A New Way of Analyzing Vibrational Spectra. II. Comparison of Internal Mode Frequencies

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ABSTRACT: Adiabatic internal frequencies are compared with **c**-vector frequencies and intrinsic frequencies. It is shown that **c**-vector modes are not suitable to characterize molecular fragments ϕ_n since they are not localized in ϕ_n and their definition leads to unreasonable frequency values. Intrinsic frequencies suffer from a strong dependence on the set of internal parameters chosen to describe the geometry of the molecule. Apart from this, they represent averaged frequencies, for which mass effects and electronic effects are not properly separated. Adiabatic frequencies are based on a dynamic principle, separate properly mass effects and electronic effects and do not depend in any way on the set of internal parameters. This is shown for HF/6-31G(d, p) vibrational frequencies of ethene, dichloroethene, benzene, the cyclooctatetraene dication, benzocyclobutadiene, and some of their isotopomers. © 1998 John Wiley & Sons, Inc. Int J Quant Chem **67**: 11–27, 1998

Introduction

In the first article of this series, henceforth called article I [1], we presented a new way of defining internal modes associated with molecular fragments ϕ_n and internal parameters ζ_n describing these fragments. Because of the way of constructing these new internal modes, we have coined the term ''adiabatic internal modes.'' The goal of using adiabatic internal modes is an easier and more chemically oriented understanding of vibrational spectra. Measured frequencies of vibrational spectra correspond to normal mode frequencies, which are difficult to understand since normal modes represent delocalized modes. Adiabatic internal modes, however, are localized in a molecular fragment and, therefore, they are perfectly suited to describe, e.g., the properties of chemical bonds.

Although the theory of adiabatic modes provides a new basis for analyzing and understanding vibrational spectra, it is not immediately clear

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whether such a new approach is needed. There have been previous investigations, which are relevant to the problem of defining appropriate internal vibrational motions [2–5], although in these investigations the actual intention was to analyze normal mode frequencies and force constants in dependence of the structure of the vibrating molecule rather than to define internal vibrational modes. It was the primary goal of this work to investigate these previous attempts, to unravel their basics in the context of the vibrational mode analysis, and to compare alternatives of defining internal modes with the adiabatic internal modes suggested in article I. This comparison will be done on theoretical grounds as well as by carrying out appropriate calculations.

We will pursue the objectives of this work by discussing in the next section the potential energy distribution (PED) analysis used in vibrational spectroscopy since it uses implicitly internal vibrational modes without referring to them [2–4]. In the third section, we investigate the intrinsic internal frequencies that can be considered as internal frequencies without a specific internal mode [5]. Finally, in the fourth section, the vibrational spectra of some selected molecules will be discussed that clearly show the advantages and disadvantages of the various definitions of internal vibrational modes. Throughout this article, we use the notation introduced in article I [1], in particular, we will abbreviate the differences $\Delta\mathbf{x}$, $\Delta\zeta$, etc., by $\mathbf{x}$, ζ, etc., to simplify the formulas.

Previous Attempts to Define Internal Motions

There have been several previous attempts to extract chemically useful information out of a normal mode analysis. For example, one could assume that each normal mode $\mathbf{l}_\mu$ is localized in a molecular fragment ϕ_n associated with an internal coordinate q_n. Then, the normal mode frequency ω_μ would be identical to the characteristic fragment frequency $\omega(\phi_n) = \omega_n$. It is one of the major goals in vibrational spectroscopy to determine fragment frequencies ω_n (e.g., the frequency of a C≡C bond, a C=O group, etc.), which can be used to identify and to describe functional groups in a molecule [6, 7]. However, normal modes $\mathbf{l}_\mu$ do not represent internal modes in the general case, which becomes clear when expressing the normal mode vectors in internal coordinate space yielding vectors $\mathbf{d}_\mu$ and relating $\mathbf{d}_\mu$ to $\mathbf{l}_\mu$:

$$\mathbf{l}_\mu = \mathbf{C}\mathbf{d}_\mu = \sum_{m=1}^{N} \mathbf{c}_m D_{m\mu} \tag{1}$$

($D_{m\mu}$: an element of matrix $\mathbf{D}$ [$D_{m\mu} = (\mathbf{d}_\mu)_m$], which collects $N_{vib} = 3K - L$ normal mode vectors $\mathbf{d}_\mu$; K: number of atoms; L: number of rotations and translations). A mode $\mathbf{l}_\mu$ could only function as internal mode if $(\mathbf{d}_\mu)_m = \delta_{m\mu}$ and $\mathbf{l}_\mu = \mathbf{c}_m$. However, there is always mass coupling between the $\mathbf{c}_m$ vectors because the $\mathbf{G}$ matrix is nondiagonal (see Eq. (20) of article I [1]), thus leading to $(\mathbf{d}_\mu)_m \neq \delta_{m\mu}$ and $\mathbf{l}_\mu \neq \mathbf{c}_m$. The often-used approach to get fragment frequencies from normal mode frequencies and to extract chemical information from vibrational spectra can only be useful if because of large mass differences mass coupling is not large.

