mathbf{C}) = k_{\mathrm{a,n}} = 1/(\mathbf{\Gamma}^q)_{\mathrm{nn}} = 1/\Gamma_{\mathrm{n}}. \tag{31}$$

In other words, the reciprocals of the compliance constants of Decius [16] are the local-mode force constants of Konkoli and Cremer [20]. This proves that the choice $\mathbf{U}=\mathbf{C}$ connects local and normal vibrational modes in a well-defined way, and the compliance constants of Decius present the missing link between them.

Table 1 Comparison of local-mode force constants and compliance constants calculated with different choices of **U** at the B3LYP/6-31G(d,p) level of theory[a]

Molecule	Fragment	r_n α_n	$k_{a,n}$	Γ_n **U**=**C**	$1/\Gamma_n$ **U**=**C**	$k_{a,n}$ **U**=**Z**	Γ_n **U**=**Z**	$\Delta(k_{a,n})$
1	C–H	1.092	5.367309	0.186313	5.367309	5.367309	0.186313	0.000000
	H–C–H	109.5	0.667215	1.498767	0.667215	0.667215	1.498767	0.000000
2	C–H$_i$	1.093	5.300379	0.188666	5.300379	5.300377	0.188666	0.000002
	C–H$_o$	1.101	4.949980	0.202021	4.949980	4.949971	0.202021	0.000009
	C–O	1.418	4.891419	0.204440	4.891419	4.891420	0.204440	−0.000001
	O–H	0.965	8.149843	0.122702	8.149843	8.149847	0.122702	−0.000004
	H–C–H	107.7	0.721482	1.386037	0.721482	0.721479	1.386042	0.000003
	H$_i$–C–O	106.9	0.983985	1.016275	0.983985	0.983959	1.016302	0.000026
	H$_o$–C–O	112.8	0.985189	1.015033	0.985189	0.985202	1.015020	−0.000013
	H–O–C	107.7	0.759139	1.317283	0.759139	0.759172	1.317224	−0.000033
3	C–H	1.086	5.560108	0.179853	5.560108	5.560106	0.179853	0.000002
	C–C	1.396	6.598466	0.151550	6.598466	6.598463	0.151550	0.000003
	H–C–C	120.0	0.944305	1.058980	0.944305	0.944274	1.059014	0.000031
	C–C–C	120.0	2.373331	0.421349	2.373331	2.373331	0.421349	0.000000
5	C–C	1.205	17.642909	0.056680	17.642909	17.642909	0.056680	0.000000
	H–C	1.066	6.469399	0.154574	6.469399	6.469399	0.154574	0.000000
	H–C–C	180.0	0.192791	5.186951	0.192791	0.192796	5.186839	−0.000005

[a] Molecules **1**, **2**, **3**, and **5** are shown in Fig. 1. Diatomic fragments A–B denote bond lengths r_n (given in Å), whereas triatomic fragments A–B–C denote bond angles α_n (given in degrees). Stretching force constants are given in mdyn/Å and the corresponding compliance constants in Å/mdyn. Bending force constants are given in (mdyn Å)/rad^2, and the corresponding compliance constants in rad^2/(mdyn Å). $\Delta(k_{a,n})=1/\Gamma_n(\mathbf{C})-1/\Gamma_n(\mathbf{Z})$

In the second case, the transformation is carried out according to

$$\mathbf{F}^q = \mathbf{Z}^\dagger \mathbf{f}^x \mathbf{Z} = \left(\mathbf{B}^\dagger \mathbf{B}\right)^{-1} \mathbf{B} \mathbf{f}^x \mathbf{B}^\dagger \left(\mathbf{B}\mathbf{B}^\dagger\right)^{-1}. \tag{32}$$
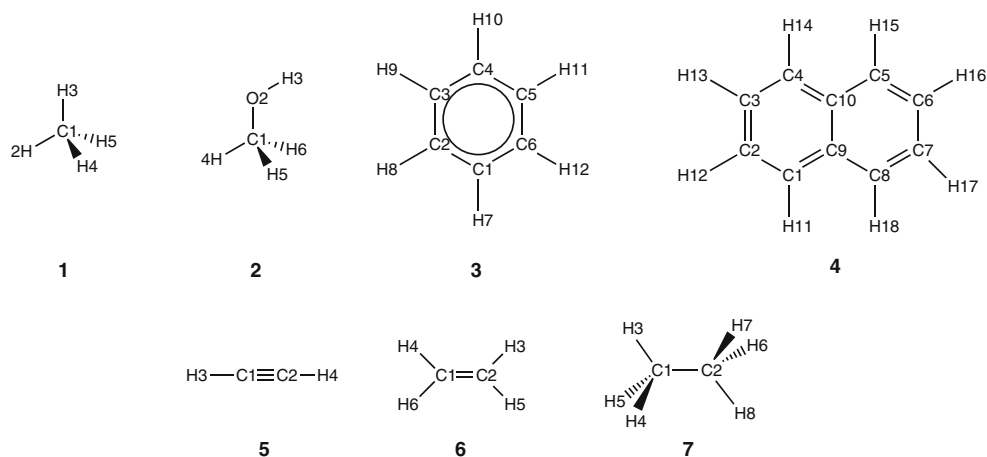
Because of

$$\mathbf{C}^\dagger \mathbf{f}^x \mathbf{C} = \left(\mathbf{B}^\dagger \mathbf{B}\right)^{-1} \mathbf{B} \mathbf{f}^x \mathbf{B}^\dagger \left(\mathbf{B}\mathbf{B}^\dagger\right)^{-1}, \tag{33}$$

the proof given in Eqs. 29–35 also holds for the choice **U**=**Z**

Table 2 Comparison of experimentally based local-mode force constants and compliance constants calculated with different choices of **U**[a]

