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Information on the electronic structure of a molecule and its chemical bonds is encoded in the molecular normal vibrational modes. However, normal vibrational modes result from a coupling of local vibrational modes, which means that only the latter can provide detailed insight into bonding and other structural features. In this work, it is proven that the adiabatic internal coordinate vibrational modes of Konkoli and Cremer [Int. J. Quantum Chem. **67**, 29 (1998)] represent a unique set of local modes that is directly related to the normal vibrational modes. The missing link between these two sets of modes are the compliance constants of Decius, which turn out to be the reciprocals of the local mode force constants of Konkoli and Cremer. Using the compliance constants matrix, the local mode frequencies of any molecule can be converted into its normal mode frequencies with the help of an adiabatic connection scheme that defines the coupling of the local modes in terms of coupling frequencies and reveals how avoided crossings between the local modes lead to changes in the character of the normal modes. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4747339]

I. INTRODUCTION

Determining the strength of the chemical bond is a difficult task because bonds are not observable.[1–5] This difficulty results from the fact that the chemical bond is just a concept (rather than a measurable quantity) for explaining structure and stability of molecules. There is a multitude of interactions between the nuclei and the electrons of a molecule with the consequence that some atoms are strongly attracted to each other, whereas other atoms only weakly attract or even repel each other. There is no way of deriving from these complex interactions an exact definition of the chemical bond in the quantum mechanical sense because this would imply a set of hermitian operators for bond properties such as bond energy, bond length, bond density, etc. Since this is not possible, one can describe the chemical bond only on the basis of one of the many models of bonding.[1–7] Some of these models are based on observable molecular properties such as relative energy, geometry, or electron density distribution whereas others revert to quantum mechanics and use molecular orbitals, the molecular wave function, or molecular density matrices as a means to describe bonding.[1–7]

The commonly used approach for assessing the strength of a chemical bond is based on measured or calculated bond dissociation energies (BDEs).[8,9] If a chemical bond is fully destroyed in a dissociation reaction, the energy needed for this process should provide a dynamic measure for the bond strength where the term dynamic is used to distinguish from static bond strength descriptors such as bond length, bond density, or bond polarity. The use of BDEs as bond strength descriptors is problematic in several ways. For example, in the hydrogen molecule electron density is drawn from the outside into the bonding region. If the HH bond is cleaved there is a relaxation of the bond density in the way that the spherical charge distribution of the H atom is reestablished. By measur-

ing the bond strength relative to the density-relaxed H atom, the actual bond strength of the HH bond is underestimated and can no longer be related to any other bond strength because density relaxation is different in each case and accordingly a flawed comparison of bond strengths results.[10,11]

If in the dissociation process larger fragments are generated, there is, besides the relaxation of the electron density of the original molecules, also a relaxation of the geometries of the fragments thus yielding more stable fragment structures. Hence, the stabilization energies (SE) of the fragments caused by both electron density and geometry relaxation have to be added to the BDE of a bond to obtain the intrinsic BDE, IBDE:

$$IBDE(H_m A\text{-}BH_n) = BDE(H_m A\text{-}BH_n) + SE(H_m A\cdot)$$
$$+ SE(\cdot BH_n), \quad (1)$$

which is a true measure of the strength of bond $A - B$ in molecule $H_m A\text{-}BH_n$. In the case of the CH bonds in methane, SE can take values as large as 40 kcal/mol, i.e., BDE and IBDE differ significantly in magnitude.[11] Also, SE values of the same type of bond in different molecules can differ considerably so that *a priori* no relationship between BDE and IBDE values can be expected. Since there is currently no generally applicable way of calculating SEs, and by this IBDEs, from known BDE values, measured or calculated BDEs are commonly used as bond strength descriptors despite the fact that they may not be reliable and often be misleading when comparing the strength of a bond $A - B$ in different molecules.

The assessment of bond strength via a dynamic process is in principle a viable way, however it should be done without changing the electron density distribution or molecular geometry so that there is no need of determining SE

values. An infinitesimally small change in the bonding situation leads to a better bond strength descriptor than any finite or ultimate change in bonding because it does not imply any electron density or geometry relaxation and leaves the chemical bond intact. Molecular vibrations probe chemical bonding and, therefore, can be considered a possible source for reliable bond strength descriptors. Each K-atomic molecule possesses $3K - L$ normal mode vibrations (L: sum of translations and rotations). These are characterized by normal mode frequency ω_μ and normal mode force constant k_μ, which refer to infinitesimally small changes in the positions of the nuclei of the molecule during a normal mode vibration $\mathbf{l}_\mu$. Hence, these properties should be suitable dynamic descriptors of the strength of the chemical bond.[11]

There are two obstacles that have to be overcome before using these vibrational properties as strength indicators. The first has to do with the mass dependence of the frequencies. For example, the molecules HH and DD possess the same electronic structure and the same bond strength whereas their vibrational frequencies strongly differ because of the different reduced masses. For the purpose of eliminating the mass dependence, one has to refer to vibrational force constants, which are independent of the reduced masses and, thereby, directly reflect the electronic factors determining the strength of the chemical bond.[12, 13]

The second problem is more serious and concerns the delocalized character of the normal vibrational modes.[12, 13] It is misleading to describe individual bonds of a molecule by a specific normal vibrational mode. Accurate bond strength descriptors are only obtained when referring to localized rather than delocalized vibrational modes, where the former can be associated with specific (diatomic) bond units. The vibrational force constants of localized (or shortly *local*) vibrational modes are the key for obtaining reliable bond strength descriptors. Because of this, we will review in Sec. II how local modes are determined either experimentally or computationally. In Sec. III, it is proven that normal and local vibrational modes are directly related, where the link between them is provided by the inverse force constant matrix. Computational evidence for this proof is given for a test set of 40 typical organic molecules. The relationship between local and normal vibrational modes will be explored in Sec. IV by determining and analyzing the coupling between vibrational modes. Conclusions of this work will be drawn in Sec. V.

II. DETERMINATION OF LOCAL VIBRATIONAL MODES

There has been 60 years of work in vibrational spectroscopy which focused on the determination of unique local vibrational modes that do not depend on the coordinates used to describe the molecule and can be clearly associated with just one (diatomic, triatomic, etc.) fragment of the molecule.[12, 14–20] Most of this work has led to information on local stretching modes in special cases such as the CH or NH bonds[18–20] without any possibility of generalization. In this connection, it should be mentioned that the determination of functional group frequencies for ketones, aldehydes, alkenes,

alkanes, alcohols, etc. does not lead to local mode frequencies because the functional group frequencies are always contaminated by coupling with other modes and are far from providing any quantitative measure of the bond strength.