The potential energy distribution (PED) analysis that is based on the work of Morino and Kuchitsu [2], Pulay and Török [3], and others [4] provides a more advanced approach to the problem of extracting chemical information from measured vibrational spectra. However, it requires knowledge of the force constant matrix $\mathbf{f}$ and normal mode vectors $\mathbf{l}_\mu$ as determined, e.g., by quantum chemical calculations. In the PED analysis, a density matrix $\mathbf{P}$ is defined, the elements of which give the distribution of normal modes $\mathbf{l}_\mu$ over internal modes $\mathbf{v}_n$. The latter are implicitly chosen to be the $\mathbf{c}$-vectors* of Eq. (1) without making any reference to this fact [2–4]:

$$\mathbf{v}_m = \mathbf{c}_m \tag{2a}$$

$$\zeta_m = q_m \qquad (m = 1, \ldots, N) \tag{2b}$$

(N: number of internal parameters or coordinates). The standard expression for the normal mode frequencies:

$$\omega_\mu^2 = \frac{\mathbf{l}_\mu^+ \mathbf{f}\mathbf{l}_\mu}{\mathbf{l}_\mu^+ \mathbf{M}\mathbf{l}_\mu} = \frac{k_\mu}{G_{\mu\mu}^{-1}} = k_\mu G_{\mu\mu}, \tag{3}$$

relates the square of ω_μ to the force constant k_μ of normal mode μ and the diagonal element $G_{\mu\mu}$ of Wilsons $\mathbf{G}$ matrix [6]. One obtains the PED density matrix for normal mode $\mathbf{l}_\mu$ by inserting Eq. (1) into the expression for the force constant $k_\mu = \mathbf{l}_\mu^+ \mathbf{f}\mathbf{l}_\mu$

* We use the term $\mathbf{c}$-vectors according to the notation introduced by Neto. See [8].

and dividing this expression by k_μ:

$$(P^{\mu}_{n,m})_{PED} = \frac{D_{n\mu} D_{m\mu} \mathbf{c}_n^+ \mathbf{f} \mathbf{c}_m}{\mathbf{l}_\mu^+ \mathbf{f} \mathbf{l}_\mu} = \frac{D_{n\mu} D_{m\mu} F_{nm}}{k_\mu}. \quad (4)$$

By using Eq. (4), normal mode $\mathbf{l}_\mu$ can be characterized in terms of internal vibrational modes $\mathbf{c}_m$ associated with internal coordinates q_m.

A deficiency of the PED analysis is that it does not lead to an internal mode frequency. This problem was solved by Boatz and Gordon (BG) [5], who extended the PED analysis by defining an ''intrinsic frequency'' $\omega_{m,BG}$ associated with an internal mode $\mathbf{v}_m$. Since intrinsic frequencies represent an alternative choice of defining internal mode frequencies, we will discuss them in the following section in detail, in particular, focusing on their advantages and disadvantages.

Analysis of Intrinsic Internal Frequencies

Although it was not shown in the original article of BG [5], their method for calculating intrinsic internal frequencies is based on Eq. (2), which can be shown by expressing the normal mode frequencies ω_μ of Eq. (3) with the help of Eq. (1):

$$\omega_\mu^2 = \frac{1}{\mathbf{l}_\mu^+ \mathbf{M} \mathbf{l}_\mu} \sum_{n=1}^{N} \sum_{m=1}^{N} D_{n\mu} D_{m\mu} \mathbf{c}_n^+ \mathbf{f} \mathbf{c}_m = \sum_{n=1}^{N} \omega_{n\mu}^2, \quad (5)$$

where the square of the coupling frequency $\omega_{n\mu}$ is defined by (6):

$$\omega_{n\mu}^2 = \frac{1}{\mathbf{l}_\mu^+ \mathbf{M} \mathbf{l}_\mu} \sum_{m=1}^{N} D_{n\mu} D_{m\mu} \mathbf{c}_n^+ \mathbf{f} \mathbf{c}_m. \quad (6)$$

By adding the coupling frequencies for a particular internal parameter (coordinate) ζ_n (q_n) over all normal modes $\mathbf{l}_\mu$, one obtains the intrinsic frequencies $\omega_{n,BG}$ of BG as

$$\omega_{n,BG}^2 = \sum_{\mu=1}^{N} \omega_{n\mu}^2, \quad (7)$$

which is clearly related to the internal mode vector $\mathbf{c}_n$ rather than the normal mode vector $\mathbf{l}_\mu$.

One of the major disadvantages of the intrinsic frequencies $\omega_{n,BG}$ defined by BG [5] is that they represent averages over normal mode frequencies. By transforming (6) into (8),

$$\omega_{n\mu}^2 = \omega_\mu^2 \sum_{m=1}^{N} P^{\mu}_{nm}, \quad (8)$$

where the density matrix element P^{μ}_{nm} is defined in Eq. (4), one can express $\omega_{n,BG}$ according to Eq. (9):

$$\omega_{n,BG}^2 = \sum_{\mu} A_{n\mu} \omega_\mu^2, \quad (9)$$

with the amplitude $A_{n\mu}$ given by

$$A_{n\mu} = \sum_{m} P^{\mu}_{nm}. \quad (10)$$

Equation (9) reveals that the normal mode frequencies ω_μ are weighted with the corresponding amplitudes $A_{n\mu}$ for parameter (coordinate) ζ_n (q_n) in normal mode $\mathbf{l}_\mu$, i.e., they indeed represent averaged frequencies.