Molecule	Fragment	$k_{a,n}$ **U**=**C**	Γ_n **U**=**C**	$1/\Gamma_n$ **U**=**C**	$k_{a,n}$ **U**=**Z**	Γ_n **U**=**Z**	$\Delta(k_{a,n})$
1	C–H	4.896515	0.204227	4.896515	4.896515	0.204227	0.000000
	H–C–H	0.623086	1.604916	0.623086	0.623086	1.604916	0.000000
2	C–H$_i$	4.888890	0.204545	4.888890	4.888888	0.204546	0.000002
	C–H$_o$	4.598815	0.217447	4.598815	4.598806	0.217448	0.000009
	C–O	4.608809	0.216976	4.608809	4.608809	0.216976	0.000000
	O–H	7.547767	0.132490	7.547767	7.547771	0.132489	−0.000004
	H–C–H	0.686460	1.456749	0.686460	0.686457	1.456755	0.000003
	H$_i$–C–O	0.926452	1.079387	0.926452	0.926426	1.079417	0.000026
	H$_o$–C–O	0.945946	1.057143	0.945946	0.945958	1.057129	−0.000012
	H–O–C	0.716321	1.396021	0.716321	0.716355	1.395955	−0.000034
3	C–H	5.113117	0.195575	5.113117	5.113115	0.195575	0.000002
	C–C	6.211729	0.160986	6.211729	6.211726	0.160986	0.000003
	H–C–C	0.894018	1.118546	0.894018	0.893986	1.118586	0.000032
	C–C–C	2.279047	0.438780	2.279047	2.279047	0.438780	0.000000

[a] Molecules **1**, **2**, and **3** are shown in Fig. 1. Diatomic fragments A–B denote bond lengths r_n (given in Å), whereas triatomic fragments A–B–C denote bond angles α_n (given in degrees). Stretching force constants are given in mdyn/Å and the corresponding compliance constants in Å/mdyn. Bending force constants are given in (mdyn Å)/rad^2 and the corresponding compliance constants in rad^2/(mdyn Å). $\Delta(k_{a,n})=1/\Gamma_n(\mathbf{C})-1/\Gamma_n(\mathbf{Z})$. Calculation of experimental local modes was performed according to Cremer and coworkers [14]
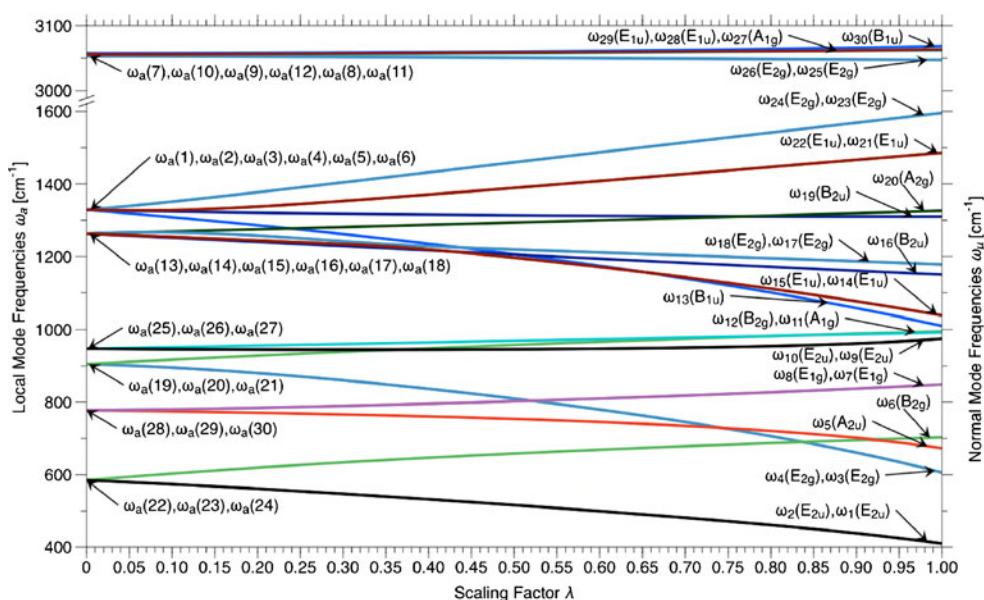
Fig. 1 Molecules investigated in this work

corresponding to **W**=**I**. Hence, the local-mode force constants and their relationship to normal-mode force constants is independent of the transformation of Cartesian to internal coordinate force constants. As in the case of the normal modes, incorrect local-mode frequencies are obtained for **W**=**I**, so we must use **U**=**C** and **W**=**M**$^{-1}$ to obtain both force constants and frequencies with the same matrix **U**.

In Tables 1 and 2, local-mode force constants and compliance constants of some typical organic molecules (Fig. 1) are compared; the values in the first table are based on B3LYP/6–31G(d,p) calculations [25, 26]) and those in the second table on experimental frequencies [27, 28] combined with DFT normal modes [14]. The local-mode force constants are calculated for **W**=**M**$^{-1}$ or **I** with the program of Konkoli and Cremer [20], and the compliance constants with a program based on Eq. 34 and written for this work. In each case, local-mode force constants are compared with the reciprocals of the compliance constants Γ_n. In total, 40 different molecules were investigated, among which only the results for methane, methanol, benzene,

and acetylene (molecules **1**, **2**, **3**, and **5** in Fig. 1) are shown in Tables 1 and 2.