McKean[18] solved the problem of measuring local mode frequencies in the case of CH stretching modes by exploiting the dependence of the vibrational frequency on the reduced masses. He synthesized isotopomers of a given molecule, in which all CH bonds except the target bond were replaced by CD bonds. The change in mass achieved by converting a CH_3 or CH_2 group into a CD_2H and CDH group decouples the remaining CH stretching mode from all CD stretching modes. Due to isotope substitution, the CH stretching mode is largely isolated, which means that it is not only decoupled from the CD stretching vibrations but also from other stretching, bending, or torsional modes. Also, all Fermi resonances for the CH stretching mode are suppressed. Hence McKean's isolated CH stretching modes can be considered to closely approximate the true local modes, which was later confirmed by Larsson and Cremer.[21]

McKean prepared a large number of isotopomers to measure isolated CH stretching frequencies and to investigate their dependence on geometric and electronic features of a given molecule.[22–25] He showed that, in this way, CH bonds can be used as sensitive antenna or probes testing the properties of molecules. While his first work focused on CH bonds, McKean and co-workers studied later other XH bonds (X: Si, Ge, P, As).[19, 26] In addition, other authors used McKean's approach to describe local XH stretching modes.[27–29]

Investigations involving bonds other than XH bonds revealed the large difficulties experiment faces when a generalization of McKean's approach is attempted. For the purpose of decoupling one internal stretching mode from other stretching modes of the same type, the change in mass by isotope substitution must be so large that it changes the mass ratio significantly. Replacement of H by deuterium results in a doubling of the mass and a satisfactory suppression of coupling and Fermi resonances so that any residual coupling for the isolated CH stretching modes is estimated to be less than 5 cm^{-1}. For a CC bond, one would obtain a very small effect if ^{12}C is replaced by ^{13}C or even ^{14}C since the change in the mass ratio is too small in these cases to play any significant role in the localization of the CC stretching motion.

A generalization of McKean's approach faces too many difficulties to play any important role in the description of, e.g., general AB bonds. The same holds for obtaining local mode information from measured overtone spectra. Henry[20] has demonstrated that the higher overtones of an XH stretching mode can be reasonably well described with an anharmonic potential of a quasidiatomic molecule.[20] Higher overtones ($\Delta v \leq 3$) of XH stretching modes reveal increasingly local mode character. For overtones with $\Delta v = 5, 6$, one observes one stretching band for each unique XH bond, even if there are several symmetry equivalent XH bonds in the molecule. This is a result of the fact that for overtones with $\Delta v = 5, 6$ the different linear combinations of symmetry equivalent XH stretchings become effectively degenerate. Because of their low intensities, these overtone spectra can only be recorded by intracavity dye laser photoacoustic

spectroscopy, which limits the applicability of this technique again to XH stretching modes.[20]

Given this difficult experimental situation, theory has made an important contribution. Cremer and co-workers[30–34] were the first to demonstrate that local vibrational modes can be determined in a similar way as normal vibrational modes are determined. Konkoli and Cremer[30] proved that this implies the calculation of adiabatically relaxed vibrational modes, which are driven by changes in an associated internal coordinate. Therefore, the term *adiabatic internal coordinate modes (AICoMs)* was coined to characterize the nature of the local vibrational modes obtained. In this work, we will use, for reasons of simplicity, the term local modes throughout. The stretching force constants obtained by Konkoli and Cremer for the local modes have been used to assess the strength of CC[34] and CF bonds.[35,36] It has been shown that local vibrational frequencies can be derived from experimental frequencies[34] and that normal vibrational modes can be characterized in terms of the local modes.[30,31] The validity of the Badger rule[37] has been demonstrated for polyatomic molecules by utilizing the local mode force constants.[10] Also, the local modes have been used to analyze and describe the changes of the generalized vibrational modes of a reaction complex along the reaction path of a chemical reaction.[38–42]

Here, we use the term *local modes* in the strict sense of its meaning as a mode driven by the displacement of just one internal coordinate such as a bond length or a bond angle. Of course, we can use also curvilinear coordinates such as the puckering or deformation coordinates of an N-membered ring,[43,44] which would lead to a local mode involving the displacement of N-atoms. Yet another possible line of application of the local modes is the use of symmetry coordinates as leading parameters, for example involving all stretching displacements of (a) given molecular group(s). This would lead to delocalized vibrational modes similar to those obtained by Reiher and co-workers.[45–47] These authors calculate unitarily transformed normal modes associated with a given band in the vibrational spectrum of a polymer where the criteria for the transformation are inspired by those applied for the localization of molecular orbitals. The authors speak in this case of *localized* vibrational modes because the modes are localized in just a few units of a polymer. Nevertheless, Reiher's modes are still delocalized within the polymer units and must not be mistaken with the local vibrational modes discussed in the current work. In passing on, we note that the frequencies of the localized vibrational modes cannot be measured (because they fulfill just the task of mathematical tools to understand measured vibrational spectra) whereas the frequencies of the local modes can be measured as was already demonstrated in selected cases.[10,21] Therefore it is desirable to use the terms local vibrational modes and localized normal vibrational modes strictly separated and distinguish between them as real and arbitrary vibrational modes.

In this work, we investigate the local vibrational modes of Konkoli and Cremer[30] for the purpose of clarifying whether they are unique, i.e., represent the only set of local vibrational modes directly related to the normal vibrational modes. This question is timely in view of the intensive work, which has been done with so-called *compliance constants*. The latter

have their roots in vibrational spectroscopy and are considered to provide a reliable measure of the bond strength.[15–17,48] They emerged when spectroscopists realized that the normal mode force constants are coordinate dependent (i.e., change with the choice of internal coordinates) and reflect the coupling between vibrational modes (i.e., correspond to delocalized rather than localized modes).[12] There were early suggestions to use the inverse of the force constant matrix[14,15] because the inverse force constants are invariant under coordinate transformations.[16] Decius[17] invented the term compliance constants for the inverse diagonal elements of the force constant matrix $\mathbf{F}$, $(\mathbf{F}^{-1})_{ii} = \Gamma_i$, and showed that they represent meaningful molecular parameters.[49] Later it was shown that bond compliance constants provide some measure of the bond strength, which is not contaminated by contributions from other bonds.[50,51] On this basis an increasing number of different bonding situations were investigated.[48,50–56]

In this work, local mode force constants and compliance constants are compared with each other. It is shown that compliance constants are the missing link between normal mode and local mode force constants. By showing this, we provide the proof that the local modes of Konkoli and Cremer[30] are the only local vibrational modes that are directly associated with the (delocalized) normal vibrational modes and accordingly they are unique. In this way, the work of Konkoli and Cremer[30–33] has to be seen as a useful extension of vibrational spectroscopy.

III. LOCAL VIBRATIONAL MODES

By solving the Euler-Lagrange equations for a vibrating molecule, the basic equation of vibrational spectroscopy given by Eq. (1) is obtained,[12]

$$\mathbf{F^q D} = \mathbf{G}^{-1}\mathbf{D\Lambda}, \qquad (2)$$

where

$$\mathbf{G} = \mathbf{B M}^{-1}\mathbf{B}^{\dagger}, \qquad (3)$$

where $\mathbf{F^q}$ is the force constant matrix, and $\mathbf{D}$ contains the normal mode vectors $\mathbf{d}_\mu$ ($\mu = 1, \ldots, N_{vib}$ with $N_{vib} = 3K - L$) given as column vectors. Both matrices are expressed in terms of internal coordinates $\mathbf{q}$. Matrix $\mathbf{G}$ is the Wilson matrix[12,57] and matrix $\mathbf{\Lambda}$ is a diagonal matrix containing the vibrational eigenvalues $\lambda_\mu = 4\pi^2 c^2 \omega_\mu^2$ where ω_μ represents the (harmonic) vibrational frequency of mode $\mathbf{d}_\mu$ given in reciprocal *cm* and c is the speed of light. The vibrational problem requires the calculation of the analytical second derivatives of the molecular energy with the help of quantumchemical methods and therefore it is solved in terms of Cartesian coordinates

$$\mathbf{f^x L} = \mathbf{M L \Lambda}, \qquad (4)$$

where $\mathbf{f^x}$ is the force constant matrix, $\mathbf{L}$ collects the vibrational eigenvectors $\mathbf{l}_\mu$, and $\mathbf{M}$ is the mass matrix of the molecule in question. Matrix $\mathbf{L}$ is renormalized according to $\boldsymbol{\ell}_\mu^{\dagger}\boldsymbol{\ell}_\mu = 1$. The force constant matrix can be written in three different ways using either Cartesian coordinates, internal coordinates