In principle, the BG method for determining intrinsic frequencies could be carried out for any set of vectors $\mathbf{v}_n$. If a nonredundant parameter set is used, the intrinsic frequencies of BG will have the same values for $\mathbf{v} = \mathbf{c}$ and for $\mathbf{v} = \mathbf{a}$ as is shown in the following:

Equation (7) can be rewritten in the form of (11):

$$\omega_{n,BG}^2 = \sum_{\mu=1}^{N_{vib}} \frac{D_{n\mu} (\mathbf{D}^+ \mathbf{F})_{\mu n}}{\mathbf{l}_\mu^+ \mathbf{M} \mathbf{l}_\mu}. \quad (11)$$

Since vectors $\mathbf{d}_\mu$ are eigenvectors of matrix $\mathbf{F}$ (see Eq. (20) of article I [1]), it follows that

$$\mathbf{D}^+ \mathbf{F} \mathbf{D} = \mathbf{k} \quad (12)$$

and

$$\mathbf{D}^+ \mathbf{F} = \mathbf{k} \mathbf{D}^{-1}, \quad (13)$$

where $\mathbf{k}$ is a diagonal matrix containing the force constants of the normal modes. Inserting (13) into (11) leads to

$$\omega_{n,BG}^2 = (\mathbf{D} \Lambda \mathbf{D}^{-1})_{nn}, \quad (14)$$

where Λ is a diagonal matrix containing the normal mode frequencies ω_μ. Eigenvalue Eq. (20) of article I [1] can be rewritten in matrix form according to

$$\mathbf{F} \mathbf{D} = \mathbf{G}^{-1} \mathbf{D} \Lambda. \quad (15)$$

From (15), it follows that

$$\mathbf{D}\Lambda\mathbf{D}^{-1} = \mathbf{GF}. \tag{16}$$

Finally, inserting (16) into (14) leads to the GF formula for the intrinsic frequencies of BG:

$$\omega_{n,BG}^2 = (\mathbf{GF})_{nn}. \tag{17}$$

When using **c**-vectors, Eq. (17) can be transformed into Eq. (18):

$$\omega_{n,BG}^2 = [(\mathbf{C}^+\mathbf{MC})^{-1}(\mathbf{C}^+\mathbf{fC})]_{nn}. \tag{18}$$

Similarly, one can use matrix **A**, in which the adiabatic vectors $\mathbf{a}_n$ given by Eq. (39) of article I [1] are stored columnwise. This leads to Eq. (19):

$$(\omega_{n,BG}^2)_{adiabatic} = [(\mathbf{A}^+\mathbf{MA})^{-1}(\mathbf{A}^+\mathbf{fA})]_{nn}, \tag{19}$$

in which the intrinsic frequencies are calculated with the help of adiabatic vectors. In the case of a nonredundant coordinate set, both Eqs. (18) and (19) give the same result as one can show in Eqs. (20)–(30).

Since adiabatic vectors $\mathbf{a}_n$ and **c**-vectors span the same space, a matrix **T** exists that transforms **C** into **A**:

$$\mathbf{A} = \mathbf{CT}. \tag{20}$$

Multiplying Eq. (20) from the left by **B** and using the identity

$$\mathbf{BC} = \mathbf{I} \tag{21}$$

leads to Eq. (22):

$$\mathbf{T} = \mathbf{BA}, \tag{22}$$

which with the help of Eqs. (38)–(40) of article I [1] can be rewritten in the form of (23):

$$T_{mn} = \sum_{\mu=1}^{N_{vib}} (BL)_{m\mu} Q_{\mu n}^0, \tag{23}$$

where matrix **L** contains the normal mode vectors $\mathbf{l}_\mu$. From Eqs. (1) and (21), it follows that

$$\mathbf{BL} = \mathbf{D}. \tag{24}$$

Using the fact that matrix **k** in (12) is diagonal, $Q_{\mu n}^0$ of Eq. (38) in article I [1] can be transformed into (25) and (26):

$$Q_{\mu n}^0 = \frac{\sum_{\nu=1}^{N_{vib}} (\mathbf{d}^+\mathbf{Fd})_{\mu\nu}^{-1} D_{\nu n}^+}{\sum_{\nu,\rho=1}^{N_{vib}} D_{n\nu} (\mathbf{d}^+\mathbf{Fd})_{\nu\rho}^{-1} D_{\rho n}^+} \tag{25}$$

$$Q_{\mu n}^0 = \frac{(\mathbf{d}^{-1}\mathbf{F}^{-1})_{\mu n}}{(\mathbf{F}^{-1})_{nn}}. \tag{26}$$

Combining Eqs. (26), (24), and (23), one obtains

$$\mathbf{T} = \mathbf{F}^{-1}\varepsilon, \tag{27}$$

where ε is a diagonal matrix given by

$$\varepsilon_{nm} = \frac{\delta_{nm}}{(\mathbf{F}^{-1})_{nn}}. \tag{28}$$

Inserting (20) into Eq. (19) leads to

$$(\omega_{n,BG}^2)_{adiabatic} = (\mathbf{T}^{-1}\mathbf{GFT})_{nn}, \tag{29}$$

and inserting (27) and (28) into (29) leads to Eq. (30):

$$(\omega_{n,BG}^2)_{adiabatic} = (\mathbf{FG})_{nn}. \tag{30}$$

From Eq. (30), (17) or, equivalently, (18) immediately follows because **F** and **G** are symmetric. This is proof that the same intrinsic frequencies are obtained no matter whether they are calculated with either adiabatic vectors (**v** = **a**) or **c**-vectors (**v** = **c**) provided that a nonredundant coordinate set is used.

The intrinsic frequencies defined by BG [5] suffer from several disadvantages:

1. The intrinsic frequencies $\omega_{n,BG}$ are not based on a dynamical principle, but are constructed as averages over all normal mode frequencies ω_μ using amplitudes $A_{n\mu}$ [see Eq. (9)]. Accordingly, one can expect that some of the physics of the vibrational motion is lost in the intrinsic frequencies.
2. Frequencies $\omega_{n,BG}$ depend on the parameter set used to describe the geometry of the molecule, which means that the choice of coordinates q_m $(m \neq n)$ indirectly determines the frequency value of the internal mode associated with parameter $\zeta_n = q_n$. This is a result of the definition of amplitudes $A_{n\mu}$, as sums over density matrix elements $P_{nm}^{(\mu)}$ [see Eq. (10)], which are unstable due to a strong parameter set dependence (for a detailed discussion, see article III [9]). As a consequence, the internal frequencies of a molecule can

vary considerably if the set of internal parameters is altered (see also the fourth section).