For all cases investigated, Eq. 34 is exactly fullfilled (i.e., the local-mode force constants are the reciprocals of the compliance constants with an uncertainty of <10^{-8}). It is also true that the force constants k_a do not depend on whether **W**=**M**$^{-1}$ or **I**. However, in this case, there are small differences between the two sets, on the order of 10^{-5} force constant units or less (see Table 1). Analysis of the deviations reveals that these deviations have two different causes. First, they are a result of the DFT (density functional theory) approach used, which implies numerical integrations and, in the SCF (self-consistent field) and geometry optimization, finite convergence criteria. In the DFT calculations, an ultrafine grid and tight convergence criteria were used, which of course do not exclude the possibility that better agreement would have been obtained with even higher numerical accuracy. However, the very small differences between the k_a and $1/\gamma$ values obtained for **U**=**C** indicate a second reason for the deviations between $\Gamma(\mathbf{C})$ and $\Gamma(\mathbf{Z})$. For **U**=**Z**, the local

Fig. 2 Adiabatic connection scheme of benzene (**3**) based on experimental frequencies. For the numbering of local-mode frequencies, local-mode parameters, normal-mode symmetries, and normal-mode frequencies, see Table 3
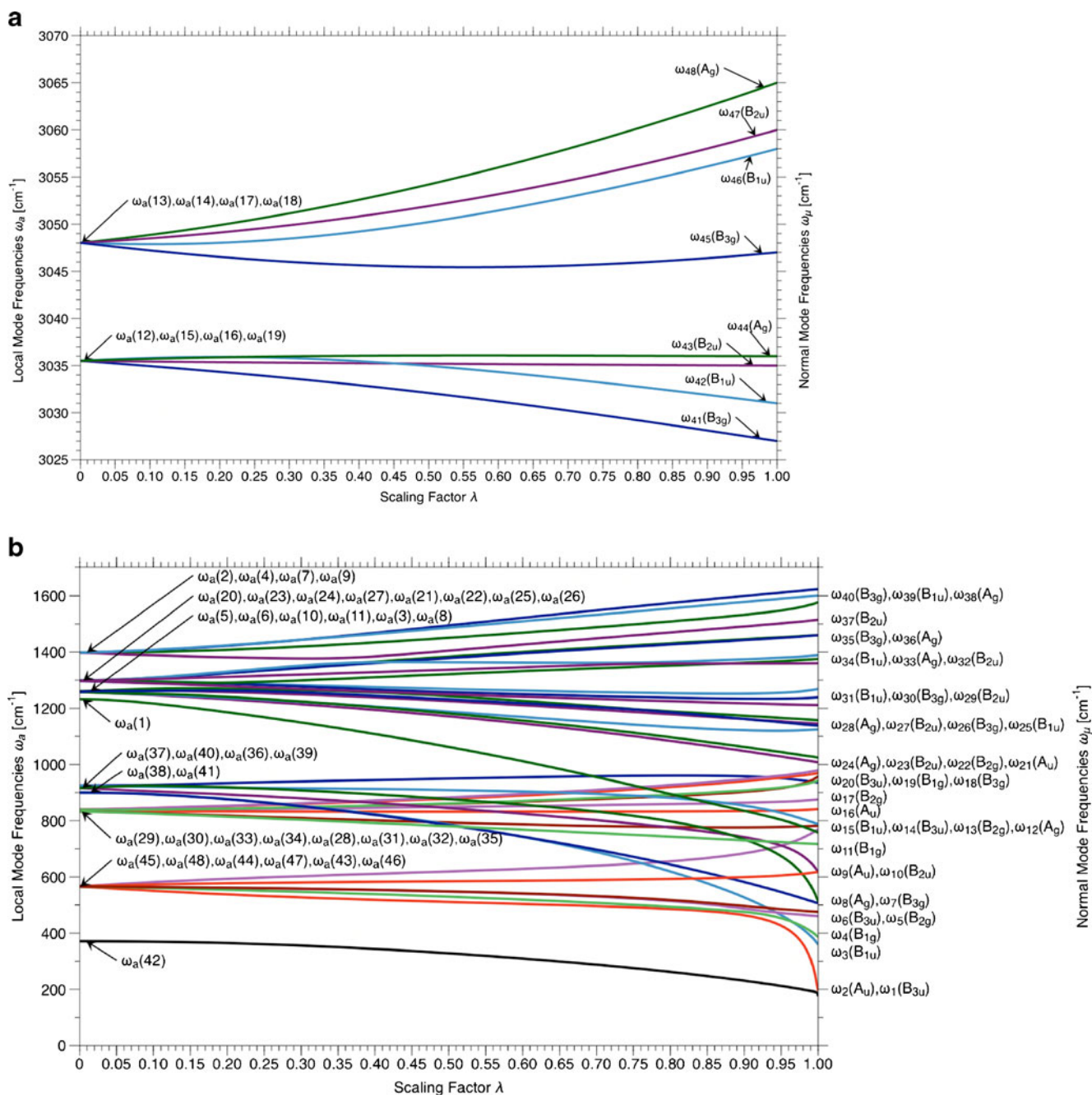
Fig. 3a–b Adiabatic connection scheme of naphthalene (**4**) based on experimental frequencies. **a** Upper and **b** lower frequency ranges. For the numbering of local-mode frequencies, local-mode parameters, normal-mode symmetries, and normal-mode frequencies, see Table 3

force constants are sensitive to residual contaminations from translational and rotational modes resulting from the fact that the geometry optimization does not lead to the exact minimum of a molecule because of numerical difficulties. This also argues against the use of $\mathbf{U=Z}$ when calculating force constants (apart from the fact that the calculation of the frequencies becomes inconsistent, as discussed above).

Similar observations can be made for the experimentally based local-mode force constants [14] derived with either $\mathbf{U=C}$

or $\mathbf{U=Z}$ (see Table 2), because the DFT normal modes were used for their determination. Upon taking the reciprocals of the compliance constants, identity (35) is again confirmed.