$\mathbf{q}$, or normal coordinates $\mathbf{Q}$,

$$\mathbf{F^q} = \mathbf{C}^\dagger \mathbf{f^x} \mathbf{C}, \qquad (5)$$

$$\mathbf{F^Q} = \mathbf{K} = \mathbf{L}^\dagger \mathbf{f^x} \mathbf{L}. \qquad (6)$$

Matrix $\mathbf{C}$ transforms normal modes from internal coordinate space to Cartesian space[58,59]

$$\mathbf{l}_\mu = \mathbf{C} \mathbf{d}_\mu \qquad (7)$$

and is given by

$$\mathbf{C} = \mathbf{M}^{-1} \mathbf{B}^\dagger \mathbf{G}^{-1}. \qquad (8)$$

The elements of the $\mathbf{B}$ matrix are defined by the partial derivatives of internal coordinates with regard to Cartesian coordinates.[12] Matrices $\mathbf{B}$ and $\mathbf{C}$ are closely related,

$$\mathbf{BC} = \mathbf{B} \mathbf{M}^{-1} \mathbf{B}^\dagger \mathbf{G}^{-1} = \mathbf{GG}^{-1} = \mathbf{I}. \qquad (9)$$

Matrix $\mathbf{B}$ is used to convert from vibrational modes expressed in Cartesian coordinates to modes expressed in internal coordinates according to

$$\mathbf{D} = \mathbf{BL}. \qquad (10)$$

Konkoli and Cremer[30] determined the local vibrational modes directly from the Euler-Lagrange equations by setting all masses equal to zero with the exception of those of the molecular fragment (e.g., bond AB) carrying out a localized vibration. They proved that this is equivalent to requiring an adiabatic relaxation of the molecule after enforcing a local displacement of atoms by changing a specific internal coordinate as, e.g., a bond length in the case of a diatomic molecular fragment (*leading parameter principle*).[30] The local modes obtained in this way take the form,[30]

$$\mathbf{a}_i = \frac{\mathbf{K}^{-1} \mathbf{d}_i^\dagger}{\mathbf{d}_i \mathbf{K}^{-1} \mathbf{d}_i^\dagger} \qquad (11)$$

where the subscript i specifies an internal coordinate q_i and the local mode is expressed in terms of normal coordinates $\mathbf{Q}$ associated with force constant matrix $\mathbf{K}$ of Eq. (6). Note that $\mathbf{d}_i$ is now a row vector of the matrix $\mathbf{D}$. The local mode force constant $k_a^{(i)}$ of mode i is obtained from Eq. (12),

$$k_a^{(i)} = \mathbf{a}_i^\dagger \mathbf{K} \mathbf{a}_i = (\mathbf{d}_i \mathbf{K}^{-1} \mathbf{d}_i^\dagger)^{-1}. \qquad (12)$$

Local mode force constants, contrary to normal mode force constants, have the advantage of being independent of the choice of the coordinates to describe the molecule in question. This relates them to the compliance constants Γ_i. In the following, we derive a simple relationship between $k_a^{(i)}$ and Γ_i.

Utilizing Eqs. (5)–(7), the internal coordinate force constant matrix can be written as

$$\mathbf{F^q} = (\mathbf{D}^{-1})^\dagger \mathbf{L}^\dagger \mathbf{f^x} \mathbf{L} \mathbf{D}^{-1} = (\mathbf{D}^{-1})^\dagger \mathbf{K} \mathbf{D}^{-1}. \qquad (13)$$

Hence, the inverse force constant matrix, i.e., the compliance matrix $\mathbf{\Gamma^q}$, and its diagonal elements are given by

$$\mathbf{\Gamma^q} = (\mathbf{F^q})^{-1} = \mathbf{D} \mathbf{K}^{-1} \mathbf{D}^\dagger, \qquad (14)$$

$$(\mathbf{\Gamma^q})_i = \mathbf{d}_i \mathbf{K}^{-1} \mathbf{d}_i^\dagger, \qquad (15)$$

which proves that in view of Eq. (12)

$$k_a^{(i)} = 1/(\mathbf{\Gamma^q})_{ii} = 1/\Gamma_i, \qquad (16)$$

i.e., the inverse of the local mode force constants of Konkoli and Cremer[30] are the compliance constants of Decius.[17]

This can be confirmed by starting directly from the Konkoli-Cremer equation for the local vibrational modes,[30] which implies a constrained minimization of the molecular geometry for the situation that the internal displacement coordinate q_i leading the local mode of a molecular fragment ϕ_i is set to a constant $q_i^\star$,

$$\frac{\partial}{\partial q_i} \left[\frac{1}{2} \mathbf{q}^\dagger \mathbf{F}^q \mathbf{q} - \eta_i(q_i - q_i^\star) \right] = 0 \qquad (17)$$

for $i = 1, 2, \ldots, N_{vib}$ where the harmonic approximation of the potential V is used. This leads to the column vector $\boldsymbol{\eta}$

$$\boldsymbol{\eta} = \mathbf{F}^q \mathbf{q}, \qquad (18)$$

$$\mathbf{q} = (\mathbf{F}^q)^{-1} \boldsymbol{\eta} = \mathbf{\Gamma}^q \boldsymbol{\eta}, \qquad (19)$$

or for a specific internal coordinate q_i

$$\frac{\eta_i}{q_i^\star} = \frac{1}{(\mathbf{\Gamma}^q)_{ii}} = \Gamma_i^{-1}, \qquad (20)$$

where the constraint $q_i = q_i^\star$ is used. The result is that the ratio of the Langrange multiplier η_i, which has the unit of a force, and the displacement $q_i^\star$ (in Å) is equal to a constant, which is the reciprocal of the compliance constant given in the units of a force constant. From the work of Konkoli and Cremer,[30] one can prove that

$$\frac{\eta_i}{q_i^\star} = (\mathbf{d}_i \mathbf{K}^{-1} \mathbf{d}_i^\dagger)^{-1} = k_a^{(i)}, \qquad (21)$$

i.e., again the local mode force constant $k_a^{(i)}$ of local mode $\mathbf{a}_i$ is equal to the reciprocal of the corresponding compliance constant Γ_i.

In Figure 1, 38 typical organic molecules augmented by two H-bonded base pairs are shown, for which the local mode force constants according to Konkoli and Cremer[30] and the compliance constants according to Decius[17] are calculated using density functional theory at the B3LYP/6-31G(d,p) level of theory.[60–62] Relevant data are listed in Table I. The stretching force constants range from 0.06 (H-bonding) to 20.3 mdyn/Å (CN stretching in HCN, i.e., from very weak to very strong bonding interactions. The data in Table I and Figure 2(a) reveal that the local mode force constants order different types of bonds according to their strength where this order is in agreement with common chemical understanding of strength increase with bond order, orbital overlap, bond polarity, ring strain, or conjugation possibilities. The same applies to the local mode bending force constants, which increase with the stiffness of the bonds, the multiple bond character of the two bonds involved, or ring strain (see Figure 2(b)).