3. The BG intrinsic frequencies can be negative because amplitudes $A_{n\mu}$ are sometimes negative. In case of a molecule in its equilibrium geometry, this leads to false information on the potential energy surface in question.
4. As a result of the parameter set dependence, a nonsymmetric choice of parameters can lead to the fact that parameters, which are symmetry-equivalent, have different intrinsic frequencies. BG avoided this problem by adding redundant parameters to the parameter set [5]. Judging from our experience, this leads to a *more symmetric choice of* **c***-vectors* and, by this, the latter approach the form of adiabatic vectors. At the same time, however, the **c**-vectors lose their normalization, which means that ζ_n is no longer equal to ζ_n^* and calculated intrinsic frequencies $\omega_{n,BG}$ correspond to $\zeta_n/\mathbf{b}_n^+\mathbf{c}_n$ rather than to ζ_n itself. The fact that $\mathbf{b}_n^+\mathbf{c}_n \neq 1$ has to do with the calculation of $\mathbf{G}^{-1}$ needed for solving Eq. (31):

$$\mathbf{C} = \mathbf{M}^{-1}\mathbf{B}^+\mathbf{G}^{-1}, \tag{31}$$

even in those cases where $\mathbf{G}^{-1}$ does not exist. This is done by calculating the generalized inverse $\mathbf{G}^-$ [10]. It can easily be shown that $\mathbf{G}\mathbf{G}^- \neq \mathbf{I}$ and, therefore, $\mathbf{b}_n^+\mathbf{c}_n \neq 1$.
5. For intrinsic frequencies $\omega_{n,BG}$, electronic and mass effects are not separated properly. This can be seen from Eq. (32):

$$\omega_{n,BG}^2 = (\mathbf{GF})_{nn} = G_{nn}F_{nn} + \sum_{m\neq n} G_{nm}F_{nm}, \tag{32}$$

which results directly from Eq. (17). The first term in Eq. (32) represents the direct contribution of internal mode $\mathbf{v}_n$ associated with internal parameter ζ_n to frequency $\omega_{n,BG}^2$, while the second term represents contributions that result from couplings between internal mode $\mathbf{v}_n$ (associated with parameter ζ_n) and other internal modes $\mathbf{v}_m$ (associated with parameters $(\zeta_m, m \neq n)$. The term $G_{nn}F_{nn}$ of (32) corresponds to ω_n as defined in Eq. (54) of article I [1] with $\mathbf{v}_n = \mathbf{c}_n$. If a nonredundant parameter set is used, $\mathbf{b}_n^+\mathbf{c}_n$ will not appear in the denominator of (54) of article I [1] since it is equal to 1.

The problems caused by the second term in Eq. (32) can be demonstrated considering isotopomers $X{-}Y$ and $X^*{-}Y^*$, where the stars indicate isotopes of X and Y. The BG intrinsic frequencies for the stretching motions of $X{-}Y$ and $X^*{-}Y^*$ should differ just because of the difference in the isotope masses, i.e., the ratio of the two frequencies should be equal to the ratio of the reduced masses of $X{-}Y$ and $X^*{-}Y^*$, respectively, since electronic effects should be the same:

$$\omega_{n,BG}^2 \frac{1}{G_{nn}} = (\omega_{n,BG}^*)^2 \frac{1}{G_{nn}^*}, \tag{33}$$

where $\omega_{n,BG}$ is the intrinsic stretching frequency of fragment $X{-}Y$; $\omega_{n,BG}^*$, the corresponding frequency of fragment $X^*{-}Y^*$; $1/G_{nn}$, the reduced mass for $X{-}Y$; and $1/G_{nn}^*$, the reduced mass for $X^*{-}Y^*$. Equation (33) compares the stretching force constants of $X{-}Y$ and $X^*{-}Y^*$ according to the definition given by BG [see, e.g., Eq. (21) in [5]), which have to be the same because of identical electronic structures for $X{-}Y$ and $X^*{-}Y^*$.

Using Eq. (32) to calculate the ratio $\omega_{n,BG}^2/(\omega_{n,BG}^*)^2$ (starred values refer to fragment $X^*{-}Y^*$), one obtains

$$\frac{\omega_{n,BG}^2}{(\omega_{n,BG}^*)^2} = \frac{G_{nn}}{G_{nn}^*}\frac{F_{nn} + \Sigma_{m\neq n}G_{nm}/G_{nn}F_{nm}}{F_{nn} + \Sigma_{m\neq n}G_{nm}^*/G_{nn}^*F_{nm}}. \tag{34}$$

The first term in the product on the right-hand side of Eq. (34) leads to Eq. (33). However, Eq. (34) will only become identical to Eq. (33) if the second factor of the product is equal to one. There is no reason to believe that this is the case and, therefore, Eq. (34) clearly shows that the definition of intrinsic vibrational frequencies suggested by BG [Eq. (32)] leads to force constants depending on both electronic structure and mass effects contrary to what is required by Eq. (33). In other words, electronic and mass effects are not separated properly in the definition of the intrinsic frequencies as can be seen from Eq. (32), in which only the first term on the right side provides a correct separation of electronic and mass effects.