Transforming local modes into normal modes

This task can be accomplished by solving the Wilson equation once for local and once for normal vibrational modes. To do this, two problems must be solved: (i) the force

Table 3 Measured normal-mode frequencies ω_μ and the corresponding local-mode force constants k_a, local-mode frequencies ω_a, and coupling frequencies ω_{coup} of benzene (**3**)[a]

μ	Sym.	ω_μ (cm^{-1})	Param. type	Param. #	k_a (mdyn Å^{-1})	ω_a (cm^{-1})	ω_{coup} (cm^{-1})	Bond order n
30	B$_{1u}$	3068	C1–H7	7	5.113	3055	13	1.010
29	E$_{1u}$	3063	C4–H10	10	5.113	3055	8	1.010
28	E$_{1u}$	3063	C3–H9	9	5.113	3055	8	1.010
27	A$_{1g}$	3062	C6–H12	12	5.113	3055	7	1.010
26	E$_{2g}$	3047	C2–H8	8	5.113	3055	−8	1.010
25	E$_{2g}$	3047	C5–H11	11	5.113	3055	−8	1.010
24	E$_{2g}$	1596	C1–C2	1	6.242	1329	267	1.468
23	E$_{2g}$	1596	C2–C3	2	6.242	1329	267	1.468
22	E$_{1u}$	1486	C3–C4	3	6.242	1329	157	1.468
21	E$_{1u}$	1486	C4–C5	4	6.242	1329	157	1.468
20	A$_{2g}$	1326	H12–C6–C1	18	0.893	1263	63	
19	B$_{2u}$	1310	C6–C1	6	6.242	1329	−19	1.468
18	E$_{2g}$	1178	H7–C1–C2	13	0.893	1263	−85	
17	E$_{2g}$	1178	H8–C2–C3	14	0.893	1263	−85	
16	B$_{2u}$	1150	H9–C3–C4	15	0.893	1263	−113	
15	E$_{1u}$	1038	H10–C4–C5	16	0.893	1263	−225	
14	E$_{1u}$	1038	H11–C5–C6	17	0.893	1263	−225	
13	B$_{1u}$	1010	C5–C6	5	6.242	1329	−319	1.468
12	B$_{2g}$	995	C1–C2–C3	19	2.258	905	90	
11	A$_{1g}$	992	H9–C3–C4–H10	26	0.186	948	44	
10	E$_{2u}$	975	H11–C5–C6–H12	27	0.186	948	27	
9	E$_{2u}$	975	H7–C1–C2–H8	25	0.186	948	27	
8	E$_{1g}$	849	H7–C1–C2–C3	28	0.268	778	71	
7	E$_{1g}$	849	H9–C3–C4–C5	29	0.268	778	71	
6	B$_{2g}$	703	C1–C2–C3–C4	22	0.354	585	118	
5	A$_{2u}$	673	H11–C5–C6–C1	30	0.268	778	−105	
4	E$_{2g}$	606	C3–C4–C5	20	2.259	905	−299	
3	E$_{2g}$	606	C5–C6–C1	21	2.258	905	−299	
2	E$_{2u}$	410	C3–C4–C5–C6	23	0.354	585	−175	
1	E$_{2u}$	410	C5–C6–C1–C2	24	0.354	585	−175	
ZPE (kcal mol^{-1}):		61.2				62.2	−1.0	

[a] Bending and torsion force constants are given in (mdyn Å)/rad^2. *ZPE* denotes the zero-point energy calculated from normal-mode frequencies. It has to be identical to the sum of the local-mode frequency contribution and the coupling frequency contribution. For the numbering of atoms, see Fig. 1

constant matrix must be related to local vibrational modes; (ii) it must be possible to split the force constant matrix and the **G** matrix into diagonal and nondiagonal parts. In this case, the diagonal parts should lead to the local-mode results, whereas including the off-diagonal parts should give the normal-mode quantities.

If matrix **A** contains the local-mode vectors **a**, a transformed force constant matrix based on local vibrational rather than normal vibrational modes can be obtained via

$$\mathbf{A}^\dagger \mathbf{K} \mathbf{A} = \mathbf{F}^a, \tag{34}$$

where the superscript "a" indicates adiabatic (local) modes, and **A** is given by

$$\mathbf{A} = \mathbf{K}^{-1}\mathbf{D}^\dagger \left[\left(\mathbf{D}\mathbf{K}^{-1}\mathbf{D}^\dagger \right)_d \right]^{-1} \tag{35}$$

(subscript "d" refers to diagonal terms of the matrix product).To fulfill the second requirement, the Wilson equation given in Eq. 2 is rewritten by multiplying it by matrix **G** and replacing the force constant matrix **F**^{q} with the compliance matrix $\mathbf{\Gamma}^q$:

$$\mathbf{G}(\mathbf{\Gamma}^q)^{-1}\mathbf{D} = \mathbf{D}\mathbf{\Lambda} \\ = \mathbf{\Gamma}^q(\mathbf{\Gamma}^q)^{-1}\mathbf{D}\mathbf{\Lambda} \tag{36}$$

Table 4 Measured normal-mode frequencies ω_μ and the corresponding local-mode force constants k_a, local-mode frequencies ω_a, and coupling frequencies ω_{coup} of naphthalene (**4**)[a]