As shown in Figures 2(a) and 2(b), and in Table I the correctness of Eq. (16) is fully confirmed. An accurate calculation of $\mathbf{\Gamma}$ exactly fulfills Eq. (16). When working with local mode force constants and compliance constants, a number of disadvantages of the latter become obvious:
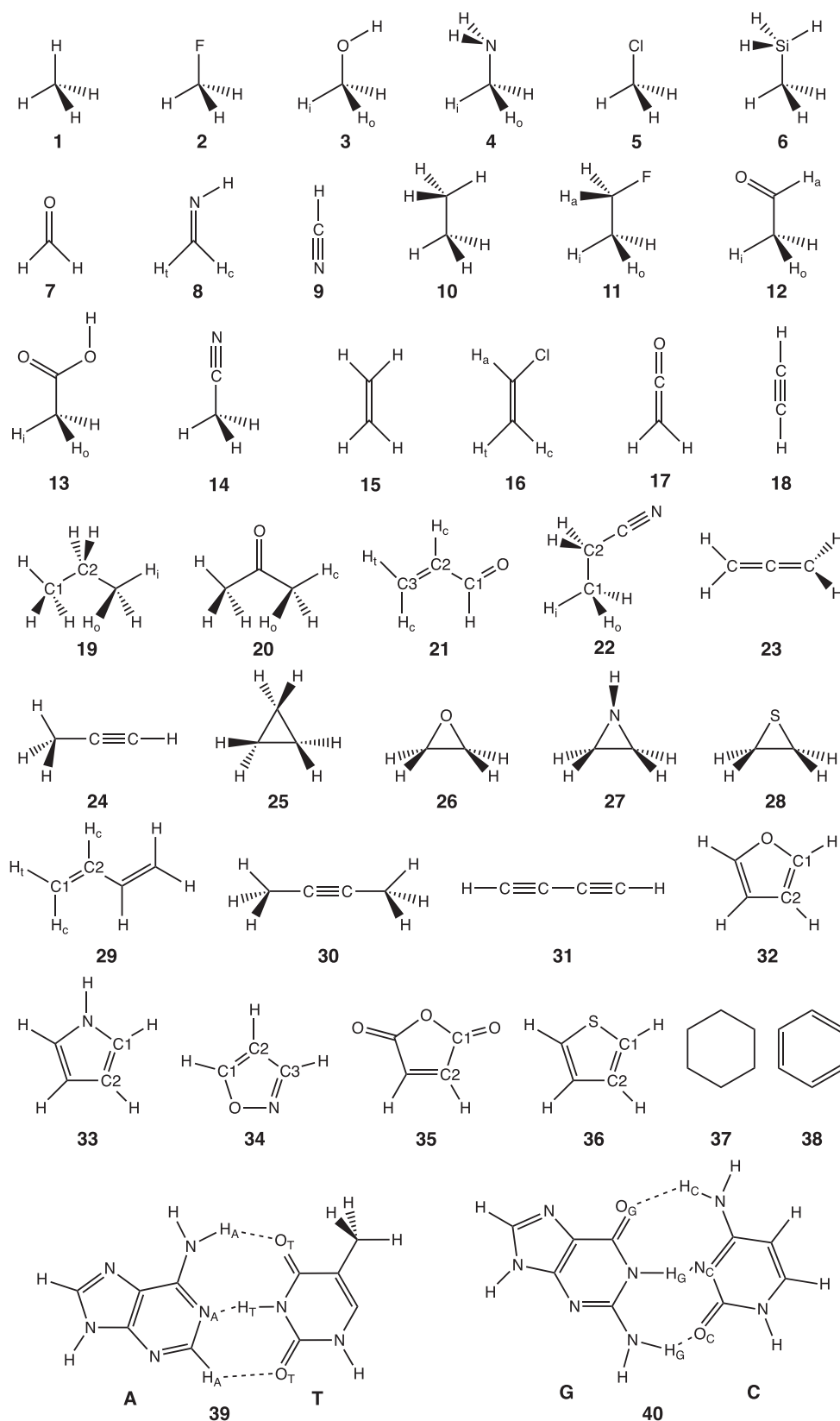
FIG. 1. Molecules investigated in this work.

- The compliance constants of Decius are not associated with a vibrational mode. There are no *compliance frequencies* or *compliance masses.* With the proof given above, they can now be related to the local vibrational modes of Konkoli and Cremer.[30]

- Since compliance constants are a measure for the weakness of a bond (the larger their value, the weaker is a bond), their usefulness as bond strength descriptors is limited. It is difficult to associate certain types of atom-atom interactions (electrostatic, dispersion, etc.)

TABLE I. Comparison of bond lengths R, local mode force constants $k_a^{(i)}$, and local mode frequencies $\omega_a^{(i)}$ with compliance constants Γ_i for the bonds in molecules **1-40** (see Figure 1). B3LYP/6-31G(d,p) calculations.