6. In their article, BG claimed that intrinsic stretching frequencies are not so sensitive to

the choice of the parameter set, which means that they do not couple so much [5]. In the same article, the authors defined special rules for torsional motions since they couple with other internal motions more strongly than stretching motions do. This can directly be explained using Eq. (32), in which the coupling is reflected by **G** matrix elements $G_{nm} = \mathbf{b}_n^+ \mathbf{M}^{-1} \mathbf{b}_m$, where **b** is a column vector of the **B** matrix with elements

$$B_{ni} = \left(\frac{\partial q_n(\mathbf{x})}{\partial x_i} \right)_{\mathbf{x}=\mathbf{x}_0}.$$

If parameter q_n is associated with a stretching motion, then there will be not so many parameters q_m $(m \neq n)$ that can couple to q_n via the matrix element G_{nm}. However, in the case of bending or torsional motions, the B matrix elements corresponding to the internal parameters representing these motions will lead to more elements G_{nm} different from zero. Coupling of internal motions increases with the number of atoms participating in the motion. This means that torsional motions will couple more than bending or stretching motions. Symmetry-adapted combinations of primitive motions such as stretching, bending, or torsional motions will lead to even larger couplings since more atoms participate in these vibrations.

From a theoretical point of view, the intrinsic frequencies have a number of deficiencies that have to be considered when using them for the analysis of vibrational spectra. We will investigate in the next section to what extent these shortcomings of the intrinsic frequencies can influence the interpretation of calculated vibrational spectra.

Analysis of Vibrational Spectra In Terms of Internal Modes

Vibrational spectra of a series of acyclic, cyclic, and polycyclic molecules were investigated using ab initio theory and the harmonic approximation of vibrational modes. Calculated vibrational normal modes were analyzed in terms of internal modes with the help of the program routine ADIA [11] that is based on the theory described in this and article I [1] and that was included in the program package COLOGNE [12].

Adiabatic mode vectors $\mathbf{a}_m$ were calculated with Eqs. (38) and (39) of article I [1]. The corresponding force constants k_a, fragment masses m_a, and adiabatic frequencies ω_a were evaluated according to Eqs. (35)–(37):

$$k_a = \mathbf{a}_n^+ \mathbf{f} \mathbf{a}_n \tag{35}$$

$$m_a = \frac{1}{\mathbf{b}_n^+ \mathbf{M}^{-1} \mathbf{b}_n} = \frac{1}{G_{nn}} \tag{36}$$

$$\omega_a^2 = \frac{\mathbf{a}_n^+ \mathbf{f} \mathbf{a}_n}{1/G_{nn}} = \mathbf{a}_n^+ \mathbf{f} \mathbf{a}_n \cdot G_{nn} = k_a \cdot G_{nn}. \tag{37}$$

All geometries and vibrational frequencies discussed in the following were calculated at the Hartree–Fock (HF) level employing the standard VDZP basis 6-31G(d, p) of Pople and co-workers [13]. Most of the HF/6-31G(d, p) results, although interesting from a chemical point of view, will not be interesting for the present comparison of internal mode frequencies and, therefore, will be published elsewhere [14]. For most acyclic molecules, it is difficult to judge whether one definition of an internal frequency is more useful than the other although calculated internal frequencies for the same internal parameter may differ considerably. Advantages and disadvantages of different types of internal frequencies become obvious when cyclic molecules are investigated and, therefore, we will focus in this article on some selected cases that clearly demonstrate which definition of internal frequencies is more suitable for chemical purposes.

In particular, we will compare the internal mode frequencies ω_n (Eq. (54) of article I [1]), $\omega_{n,BG}$ [Eq. (9)], and Ω_n [Article I, Eq. (45 [1]) to confirm the properties of internal modes derived theoretically. For each molecule investigated, we consider both adiabatic internal modes $(\mathbf{v}_n = \mathbf{a}_n)$ and **c**-vector modes $(\mathbf{v}_n = \mathbf{c}_n)$. Results referring to the first choice will be indicated by subscript a, while those referring to the second choice will be denoted by subscript c. The internal frequencies will explicitly be given in the form $\omega_a(AB)$, $\omega_c(ABC)$, etc. For all examples studied, we have used $\zeta_n = q_n$ since internal coordinates are mostly used in chemistry. Beside bond lengths $r(AB)$, angles $\alpha(ABC)$, and dihedral angles $\tau(ABCD)$, we will use also out-of-plane angles $\gamma(ABCD)$, where atoms C and D are bonded to B and the angle γ describes the bending of A out of the plane BCD. Only planar hydrocarbon molecules are discussed to remove coupling between in-plane and out-of-plane parameters.

FRAGMENT FREQUENCIES Ω_n

The fragment frequencies Ω_n defined in Eq. (45) of article I [1] are not suitable candidates for the internal frequencies of a molecule because all atomic masses of the molecule influence the value of Ω_n rather than just the atomic masses of the fragment ϕ_n described by the internal parameter q_n. This is confirmed by the data presented in Table I and Figure 1, in which internal frequencies ω_a, ω_{BG}, ω_c, Ω_a, and Ω_c are listed for ethene and 1,2-dichloroethene. Since Cl possesses an electronegativity ($\chi = 2.83$) comparable to that of C ($\chi = 2.50$) [15] and since conjugation of Cl with the C=C double bond is small as a result of insufficient Cl($3p\pi$)–C($2p\pi$) overlap, the C=C double bond should possess similar properties in both molecules. This, e.g., is confirmed by the HF/6-31G(d, p) CC bond lengths given in Figure 1 (C_2H_4: 1.316 Å; $C_2H_2Cl_2$: 1.312 Å).