μ	Sym.	ω_μ (cm^{-1})	Param. type	Param. #	k_a (mdyn Å^{-1})	ω_a (cm^{-1})	ω_{coup} (cm^{-1})	Bond order n
48	A$_g$	3065	C2–H12	13	5.089	3048	17	1.009
47	B$_{2u}$	3060	C3–H13	14	5.089	3048	12	1.009
46	B$_{1u}$	3058	C6–H16	17	5.089	3048	10	1.009
45	B$_{3g}$	3047	C7–H17	18	5.089	3048	−1	1.009
44	A$_g$	3036	C1–H11	12	5.047	3036	1	1.007
43	B$_{2u}$	3035	C4–H14	15	5.047	3036	−1	1.007
42	B$_{1u}$	3031	C5–H15	16	5.047	3036	−5	1.007
41	B$_{3g}$	3027	C8–H18	19	5.047	3036	−9	1.007
40	B$_{3g}$	1624	C1–C2	2	6.909	1398	226	1.603
39	B$_{1u}$	1601	C3–C4	4	6.909	1398	203	1.603
38	A$_g$	1577	C5–C6	7	6.909	1398	179	1.603
37	B$_{2u}$	1515	C7–C8	9	6.909	1398	117	1.603
35	B$_{3g}$	1460	C9–C1–H11	20	0.249	1298	162	
36	A$_g$	1460	C3–C4–H14	23	0.249	1298	162	
34	B$_{1u}$	1389	C10–C5–H15	24	0.249	1298	91	
33	A$_g$	1376	C7–C8–H18	27	0.249	1297	79	
32	B$_{2u}$	1361	C1–C2–H12	21	0.248	1298	63	
31	B$_{1u}$	1269	C2–C3–H13	22	0.248	1297	−28	
30	B$_{3g}$	1239	C5–C6–H16	25	0.248	1297	−58	
29	B$_{2u}$	1212	C6–C7–H17	26	0.248	1297	−85	
28	A$_g$	1158	C2–C3	3	5.614	1260	−102	1.339
27	B$_{2u}$	1145	C6–C7	8	5.614	1260	−115	1.339
26	B$_{3g}$	1138	C1–C9	5	5.595	1258	−120	1.335
25	B$_{1u}$	1125	C4–C10	6	5.595	1258	−133	1.335
24	A$_g$	1025	C5–C10	10	5.595	1258	−233	1.335
23	B$_{2u}$	1008	C8–C9	11	5.595	1258	−250	1.335
22	B$_{2g}$	980	H12–C2–C1–C3	29	0.298	839	141	
21	A$_u$	970	H13–C3–C2–C4	30	0.298	839	131	
20	B$_{3u}$	958	H16–C6–C5–C7	33	0.298	839	119	
19	B$_{1g}$	943	H17–C7–C6–C8	34	0.298	839	104	
18	B$_{3g}$	935	C9–C1–C2	37	2.353	925	10	
17	B$_{2g}$	876	H11–C1–C9–C2	28	0.293	833	43	
16	A$_u$	841	H14–C4–C3–C10	31	0.293	833	8	
15	B$_{1u}$	788	C10–C5–C6	40	2.353	925	−137	
14	B$_{3u}$	783	H15–C5–C10–C6	32	0.293	833	−50	
13	B$_{2g}$	770	C1–C2–C3–C4	45	0.327	568	203	
12	A$_g$	758	C9–C10	1	5.368	1232	−474	1.288
11	B$_{1g}$	717	H18–C8–C7–C9	35	0.293	833	−116	
10	A$_u$	618	C10–C9–C1	36	2.439	917	−299	
9	B$_{2u}$	618	C5–C6–C7–C8	48	0.327	568	51	
8	A$_g$	512	C9–C10–C5	39	2.439	917	−405	
7	B$_{3g}$	506	C5–C6–C7	41	2.230	900	−394	
6	B$_{3u}$	476	C9–C1–C2–C3	44	0.325	566	−90	
5	B$_{2g}$	461	C10–C5–C6–C7	47	0.325	566	−105	
4	B$_{1g}$	386	C10–C9–C1–C2	43	0.340	566	−180	
3	B$_{1u}$	359	C1–C2–C3	38	2.230	900	−541	
2	A$_u$	195	C9–C10–C5–C6	46	0.340	566	−371	
1	B$_{3u}$	176	C8–C9–C10–C4	42	0.378	371	−195	
ZPE (kcal mol^{-1}):		89.6				93.0	−3.4	

[a] Bending and torsion force constants are given in (mdyn Å)/rad^2. *ZPE* denotes the zero-point energy calculated from normal-mode frequencies. It has to be identical to the sum of the local-mode frequency contribution and the coupling frequency contribution. For the numbering of atoms, see Fig. 1

Upon defining a new normal-mode eigenvector matrix $\mathbf{R} = (\mathbf{\Gamma}^q)^{-1}\mathbf{D}$, the Wilson equation adopts the form

$$\mathbf{GR} = \mathbf{\Gamma}^q\mathbf{R}\mathbf{\Lambda}, \tag{37}$$

which leads to the same eigenvalues as the Wilson equation itself:

$$\mathbf{R}^\dagger\mathbf{GR} = \mathbf{D}[(\mathbf{\Gamma}^q)^{-1}]^\dagger\mathbf{\Gamma}^q(\mathbf{\Gamma}^q)^{-1}\mathbf{D} = \mathbf{D}^\dagger\mathbf{F}^q\mathbf{D} = \mathbf{\Lambda}. \tag{38}$$

We then split the matrices $\mathbf{G}$ and $\mathbf{\Gamma}^q$ in Eq. 41 into diagonal and off-diagonal parts, where the latter are switched on slowly using a scaling parameter λ increasing from $\lambda=0$ (local vibrational modes) to $\lambda=1$ (normal vibrational modes):

$$(\mathbf{G}_d + \lambda\mathbf{G}_o)\mathbf{R}_\lambda = (\mathbf{\Gamma}^q_d + \lambda\mathbf{\Gamma}^q_o)\mathbf{R}_\lambda\mathbf{\Lambda}_\lambda. \tag{39}$$

This results in an adiabatic connection scheme (ACS) that leads from local to normal modes. By definition, an ACS must have $N_{vib} = 3N - \Sigma$ local modes to match the normal modes. To achieve this, N_{vib} internal coordinates must be selected that *lead* the local vibrational modes according to the leading parameter principle of Konkoli and Cremer [20]. For a given molecule, there may be multiple options for internal coordinates. In this situation, the following procedure may help. (i) For the molecule in question, the normal vibrational modes $\mathbf{d}_\mu$ are calculated. (ii) Each of the N_{vib} normal vibrational modes $\mathbf{d}_\mu$ is decomposed into local vibrational modes $\mathbf{a}_n$, where different sets of internal coordinates $\mathbf{q}$ are tested. (iii) The set $\mathbf{q}$ that leads to the largest overlap between the normal and local vibrational modes is chosen for the ACS.

For an acyclic N-atom molecule, such a set is normally given by $N - 1$ bond lengths, $N - 2$ bond angles, and $N - 3$ bond dihedral angles, whereas in the case of an N-membered ring, N ring bonds, $N - 3$ bond angles, and $N - 3$ bond dihedral angles should be used (a bond dihedral angle is defined by four atoms which form a string of bonds that are directly connected to each other). Regardless of how the set of N_{vib} is chosen, the form and the properties of a local mode associated with internal coordinate q_n is independent of the choice of all other internal coordinates [20].