No	Bond	R [Å]	$k_a^{(i)}$ [mdyn/Å]	ω_a [cm^{-1}]	Γ_i [Å/mdyn]	No	Bond	R [Å]	$k_a^{(i)}$ [mdyn/Å]	ω_a [cm^{-1}]	Γ_i [Å/mdyn]
1.1	C–H	1.092	5.365	3129	0.186	22.3	C2–H	1.096	5.170	3072	0.193
2.1	C–H	1.096	5.178	3075	0.193	22.4	C1–C2	1.539	3.916	1052	0.255
2.2	C–F	1.383	5.405	1117	0.185	22.5	C–C2	1.466	4.834	1169	0.207
3.1	C–O	1.418	4.908	1102	0.204	22.6	C≡N	1.161	19.750	2278	0.051
3.2	C–H$_i$	1.093	5.298	3110	0.189	23.1	C–H	1.087	5.521	3175	0.181
3.3	C–H$_o$	1.101	4.946	3005	0.202	23.2	C=C	1.306	10.569	1729	0.095
3.4	O–H	0.965	8.150	3820	0.123	24.1	C–H	1.095	5.195	3080	0.192
4.1	C–H$_i$	1.104	4.798	2960	0.208	24.2	C–H$_r$	1.065	6.488	3442	0.154
4.2	C–H$_o$	1.095	5.211	3084	0.192	24.3	C–C	1.459	5.250	1219	0.190
4.3	C–N	1.464	4.426	1078	0.226	24.4	C≡C	1.207	17.373	2217	0.058
4.4	N–H	1.017	6.783	3499	0.147	25.1	C–H	1.086	5.540	3180	0.181
5.1	C–H	1.089	5.445	3153	0.184	25.2	C–C	1.508	4.137	1082	0.242
5.2	C–Cl	1.803	2.903	743	0.344	26.1	C–H	1.090	5.366	3130	0.186
6.1	C–H	1.094	5.258	3098	0.190	26.2	C–C	1.469	5.349	1230	0.187
6.2	C–Si	1.888	2.738	744	0.365	26.3	C–O	1.430	4.068	1004	0.246
6.3	Si–H	1.488	2.838	2225	0.352	27.1	C–H$_t$	1.087	5.477	3162	0.183
7.1	C–H	1.110	4.687	2925	0.213	27.2	C–H$_c$	1.088	5.419	3145	0.185
7.2	C=O	1.207	13.612	1836	0.073	27.3	C–C	1.485	4.769	1162	0.210
8.1	C–H$_c$	1.099	5.062	3040	0.198	27.4	C–N	1.473	3.733	990	0.268
8.2	C–H$_t$	1.094	5.314	3115	0.188	27.5	N–H	1.019	6.734	3487	0.149
8.3	C=N	1.270	11.155	1712	0.090	28.1	C–H	1.086	5.538	3179	0.181
8.4	N–H	1.026	6.448	3412	0.155	28.2	C–C	1.481	4.559	1136	0.219
9.1	C–H	1.069	6.346	3404	0.158	28.3	C–S	1.837	2.552	705	0.392
9.2	C≡N	1.157	20.287	2308	0.049	29.1	C1–H$_c$	1.087	5.554	3184	0.180
10.1	C–H	1.095	5.215	3085	0.192	29.2	C1–H$_t$	1.085	5.636	3208	0.177
10.2	C–C	1.530	4.149	1083	0.241	29.3	C2–H$_c$	1.090	5.429	3148	0.184
11.1	C–H$_i$	1.095	5.237	3092	0.191	29.4	C1=C2	1.340	9.301	1622	0.108
11.2	C–H$_o$	1.094	5.284	3106	0.189	29.5	C2–C2	1.457	5.153	1207	0.194
11.3	C–H$_a$	1.097	5.096	3050	0.196	30.1	C–H	1.096	5.164	3070	0.194
11.4	C–C	1.516	4.269	1099	0.234	30.2	C–C	1.461	5.242	1218	0.191
11.5	C–F	1.393	5.040	1079	0.198	30.3	C≡C	1.209	17.153	2203	0.058
12.1	C–H$_o$	1.097	5.148	3066	0.194	31.1	C–H	1.065	6.493	3443	0.154
12.2	C–H$_i$	1.091	5.407	3142	0.185	31.2	C≡C	1.212	16.679	2172	0.060
12.3	C–H$_a$	1.114	4.540	2879	0.220	31.3	C–C	1.369	7.685	1474	0.130
12.4	C–C	1.507	4.081	1074	0.245	32.1	C2–H	1.080	5.828	3262	0.172
12.5	C=O	1.211	13.234	1810	0.076	32.2	C1–H	1.079	5.913	3286	0.169
13.1	C–H$_o$	1.094	5.224	3088	0.191	32.3	C2–C2	1.435	5.573	1256	0.179
13.2	C–H$_i$	1.089	5.485	3164	0.182	32.4	C1=C2	1.361	8.028	1507	0.125
13.3	C–C	1.507	4.268	1099	0.234	32.5	C1–O	1.364	5.589	1176	0.179
13.4	C–O	1.358	5.666	1184	0.176	33.1	C2–H	1.081	5.794	3252	0.173
13.5	C=O	1.210	12.933	1789	0.077	33.2	C1–H	1.080	5.847	3267	0.171
13.6	O–H	0.972	7.817	3741	0.128	33.3	C2–C2	1.425	5.808	1282	0.172
14.1	C–H	1.093	5.299	3110	0.189	33.4	C1=C2	1.378	7.376	1445	0.136
14.2	C–C	1.460	5.105	1202	0.196	33.5	C1–N	1.375	6.463	1303	0.155
14.3	C≡N	1.160	19.820	2282	0.050	33.6	N–H	1.007	7.523	3685	0.133
15.1	C–H	1.087	5.572	3189	0.179	34.1	C1–O	1.345	5.881	1207	0.170
15.2	C=C	1.330	9.911	1674	0.101	34.2	C2–H	1.079	5.909	3284	0.169
16.1	C–H$_a$	1.084	5.688	3222	0.176	34.3	C3–H	1.082	5.783	3249	0.173
16.2	C–H$_t$	1.085	5.642	3209	0.177	34.4	C1=C2	1.360	8.024	1507	0.125
16.3	C–H$_c$	1.084	5.688	3222	0.176	34.5	C2–C3	1.424	5.801	1281	0.172
16.4	C=C	1.327	9.818	1667	0.102	34.6	C3–N	1.313	8.232	1470	0.121
16.5	C–Cl	1.752	3.320	794	0.301	34.7	O–N	1.399	3.713	919	0.269
17.1	C–H	1.082	5.757	3242	0.174	35.1	C–H	1.082	5.816	3258	0.172
17.2	C=C	1.314	9.815	1666	0.102	35.2	C=C	1.335	9.469	1637	0.106
17.3	C=O	1.171	16.290	2008	0.061	35.3	C–C	1.491	4.268	1099	0.234
18.1	C–H	1.066	6.472	3437	0.155	35.4	C=O	1.198	13.595	1835	0.074
18.2	C≡C	1.205	17.645	2234	0.057	35.5	C–O	1.394	3.835	975	0.261

TABLE I. (*Continued.*)

No	Bond	R [Å]	$k_a^{(i)}$ [mdyn/Å]	ω_a [cm^{-1}]	Γ_i [Å/mdyn]	No	Bond	R [Å]	$k_a^{(i)}$ [mdyn/Å]	ω_a [cm^{-1}]	Γ_i [Å/mdyn]
19.1	C1–H$_o$	1.096	5.178	3074	0.193	36.1	C2–H	1.084	5.679	3220	0.176
19.2	C1–H$_i$	1.095	5.217	3086	0.192	36.2	C1–H	1.081	5.827	3261	0.172
19.3	C2–H	1.098	5.088	3048	0.197	36.3	C2–C2	1.430	5.690	1269	0.176
19.4	C1–C2	1.532	4.066	1072	0.246	36.4	C1=C2	1.367	7.657	1472	0.131
20.1	C–H$_o$	1.096	5.100	3051	0.196	36.5	C–S	1.736	3.653	843	0.274
20.2	C–H$_i$	1.091	5.421	3146	0.184	37.1	C–H	1.097	5.115	3026	0.199
20.3	C–C	1.520	3.853	1044	0.260	37.2	C–H	1.100	5.016	3056	0.196
20.4	C=O	1.216	12.777	1779	0.078	37.3	C–C	1.537	3.923	1054	0.255
21.1	C3–H$_c$	1.088	5.539	3180	0.181	38.1	C–H	1.086	5.564	3187	0.180
21.2	C3–H$_t$	1.085	5.651	3212	0.177	38.2	C–C	1.396	6.600	1366	0.152
21.3	C2–H$_c$	1.087	5.574	3190	0.179	39.1	(N)O$_A$...H$_T$	1.923	0.178	564	5.618
21.4	C1–H$_a$	1.114	4.555	2884	0.220	39.2	H$_A$...O$_T$	2.798	0.059	326	16.949
21.5	C2=C3	1.337	9.410	1632	0.106	39.3	N$_A$...H$_T$	1.796	0.280	713	3.571
21.6	C1–C2	1.475	4.577	1138	0.218	40.1	O$_G$...H$_C$(N)	1.748	0.274	699	3.650
21.7	C1=O	1.215	12.719	1774	0.079	40.2	(N)H$_G$...O$_C$	1.902	0.250	667	4.000
22.1	C1–H$_i$	1.093	5.299	3110	0.189	40.3	H$_G$...N$_C$	1.895	0.467	921	2.141
22.2	C1–H$_o$	1.093	5.319	3116	0.188						

with increasing Γ_i values. This is the reason why chemists did not use compliance constants for a long time. One has tried to rectify this problem by using the inverse of the compliance constants as local force constants. However, this implies that the inverse of the diagonal elements of the inverse normal mode force constant matrix is a local mode force constant, which has never been proven. Equation (16) provides this proof.

- A significant problem with the interpretation of the compliance matrix $\boldsymbol{\Gamma}$ are the existence of off-diagonal elements, the meaning of which and their relevance for the diagonal elements is not known. On the diagonal of $\boldsymbol{\Gamma}$, there are sometimes small compliance constants between atoms that are separated by many Å, thus erroneously suggesting strong non-covalent interactions. The occurrence of these terms led Baker and Pulay to the conclusion that compliance constants cannot be used to accurately describe the strength of weak bonds.[55] For the local mode force constants this problem does not exist because they are driven by one internal coordinate each (leading parameter principle), are not associated with off-diagonal elements, and lead to meaningful values associated with meaningful molecular internal coordinates.
- The determination of compliance constants implies the calculation of an inverse matrix. This requires more computational work and leads to reduced accuracy in the compliance constants compared to that of the local mode force constants.