Internal CC stretching frequencies ω_a, ω_{BG}, and ω_c are in line with this prediction since $\Delta\omega = \omega(\mathrm{CC}, C_2H_4) - \omega(\mathrm{CC}, C_2H_2Cl_2) < 10\ \mathrm{cm}^{-1}$ in each of these cases (Fig. 1). However, both Ω_a and Ω_c reveal a dramatic decrease of the stretching frequency by 294 (Ω_a, Fig. 1) and 766 cm^{-1} (Ω_c, Fig. 1) when substituting ethene by two Cl atoms, which chemically is not justified and simply reflects an increase in masses M_n when converting C_2H_4 into $C_2H_2Cl_2$. Clearly, both Ω_a and Ω_c are not suitable internal vibrational mode frequencies as was anticipated already in article I. Internal frequencies ω_a, ω_{BG}, and ω_c are better suited to reveal the similarity of the C=C double bonds in the two molecules. Therefore, we will concentrate

TABLE I

Internal parameters q_n and internal frequencies ω_n (Ω_n) ($n = a$: adiabatic internal frequencies; n = BG: intrinsic frequencies; $n = c$: c-vector frequencies) calculated for ethene and 1,2-dichloroethene at the HF/6-31G(d, p) level of theory.[a]

	Parameter set									
n	A	B	C	D	q_n	ω_a	ω_{BG}	ω_c	Ω_a	Ω_c
Ethene										
1	C2	C1			1.316	1798	1770	1813	1729	1677
2	H3	C2			1.076	3344	3345	3353	3324	3307
3	H4	C1			1.076	3344	3345	3353	3324	3307
4	H5	C2			1.076	3344	3345	3353	3324	3307
5	H6	C1			1.076	3344	3345	3353	3324	3307
6	H3	C2	C1		121.7	1279	1395	1448	1118	1385
7	H5	C2	C1		121.7	1279	1395	1448	1118	1385
8	H4	C1	C2		121.7	1279	1395	1448	1118	1385
9	H6	C1	C2		121.7	1279	1395	1448	1118	1385
10	H4	C1	C2	H3	0	1119	1126	1417	1118	1118
11	H6	C1	C2	H5	0	1119	1126	1417	1118	1118
12	H5	C2	C1	H4	180.0	1118	1092	1488	1117	1092
cis-1,2-Dichloroethene										
1	C2	C1			1.312	1798	1768	1821	1435	911
2	Cl3	C2			1.721	909	853	938	792	699
3	Cl4	C1			1.721	909	853	938	792	699
4	H5	C2			1.072	3402	3402	3406	3330	3289
5	H6	C1			1.072	3402	3402	3406	3330	3289
6	Cl3	C2	C1		125.7	646	557	735	267	271
7	Cl4	C1	C2		125.7	646	557	735	267	271
8	H5	C2	C1		120.2	1315	1424	1513	517	1367
9	H6	C1	C2		120.2	1315	1424	1513	517	1367
10	Cl4	C1	C2	Cl3	0	510	469	635	473	526
11	H6	C1	C2	H5	0	1060	1058	1360	1059	899
12	H5	C2	C1	Cl4	180.0	796	813	1096	669	813

[a] Distances in Å, angles in degrees, frequencies in cm^{-1}. Nuclei A, B, C, and D are numbered as in Figure 1.

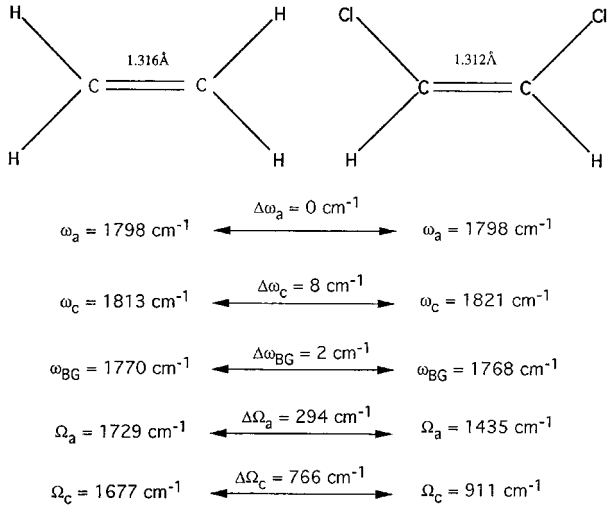


FIGURE 1. HF / 6-31G(d, p) bond length and internal frequency ω of the CC bonds in C_2H_4 and $C_2H_2Cl_2$ (see text).

in the following on these frequencies and refrain from any further discussion of frequencies Ω_a or Ω_c.

COMPARISON OF INTERNAL FREQUENCIES ω_a, ω_c, AND ω_{BG}.

Differences in internal frequencies ω_a, ω_c, and ω_{BG} become obvious for molecules, for which internal coordinates couple strongly or for which a chemically useful choice of a parameter set is difficult. These problems are encountered for ring compounds and, accordingly, we will investigate benzene (**1a**) and the cyclooctatetraene-dication (**2a**) as appropriate nontrivial examples.

In Figures 2 and 3, the parameter sets used for **1a** and **2a** are shown. Adiabatic frequencies (ω_a), **c**-vector frequencies (ω_c), and for the sake of comparison, intrinsic frequencies of BG (ω_{BG}) [5] are given in Tables II and III. Results show that (a) frequencies ω_a, ω_c, and ω_{BG} all fulfill the symmetry criteria (symmetry-equivalent internal modes have to have the same frequency values) and (b) internal frequencies for related internal modes associated with similar internal parameters are about the same. However, there are some important differences, which will be discussed.