Adiabatic connection schemes for benzene and napthalene

Figures 2 and 3 show the ACSs of benzene and naphthalene, based on experimental frequencies [29, 30]. For benzene, six C–H bond lengths, six C–C bond lengths, three C–C–C bond angles, six H–C–C bond angles, three H–C–C–H bond dihedral angles, three C–C–C–C bond dihedral angles, and three H–C–C–C bond dihedral angles gave the best match between normal and local vibrational modes in the ACS.

This is reflected by the fact that the absolute values of the coupling frequencies ω_{coup}, which are defined as

$$\omega_{coup} = \omega_\mu - \omega_a, \tag{40}$$

sum to a minimum value.

The local vibrational frequencies obtained in this way must fulfill the zero-point energy (ZPE) condition of the molecule (i.e., the ZPE of the molecule must be exactly reproduced by the contributions from local and coupling frequencies). For benzene, the experimental frequencies lead to ZPE=61.2 kcal mol^{-1} (Table 3). This value is equal to the sum ZPE$_a$+ZPE$_{coup}$, which is $62.2 - 1.0 = 61.2$ kcal mol^{-1} (Table 3).

The ACS of benzene reveals that the six local C–H stretching frequencies at 3055 cm^{-1} can be split into one A_{1g}, one B_{1u}, two E_{1u}, and two E_{2g} normal modes. All coupling frequencies are smaller than 15 cm^{-1}, which is a direct reflection of the fact that mass coupling between the local C–H stretching modes is small because the C–H bonds are separated by one C–C bond and form angles of $60°$. An angle of $90°$ would suppress all couplings, whereas an angle of 0 or $180°$ would lead to the strongest coupling (Table 4).

There is considerably stronger coupling between the C–C stretching modes at 1329 cm^{-1}, which can be split into modes between 1010 and 1596 cm^{-1} according to coupling frequencies of 267 and -319 cm^{-1}. Hence, it is impossible to gauge the C–C bond strength using the normal-mode C–C stretching frequencies (e.g., by averaging). This is, however, easily achieved by utilizing local-mode properties. In this connection, the local-mode frequencies are less suitable because they always depend on the masses of the atoms involved. It is better to use the local-mode stretching force constants k_a, as given in Table 3. These should be compared with suitable references such as the local-mode C–C stretching force constants of ethane, ethylene, or acetylene, which are given in Table 5. These reveal that the C–C bonds in benzene (k_a=5.124 mdyn/Å , Table 3) are similar to the C–C bond in ethylene (k_a=5.104 mdyn/Å , Table 5).

The comparison of local-mode k_a values soon becomes tedious given the number of bonds to be compared, so it is easier to derive a C–C bond order from local-mode k_a values, as was previously shown by Kraka and Cremer [31]. For this purpose, the C–C bonds of ethane and ethylene are assigned bond orders n of 1 and 2, in line with conventional chemical concepts. Using exclusively experimental normal-mode frequencies and the local-mode frequencies and force constants derived from them, the following bond order–force constant relationship for C–C bonds is derived:

$$n(CC) = 0.30071k_a(CC)^{0.86567}. \tag{41}$$

In this way, C–C bond orders for acetylene of 3.286 and for benzene of 1.468 result, in line with general expectations.

Table 5 Measured normal-mode frequencies ω_μ and the corresponding local-mode force constants k_a, local-mode frequencies ω_a, and coupling frequencies ω_{coup} of ethane (**7**), ethylene (**6**), and acetylene (**5**)[a]

μ	Sym.	ω_μ (cm^{-1})	Param. type	Param. #	k_a (mdyn Å^{-1})[a]	ω_a (cm^{-1})	ω_{coup} (cm^{-1})
Ethane							
18	E_u	2985	C2–H7	13	4.785	2955	30
17	E_u	2985	C1–H4	14	4.785	2955	30
16	E_g	2969	C2–H8	15	4.785	2955	14
15	E_g	2969	C1–H3	16	4.785	2955	14
14	A_{2u}	2954	C1–H5	17	4.785	2955	−1
13	A_{1u}	2896	C2–H6	18	4.785	2955	−59
12	E_u	1469	H7–C2–H8	9	0.654	1433	36
11	E_u	1469	H4–C1–H5	10	0.654	1433	36
10	E_g	1468	H6–C2–H7	11	0.654	1433	35
9	E_g	1468	H3–C1–H4	12	0.654	1433	35
8	A_{1g}	1388	H5–C1–C2	3	0.734	1123	265
7	A_{2u}	1379	H6–C2–C1	4	0.734	1123	256
6	E_g	1190	H7–C2–C1	5	0.734	1123	67
5	E_g	1190	H4–C1–C2	6	0.734	1123	67
4	A_{1g}	995	H8–C2–C1	7	0.734	1123	−128
3	E_u	822	H3–C1–C2	8	0.734	1123	−301
2	E_u	822	C1–C2	2	4.007	1065	−243
1	A_{1u}	289	H3–C1–C2–H6	1	0.069	511	−222
ZPE (kcal mol^{-1}):		45.3				45.4	−0.1
Ethylene							
12	B_{2u}	3106	H3–C2	9	5.104	3052	54
11	B_{3g}	3103	H4–C1	10	5.104	3052	51
10	A_g	3026	H5–C2	11	5.104	3052	−26
9	B_{1u}	2989	H6–C1	12	5.104	3052	−63
8	A_g	1623	C2–C1	8	8.924	1589	34
7	B_{1u}	1444	H5–C2–C1	4	0.750	1170	275
6	A_g	1342	H6–C1–C2	5	0.750	1170	173
5	B_{3g}	1236	H4–C1–C2	6	0.750	1170	67
4	A_u	1023	H5–C2–C1–H4	7	0.222	1170	−147
3	B_{2g}	949	H6–C1–C2–H5	3	0.186	977	−28
2	B_{3u}	943	H4–C1–C2–H3	1	0.186	976	−33
1	B_{2u}	826	H3–C2–C1	2	0.750	976	−150
ZPE (kcal mol^{-1}):		30.9				30.6	0.3
Acetylene							
7	Σ_g	3374	H7–C1	6	5.902	3414	−40
6	Σ_u	3289	H8–C2	7	5.902	3414	−125
5	Σ_g	1974	C2–C1	5	15.836	2217	−243
3,4	Π_u	730	H3–C1–C2	1	0.208	702	28
1,2	Π_g	612	H4–C2–C1	3	0.208	702	−90
ZPE (kcal mol^{-1}):		16.2				16.9	−0.7