The proof leading to Eq. (16) and the discussion of the properties of compliance constants have two important implications. (1) The AICoM local vibrational modes of Konkoli and Cremer[30] are the only local modes that are directly related to the normal vibrational modes of a molecule. This follows from the fact that they can be directly connected via matrix $\boldsymbol{\Gamma} = \mathbf{F}^{-1}$. (ii) The compliance constants are superfluous as

bond descriptors because the local mode force constants already fulfill this task and there is no reason for working with the less accurate and more costly to calculate reciprocal of a force constant for the purpose of describing the weakness of a chemical bond. In the following, we will clarify the relationship between local and vibrational modes.

IV. AN ADIABATIC CONNECTION SCHEME FOR RELATING LOCAL TO NORMAL VIBRATIONAL MODES

For the purpose of relating local vibrational modes to normal modes, one has to express the force constants matrix in terms of local mode force constants according to

$$\mathbf{F}^a = \mathbf{A}^\dagger \mathbf{K} \mathbf{A}, \qquad (22)$$

where $\mathbf{A}$ collects the local mode vectors of Eq. (11), i. e.,

$$\mathbf{A} = \mathbf{K}^{-1}\mathbf{D}^\dagger[(\mathbf{D}\mathbf{K}^{-1}\mathbf{D}^\dagger)_d]^{-1} \qquad (23)$$

(subscript d denotes the diagonal terms of the matrix product). The diagonal part of $\mathbf{F}^a$ contains the local mode force constants $k_a^{(i)}$ whereas the off-diagonal elements provide a link to the normal vibrational modes. By using a scaling factor λ, the matrix $\mathbf{F}^a$ could be written as $\mathbf{F}_d^a + \lambda\mathbf{F}_o^a$, i.e., as the sum of a diagonal part $\mathbf{F}_d^a$ and an off-diagonal part $\mathbf{F}_o^a$. For $\lambda = 0$ the local mode force constant matrix (having on the diagonal the $k_a^{(i)}$ values) and for $\lambda = 1$ the normal mode constant matrix (expressed in local modes) would be obtained. With this objective in mind and using Eq. (13), Eq. (2) is re-written as

$$\mathbf{A}^\dagger \mathbf{K} \mathbf{A}(\mathbf{A}^{-1}) = \mathbf{F}^a(\mathbf{A}^{-1}) = \left(\mathbf{F}_d^a + \lambda\mathbf{F}_o^a\right)(\mathbf{A}^{-1})$$

$$= (\mathbf{A}^\dagger \mathbf{D}^\dagger \mathbf{G}^{-1}\mathbf{D}\mathbf{A})(\mathbf{A}^{-1})\boldsymbol{\Lambda}. \qquad (24)$$

Equation (24) reveals that partitioning into a diagonal and an off-diagonal part (as done for the force constant matrix) requires the same for matrix $\mathbf{G}^{-1}$, which is not possible.
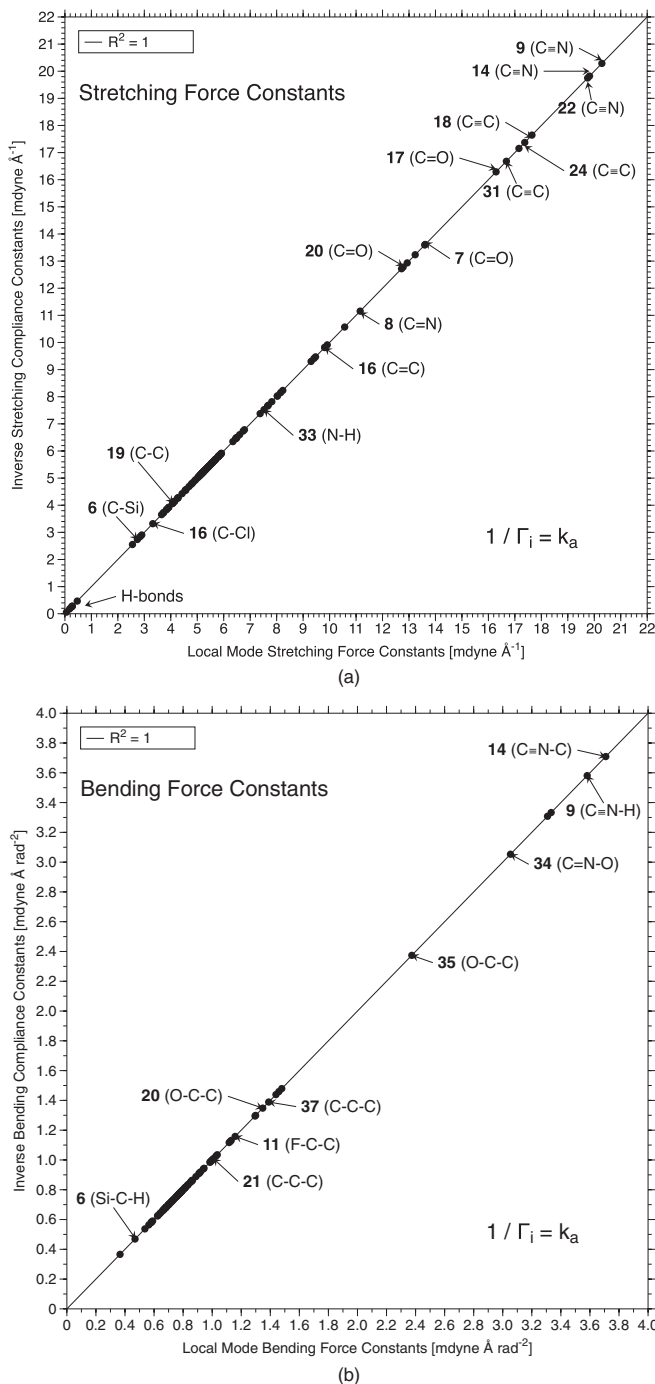
FIG. 2. Correlation of inverse compliance constants Γ_i with local mode force constants $k_a^{(i)}$. (a) Bond stretching force constants (see Table I); (b) Angle bending force constants. B3LYP/6-31G(d,p) calculations.

However, this objective can be reached with the help of compliance matrix $\boldsymbol{\Gamma}^q$ expressed in terms of internal coordinates as defined in Eq. (14). Then, Eq. (2) can be rewritten as

$$(\boldsymbol{\Gamma}^q)^{-1}\mathbf{D} = \mathbf{G}^{-1}\mathbf{D}\boldsymbol{\Lambda}. \qquad (25)$$

Next, Eq. (25) is rearranged to Eq. (26)

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

$$\mathbf{G}[(\boldsymbol{\Gamma}^q)^{-1}\mathbf{D}] = \boldsymbol{\Gamma}^q[(\boldsymbol{\Gamma}^q)^{-1}\mathbf{D}]\boldsymbol{\Lambda},$$

$$\mathbf{G}\mathbf{R} = \boldsymbol{\Gamma}^q\mathbf{R}\boldsymbol{\Lambda}, \qquad (26)$$

where a new eigenvector matrix $\mathbf{R}$ is introduced,

$$\mathbf{R} = (\boldsymbol{\Gamma}^q)^{-1}\mathbf{D} = \mathbf{F}^q\mathbf{D} = (\mathbf{D}^{-1})^{\dagger}\mathbf{K}. \qquad (27)$$

By partitioning matrices $\boldsymbol{\Gamma}^q$ and $\mathbf{G}$ into diagonal ($\boldsymbol{\Gamma}_d^q$ and $\mathbf{G}_d$) and off-diagonal ($\boldsymbol{\Gamma}_o^q$ and $\mathbf{G}_o$) parts and introducing the scaling factor λ ($0 \leq \lambda \leq 1$), Eq. (26) becomes

$$(\mathbf{G}_d + \lambda\mathbf{G}_o)\mathbf{R}_\lambda = (\boldsymbol{\Gamma}_d^q + \lambda\boldsymbol{\Gamma}_o^q)\mathbf{R}_\lambda\boldsymbol{\Lambda}_\lambda, \qquad (28)$$

where $\mathbf{R}$ and $\boldsymbol{\Lambda}$ depend on λ. Equation (28) is the basis for an adiabatic connection scheme, which relates local vibrational modes to normal vibrational modes in terms of their eigenvalues (frequencies) and eigenvectors (mode vectors).