For all cases considered, **c**-vector frequencies ω_c are always the largest ones, which is due to the constraint $\mathbf{BC} = \mathbf{I}$ [see Eq. (41)]. For the internal modes associated with the carbon frame, intrinsic frequencies of BG attain lower values than do adiabatic ones. For example, in **1a**: ω_a(CC) = 1406, ω_{BG}(CC) = 1370; ω_a(CCC) = 997, ω_{BG}(CCC) = 714 cm^{-1} [see Table II(a)], and in **2a**: ω_a(CC) = 1325, ω_{BG}(CC) = 1293; ω_a(CCC) = 802, ω_{BG}(CCC) = 671 cm^{-1} [see Table III(a)]. The intrinsic frequencies are lowered because a redundant parameter set of 15 (24) rather than 12 (18) internal parameters is used for the carbon frame of **1a** (**2a**). The decrease of intrinsic frequencies with the number of parameters used was discussed previously by BG [5] and simply reflects the fact that intrinsic frequencies are averaged frequencies that become smaller the more internal coordinates are included into the parameter set. The calculated values of ω_a, ω_c, and ω_{BG} for the CH stretching modes of **1a** [ω_a = 3348, ω_c = 3353, ω_{BG} = 3346 cm^{-1}; Table II(a)] and **2a** [ω_a = 3349, ω_c = 3351, ω_{BG} = 3347 cm^{-1}; Table III(a)] are similar since the CH stretching motion is largely decoupled from the internal motions associated with the ring parameters. The set of γ-parameters describing HCCC out-of-plane motions is nonredundant and, therefore, ω_{BG} values are larger than the corresponding ω_a values [**1a**: ω_a = 969, ω_{BG} = 1051 cm^{-1}; see Table III(a); **2a**: ω_a = 607, ω_{BG} = 1148 cm^{-1}; see Table III(a)] where differences can be as large as 500 cm^{-1}, reflecting the strong parameter dependence of intrinsic frequencies.

PARAMETER SET INDEPENDENCE OF ADIABATIC FREQUENCIES ω_a

The major advantage of adiabatic internal frequencies ω_a is that they can be calculated using only a limited number of parameters of interest without constructing a complete (nonredundant) parameter set. Alternatively, one can also use any set of redundant parameters without changing the values of the adiabatic frequencies, i.e., ω_a values are completely independent of the parameter set used to describe the molecule in question. This independence of the parameter set is an important property of ω_a, which clearly shows that the differences in calculated internal frequencies of fragments ϕ_n directly reflect differences in the electronic structure of the fragments rather than being contaminated by the choice of internal parameters.

BG tried to circumvent the problem that intrinsic frequencies depend on the choice of the parameter set by setting up four empirical rules for handling symmetric molecules so that a reasonable parameter set is obtained in this case [5]. While these rules can successfully be used in many cases,