[a] Bending and torsion force constants are given in (mdyn Å)/rad^2. *ZPE* denotes the zero-point energy calculated from normal-mode frequencies. It has to be identical to the sum of the local-mode frequency contribution and the coupling frequency contribution. For the numbering of atoms, see Fig. 1

Bonding should be stronger in acetylene than expected from ethane and ethylene because all of the repulsive C–H eclipsing interactions are removed. For benzene, one expects a bond order close to 1.5, which is confirmed by the local-mode force constants. In this connection, it should be mentioned that the C–C bond dissociation energies (BDEs) provide little guidance about the strength of the C–C bonds, because the fragments resulting from C–C bond cleavage undergo geometrical relaxation and strong electron density reorganization effects, which lower the BDE values significantly. Since these fragment stabilization effects are different for each C–C bond, and their magnitudes are not known, BDEs provide a poor measure of the bond strength.

The C-H bond order is more difficult to derive, although it is possible to do so due to the fact that local-mode XH stretching force constants have a similar dependence on the effective bond length, as discussed by Kraka and co-workers [15]. These authors showed that, in line with Badger's pioneering work [32], X–H stretching force constants can all be represented by one power relationship provided that all atoms X belong to the same period in the periodic table. Freindorf and coworkers [33] derived this power relationship for X–H bonds (X: atom of the second period) using F–H (bond order $n=1.0$) and $F \cdots H \cdots F^-$ ($n=0.5$). Since the F–H bond is stronger than a C–H bond, it is necessary to rescale this relationship so that the C–H bond in methane adopts an n value of 1.0. We derived the relationship for C–H bonds by utilizing the experimental frequencies of F–H ($4151.6 \ cm^{-1}$) [34], $F \cdots H \cdots F^-$ (583, 1286, 1331 cm^{-1}) [35], and methane [29].

$$n(CH) = 0.5243k_a(CH)^{0.29198}, \tag{42}$$

with a shift value Δn of 0.166 to obtain a bond order of 1.000 for C–H in methane. According to the bond order relationship given in Eq. 46, the C–H bonds in ethylene and benzene have bond orders of 1.010, in line with their similar nature. The acetylene C–H bond has a bond order of 1.046 and is much stronger. Actually, the ratio of the BDE values of CH in acetylene and methane (133.32 and 105.0 kcal mol^{-1} [36]) suggest a bond order of 1.270 for the former, which is far too large and a result of the unreliability of the BDE as a bond strength descriptor. The stabilization energy associated with the change in a methyl radical from a pyramidal form (adopted in ethane or the methyl portion of H_3C–H) with sp^3 hybridization to a planar form with sp^2 hybridization is much larger than that seen for an ethynyl radical, which essentially retains its structure and hybridization.

The ACS of naphthalene confirms that the molecule possesses two types of C–H bonds: those in the *peri* positions (α hydrogens: H11, H14, H15, H18) have smaller k_a values (5.047 mdyn/Å, Table 4) than those in the β positions (H12, H13, H16, H17; $k_a=5.089$ mdyn/Å). The corresponding bond orders of 1.009 and 1.007 indicate that the *peri*-exchange repulsion effects weaken the *peri*-C–H

bonds. There are four different C–C bonds with C–C stretching frequencies of 1398 (C1–C2, etc.), 1260 (C2–C3, etc.), 1258 (C4–C10, etc.), and 1232 cm^{-1} (C9–C10, see Figs. 1 and 3). The corresponding bond orders (based on the C–C stretching force constants k_a) are 1.603, 1.339, 1.335, and 1.288, respectively. This suggests that the peripheral ten-π-electron delocalization is slightly preferred over the six-π-electron delocalization in the benzene rings, which share a common π-electron pair.

The ACS of benzene and naphthalene shown in Figs. 2 and 3 contain a wealth of information that is not hampered by the deficiencies of the method and/or basis set used, the harmonic approximation, or the way of including anharmonicity corrections. Since experimental information is used throughout this work, the only possible deficiencies of the diagrams may arise from shortcomings in the experimental measurements. In future work, we will demonstrate that by introducing curvilinear coordinates, a unique set of N_{vib} coordinates can be specified, which significantly simplifies the determination and analysis of the local modes of ring molecules so that their properties can be directly related to electronic structural features.

Conclusions

In this work, we have demonstrated that, starting from a set of N_{vib} normal vibrational modes, we can determine a set of N_{vib} unique local vibrational modes, where the two sets are related by an ACS. Based on this work, the following conclusions can be drawn.

1) As a result of the fact that matrix **B** is rectangular, there are an infinite number of pseudoinverse matrices $\mathbf{U}=\mathbf{WB}^\dagger(\mathbf{BWB}^\dagger)^{-1}$ which can convert the Cartesian force constant matrix into an internal coordinate force constant matrix. The local vibrational modes are not affected by the choice of the matrix **W** [13]. It is proven that there is always just one set of local-mode force constants.

2) However, it was also shown that the choice $\mathbf{W}=\mathbf{M}^{-1}$ has some numerical advantages over the choice $\mathbf{W}=\mathbf{I}$.

3) The local-mode force constants k_a are identical to the reciprocal of the compliance constants of Decius. This was proven by deriving the relationship $\mathbf{C}=\mathbf{LD}^{-1}$. Although $\mathbf{LD}^{-1}$ does not comply with the general formula $\mathbf{U}=\mathbf{WB}^\dagger(\mathbf{BWB}^\dagger)^{-1}$, we showed that $\mathbf{LD}^{-1}$ provides a valid transformation of the force constant matrix $\mathbf{f}^x$.