For $\lambda = 0$, the adiabatic frequencies are obtained by

$$\mathbf{G}_d\mathbf{R}_0 = \boldsymbol{\Gamma}_d^q\mathbf{R}_0\boldsymbol{\Lambda}_a, \qquad (29)$$

where matrix $\boldsymbol{\Lambda}_a$ contains the local mode frequencies on its diagonal (in form of the product $4\pi^2 c^2 \omega_a^2$). This can be shown in the following way:

$$\boldsymbol{\Lambda}_a = \mathbf{G}_d(\boldsymbol{\Gamma}_d^q)^{-1} = \mathbf{G}_d[k_a^{(i)}]$$
$$= [G_{i,i} \times k_a^{(i)}] = [4\pi^2 c^2 (\omega_a)_i^2], \qquad (30)$$

where symbol [ ] denotes a diagonal matrix. For the diagonal part of Eq. (28), each local mode force constant $k_a^{(i)}$ is associated with just one internal coordinate. The corresponding local mode vector is orthonormal, i.e., it is a unit vector of length N_{vib} with 1 at the position of the internal coordinate leading the local mode.

For increasing λ, coupling between the modes is introduced and the resulting mode vectors are no longer orthogonal. They are expressed in terms of normal coordinates and collected in matrix $\mathbf{A}$. Matrix $\mathbf{A}$ is related to $\mathbf{R}$ by the following equation:

$$\mathbf{A} = \mathbf{R}^{-1}(\boldsymbol{\Gamma}_d^q)^{-1} = \mathbf{R}^{-1}[k_a]. \qquad (31)$$

Furthermore, it holds that

$$\mathbf{A} = \mathbf{D}^{-1}\boldsymbol{\Gamma}^q(\boldsymbol{\Gamma}_d^q)^{-1} = \mathbf{D}^{-1}(\boldsymbol{\Gamma}_d^q + \boldsymbol{\Gamma}_o^q)(\boldsymbol{\Gamma}_d^q)^{-1}$$
$$= \mathbf{D}^{-1}\mathbf{I} + \mathbf{D}^{-1}\boldsymbol{\Gamma}_o^q(\boldsymbol{\Gamma}_d^q)^{-1}, \qquad (32)$$

which implies that

$$\mathbf{D}\mathbf{A} = \boldsymbol{\Gamma}^q(\boldsymbol{\Gamma}_d^q)^{-1}, \qquad (33)$$

i.e., normal mode vectors and local mode vectors are connected via the compliance matrix.

If the scaling factor λ is increased stepwise from 0 to 1 (under the premise that the number of internal coordinates is equal to the number of vibrations: $N_{para} = N_{vib}$), vibrational couplings between the local modes are switched on that lead, in the case of $\lambda = 1$, to the normal mode vibrations of Eq. (2). In Figures 3(b) and 3(c), the adiabatic connection scheme is graphically displayed for 10 of the 12 vibrational modes of methanol. The corresponding frequencies are given in Table II together with the coupling frequencies, leading from local mode frequencies to normal mode frequencies as obtained at the B3LYP/6-31G(dp) level of theory. The 12 internal coordinates used for methanol are indicated in Figure 3(a), which for the purpose of fulfilling the
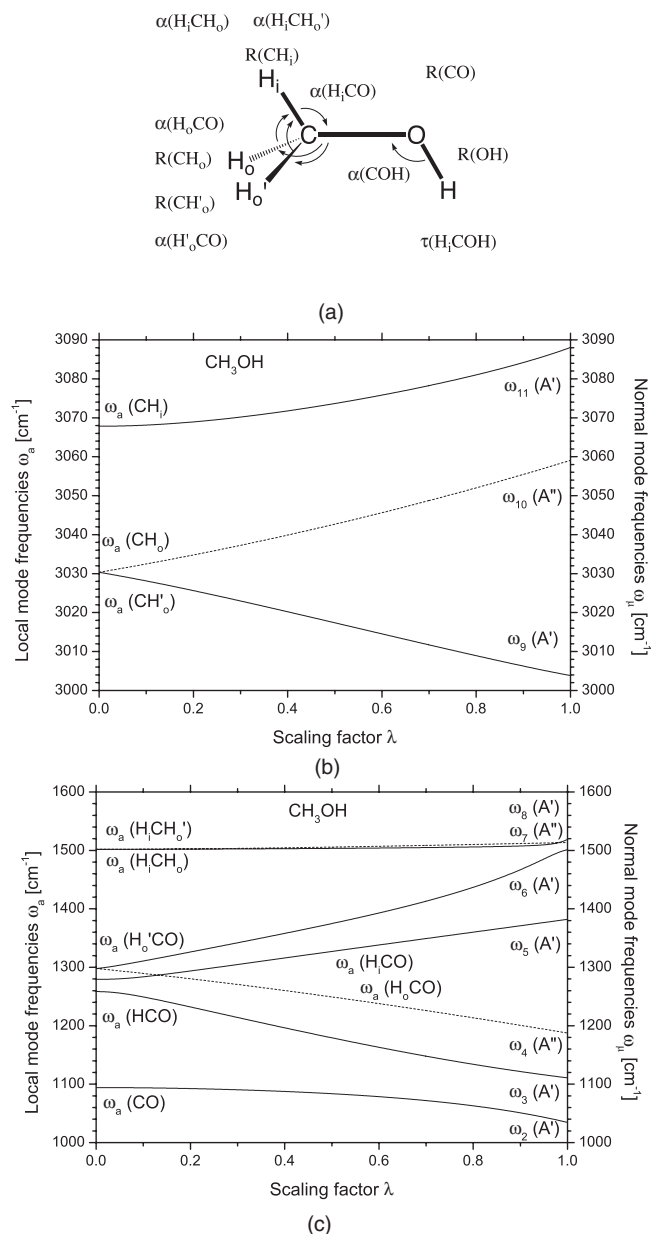
FIG. 3. (a) The 12 internal coordinates (nine of them are unique) used to describe the geometry of methanol. (b), (c) Adiabatic connection scheme relating local mode frequencies (left) with normal mode frequencies (right). The highest and the lowest frequency are not shown. B3LYP/6-31G(d,p) calculations.

requirement $N_{para} = N_{vib}$ also have to contain symmetry-equivalent internal coordinates. The application of Eq. (28) requires resolving all avoided crossings, which is handled by applying the diabatic mode ordering (DMO) algorithm of Konkoli, Kraka, and Cremer.[63] The DMO algorithm is based on overlap between the vibrational mode vectors of consecutive λ-steps rather than symmetry criteria (therefore the characterization as being *diabatic*[40]). By decreasing the step-length $\Delta\lambda$ to 0.01 or even smaller, DMO can correctly resolve any avoided crossing of vibrational eigenstates for increasing λ.

At an avoided crossing the mode character is switched or distributed between the modes depending on the type of avoided crossing. The resulting mode character can be determined by a decomposition of normal vibrational modes in terms of local modes as was first shown by Konkoli and Cremer.[31] In Table II, this decomposition is given in the last column and can be used to identify multiple couplings between different modes. For methanol, there is one avoided crossing involving modes 6 and 8, which both have A' symmetry (see Figure 3(c)) for λ close to 1. Mode 6 starts as a pure H_oCO bending mode but after the avoided crossing is slightly dominated by H_iCH_o bending character (41% compared to 38% H_oCO bending character, see Table II). The frequency of mode 8 is pushed above that of mode 7 and also adopts mixed character (64% H_iCH_o + 23% H_oCO character) due to the avoided crossing. Another avoided crossing at $\lambda = 0.8$ between modes 2 and 3 leads to a mixing of CO stretching and COH bending character (see Table II). Since mode 3 has already obtained some H_iCO and $H_oCO + H'_oCO$ character in avoided crossings with modes 5 and 6 at λ close to zero, it passes some of this character to mode 2, which becomes in this way a mixture of five different local vibrational modes (see Table II).

The change in the mode frequencies for increasing scaling parameter reflects the coupling between local modes leading to the normal vibrational modes. It is justified to consider the difference $\omega_{coup} = \omega(\lambda = 1) - \omega(\lambda = 0)$ as a coupling frequency, which reflects the changes in the local mode frequency $\omega_a = \omega(\lambda = 0)$ caused by mode-mode coupling. When adding the sum of coupling frequencies to the sum of local mode frequencies, the zero-point energy (ZPE) is recovered (see Table II). Large couplings are obtained when the starting frequencies are close or identical and the mass ratio of the vibrating atoms is comparable. For example, there are large coupling frequencies ranging from 106 to 203 cm^{-1} for the ABH bending modes close to 1300 cm^{-1} with A = C and B = O (or vice versa; see Figure 3(c) and Table II). However, for HCH bending (1500 cm^{-1}) the 12 times larger mass of the central atom acts as a wall and effectively suppresses mode-mode coupling between H_iCH_o and $H_iCH'_o$ bending (Figure 3(b)). Diagrams as the one in Figures 3(b) and 3(c) help to specify true electronic effects in a molecule via the local mode force constants (or frequencies) and to analyze the normal mode properties as a result of both electronic and kinematic effects involving mode-mode coupling. However, they do not detail the coupling between vibrational modes because they are cumulative quantities. These details are obtained from the adiabatic connection scheme or the decomposition of normal vibrational modes in terms of local modes.[31]

For the purpose of getting meaningful local mode results, it is advisable to keep $N_{para} = N_{vib}$ and to use for a K-atomic acyclic molecule K-1 bonds, K-2 bond angles, and K-3 dihedral angles (cyclic molecule: K bonds, K-3 bond angles, K-3 puckering coordinates[43]) where the angles are defined for directly bonded atoms to obtain a meaningful parameter set. The inclusion of non-bonded distances within a molecule often does not lead to useful results. However, non-bonded interactions between molecules such as H-bonding can be probed in a meaningful way by local mode force constants.

TABLE II. Vibrational analysis of methanol (B3LYP/6-31G(dp) calculations).[a]

Type	ω_a [cm^{-1}]	μ	ω_μ [cm^{-1}]	ω_{coup} [cm^{-1}]	Character of normal mode μ in terms of local mode contributions
$\omega_a(OH)$	3829.42	12	3835.01	5.59	99.9% OH
$\omega_a(CH_i)$	3067.83	11	3088.05	20.22	83.1% CH$_i$, 16.4% (CH$_o$ + CH$'_o$)
$\omega_a(CH_o)$	3030.35	10	3059.08	28.73	99.6% (CH$_o$ + CH$'_o$)
$\omega_a(CH'_o)$	3030.35	9	3003.83	−26.52	83.6% (CH$_o$ + CH$'_o$), 16.1% CH$_i$
$\omega_a(H_iCH_o)$	1501.92	8	1518.85	16.93	64.4% (H$_i$CH$_o$ + H$_i$CH$'_o$), 23.0% (H$_o$CO + H$'_o$CO), 10.1% H$_i$CO, 1.0% COH
$\omega_a(H_iCH'_o)$	1501.92	7	1513.54	11.62	91.6% (H$_i$CH$_o$ + H$_i$CH$'_o$), 7.0% (H$_o$CO + H$'_o$CO)
$\omega_a(H_oCO)$	1297.84	4	1187.46	−110.38	95.2% (H$_o$CO + H$'_o$CO), 4.4% (H$_i$CH$_o$ + H$_i$CH$'_o$)
$\omega_a(H'_oCO)$	1297.84	6	1501.29	203.45	41.4% (H$_i$CH$_o$ + H$_i$CH$'_o$), 37.6% (H$_o$CO + H$'_o$CO), 18.4% H$_i$CO, 2.2% CO
$\omega_a(H_iCO)$	1279.42	5	1382.09	102.67	67.8% COH, 24.8% H$_i$CO, 6.2% (H$_o$CO + H$'_o$CO)
$\omega_a(COH)$	1258.43	3	1110.76	−147.67	52.1% CO, 10.6% COH, 29.4% H$_i$CO, 7.6% (H$_o$CO + H$'_o$CO)
$\omega_a(CO)$	1094.16	2	1034.51	−59.65	39.5% CO, 25.3% COH, 19.7% H$_i$CO, 14.6% (H$_o$CO + H$'_o$CO)
$\omega_a(H_iCOH)$	345.62	1	292.69	−52.93	99.6% H$_i$COH
ZPE	32.22		32.20	−0.02	

[a]The zero poin energy (ZPE; in kcal/mol) is added to verify that the sum of local mode frequencies enhanced by the sum of coupling frequencies equals the sum of normal mode frequencies.

V. CONCLUSIONS

In this work, we have proven that the local vibrational modes first presented by Konkoli and Cremer[30] are the true counterparts of the delocalized normal vibrational modes. The proof given here is based on the fact that the compliance constants of Decius,[17] which are obtained from the inverse force constant matrix in internal coordinates, are directly related to the local mode force constants. Hence, the compliance matrix of Decius provides the missing link between normal and local vibrational modes. We have verified the theoretically derived relationship $k_a^{(i)} = 1/\Gamma_i$ for stretching and bending force constants for a set of 40 typical organic molecules (Figure 1) calculated with two different approaches (using the Konkoli-Cremer program for the $k_a^{(i)}$ constants and a new program developed in this work for the Γ_i constants).

The compliance matrix **Γ** provides the possibility of relating local mode frequencies directly to the normal mode frequencies via the adiabatic connection scheme given by Eq. (28). One obtains correlation diagrams that reveal the coupling between local vibrational modes, where the coupling can be expressed in terms of cumulative coupling frequencies. The sum of local mode and coupling frequency is always identical to the corresponding normal mode frequency. Detailed information about the coupling mechanism is given by the decomposition of the normal vibrational modes in terms of local modes.

Local mode force constants provide an exact measure of the relative intrinsic strength of different bonds and, therefore, are perfectly suited to discuss the electronic structure and bonding in molecules. This is true for weak atom-atom interactions (e.g., H-bonding) as well as strong triple bonds (e.g., as in nitriles). In this connection it is advantageous that local mode frequencies and force constants can be derived from experimental frequencies, as was demonstrated by Cremer and co-workers.[34] The use of compliance constants has become superfluous in view of the results presented in this work.

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