4) Local and normal vibrational modes can be related to each other by rewriting the Wilson equation with the help of the compliance matrix $\mathbf{\Gamma}^q$, partitioning compliance and the **G** matrix into diagonal and off-diagonal parts, and successively switching on the latter with the aid of the scaling parameter λ. This yields an ACS between local and normal vibrational modes that can be used to quantitatively determine mass-coupling

between local vibrational modes. This was done for the local C–H and C–C stretching modes of benzene.

5) The change in local-mode frequency in an ACS is measured by the coupling frequency ω_{coup}, which accounts for all mass couplings of a given local mode $\mathbf{a}_n$ with all other $N_{vib} - 1$ local modes. The sum of all $|\omega_{coup}|$ is a minimum if the set of local vibrational modes is unique.

6) The local vibrational modes of Konkoli and Cremer are independent of the choice of internal coordinates. However, to derive an ACS, N_{vib} internal coordinates must be determined independent of the point group symmetry of a molecule. Some general rules for selecting the set of N_{vib} internal coordinates $\mathbf{q}$ for acyclic and cyclic molecules were discussed. An appropriate set of internal coordinates will be found if the sum $\sum_n^{N_{vib}} |\omega_{n,coup}|$ is a minimum.

7) The strengths of the C–H and C–C bonds in benzene and napthalene were explored with the aid of a power relationship between the bond order n and the local-mode force constants k_a derived from experimental frequencies. To do this, it was assumed that the reference molecules ethane and ethylene have bond orders of 1 and 2. For the C–H bond, a general power relationship for X–H was derived from the experimental frequencies of F–H and F $\cdots$ H $\cdots$ F$^-$ (bond orders of 1 and 0.5). A shift value was used in connection with this relationship to obtain a bond order of 1 for the C–H bonds in methane.

8) The local-mode-based description of the electronic structure of napthalene nicely shows the degree of π-electron delocalization. It reveals that the central C–C bond in napthalene is the weakest, with only 29 % π-character. The *peri*-positioned C–H bonds are weaker than the other C–H bonds of napthalene.

The existence of just one set of local-mode force constants for a given set of internal coordinates guarantees a conceptually consistent analysis of the electronic structure and chemical bonding in molecules with the help of local-mode force constants derived from normal vibrational modes [14, 15, 31, 37, 38].

References

1. Wilson EB, Decius JC, Cross PC (1955) Molecular vibrations. McGraw-Hill, New York
2. Woodward LA (1972) Introduction to the theory of molecular vibrations and vibrational spectroscopy. Oxford University Press, Oxford
3. Califano S (1976) Vibrational states. Wiley, London
4. Wilson S (1992) In: Wilson S (ed) Methods in computational chemistry, volume 4: molecular vibrations. Plenum, New York, pp 1–32
5. Neto N (1984) Chem Phys 87:43
6. Neto N (1984) Chem Phys 91:89
7. Neto N (1984) Chem Phys 91:101
8. Cremer D, Pople JA (1975) J Am Chem Soc 97:1354
9. Cremer D, Szabo KJ (1995) In: Juaristi E (ed) Conformational behavior of six-membered rings, analysis, dynamics, and stereo-electronic effects (Methods in Stereochemical Analysis series). Wiley–VCH, New York, p 59
10. Zou W, Izotov D, Cremer D (2011) J Phys Chem A 115:8731
11. Crawford B (1952) J Chem Phys 20:77
12. Polo SR (1956) J Chem Phys 24:1133
13. Winnewisser B, Watson JKG (2001) J Mol Spectrosc 205:227
14. Cremer D, Larsson JA, Kraka E (1998) In: Parkanyi C (ed) Theoretical and computational chemistry, volume 5: theoretical organic chemistry. Elsevier, Amsterdam, p 259
15. Kraka E, Larsson JA, Cremer D (2010) In: Grunenberg J (ed) Computational spectroscopy: methods, experiments and applications. Wiley, New York, pp 105–149
16. Decius J (1963) J Chem Phys 38:241
17. Cyvin SJ, Slater NB (1960) Nature 188(4749):485
18. Cyvin SJ (1971) Molecular vibrations and mean square amplitudes. Universitetsforlaget, Oslo, pp 68–73
19. Vijay Madhav M, Manogaran S (2009) J Chem Phys 131 (17):174112
20. Konkoli Z, Cremer D (1998) Int J Quant Chem 67:1
21. Eckart C (1935) Phys Rev 47:52
22. Larsson J, Cremer D (1999) J Mol Struct 485:385
23. McKean DC (1978) Chem Soc Rev 7:399
24. Henry BR (1987) Acc Chem Res 20(12):429
25. Becke AD (1993) J Chem Phys 98:5648
26. Stevens PJ, Devlin FJ, Chablowski CF, Frisch MJ (1994) J Phys Chem 98:11623
27. Dewar MJS, Ford GP (1977) J Am Chem Soc 99:1685
28. Hehre WJ, Radom L, Schleyer PvR, Pople JA (eds) (1986) Ab initio molecular orbital theory. Wiley, New York
29. Shimanouchi T (1972) Tables of molecular vibrational frequencies consolidated, vol. I. National Bureau of Standards, Washington, DC
30. Srivastava A, Singh V (2007) Ind J Pure Appl Phys 45:714
31. Kraka E, Cremer D (2009) Chem Phys Chem 10(4):686
32. Badger RM (1934) J Chem Phys 2(3):128
33. Freindorf M, Kraka E, Cremer D (2012) Int J Quant Chem 112:3174
34. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure, IV. Constants of diatomic molecules. Van Nostrand Reinhold, New York
35. Kawaguchi K, Hirota E (1987) J Chem Phys 87:6838
36. Luo YR (2007) Comprehensive handbook of chemical bond energies. CRC, Boca Raton
37. Oomens J, Kraka E, Nguyen MK, Morton TH (2008) J Phys Chem A 112(43):10774
38. Cremer D, Kraka E (2010) Curr Org Chem 14:1524