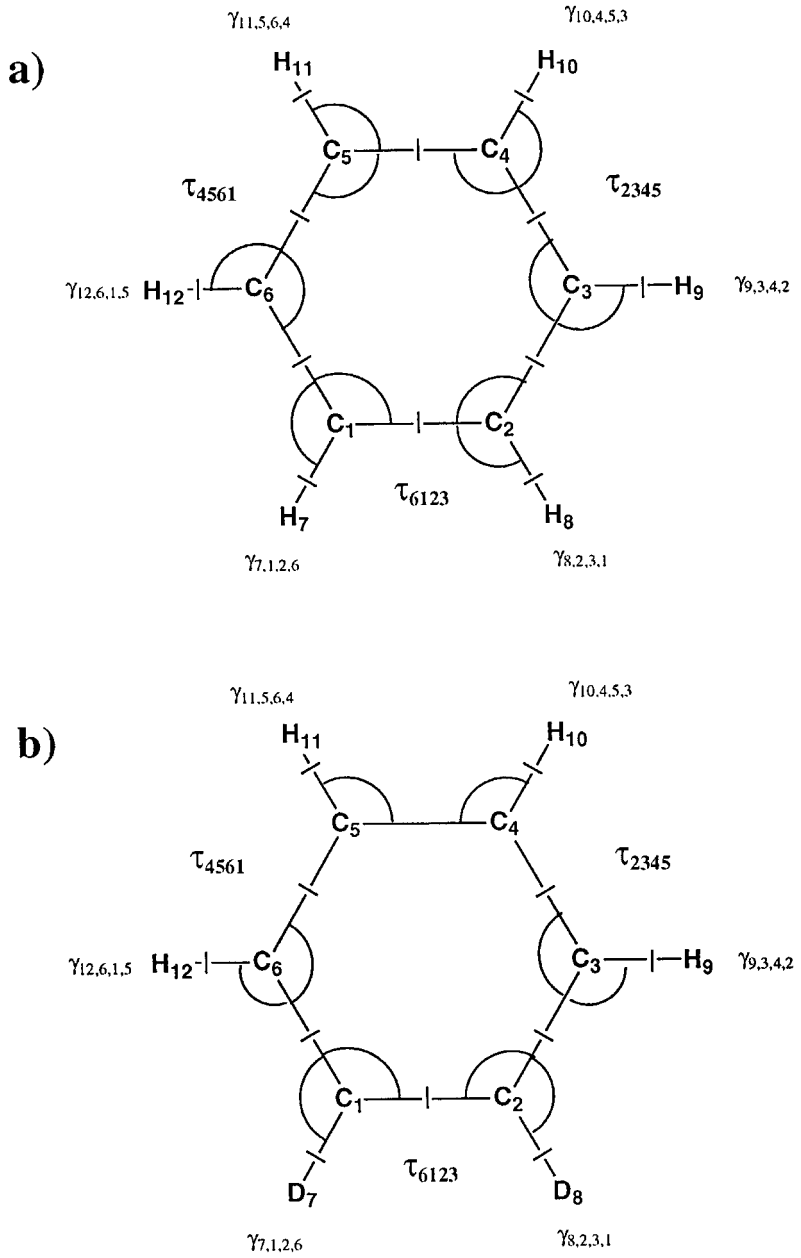


FIGURE 2. Parameter sets used for (a) benzene (**1a**) and (b) 1,2-dideuterobenzene (**1b**). Numbering of atoms and the notation of parameters (torsional angles τ and out-of-plane bending angles γ) are explicitly given. Bond lengths and bond angles covered in the parameter set are indicated by a perpendicular line through the bond line and an arc connecting the bonds involved in the bending motion.

they do not solve problems in the case of nonsymmetric molecules, for which the four BG rules cannot be applied. In the latter case, one can no longer say whether a given difference in ω_n and ω_m of two related fragments ϕ_n and ϕ_m results form the particular choice of the parameter set or is due to a difference in electronic structure. This will be illustrated in the following:

Using the parameter set chosen for **1a**, one can probably handle all substituted benzene compounds without noticing any inherent problems connected with the use of intrinsic frequencies. One simply takes as appropriate internal parameters all bond lengths, all symmetry-equivalent in-

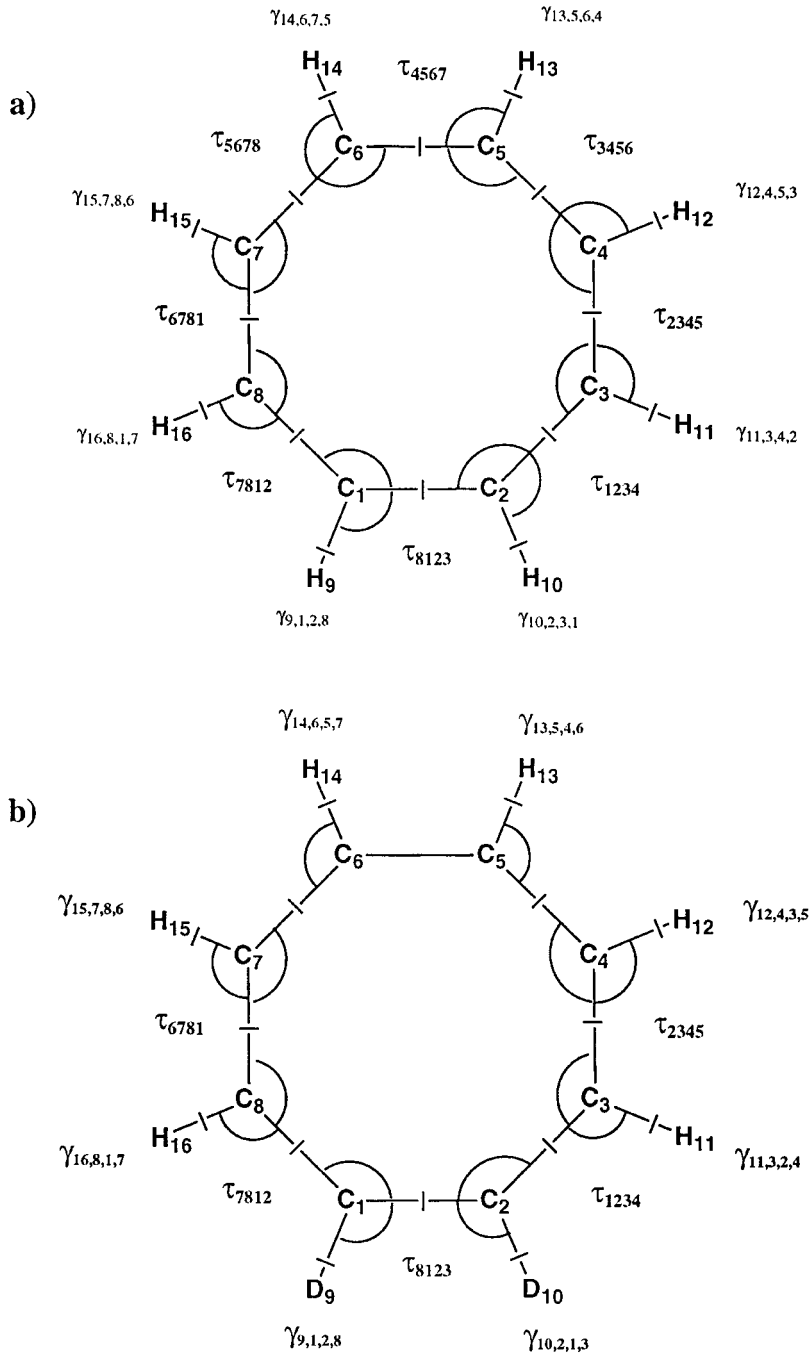


FIGURE 3. Parameter sets used for (a) the cyclooctatetraene dication (**2a**) and (b) the 1,2-dideuterocyclooctatetraene dication (**2b**). Numbering of atoms and the notation of parameters (torsional angles τ and out-of-plane bending angles γ) are explicitly given. Bond lengths and bond angles covered in the parameter set are indicated by a perpendicular line through the bond line and an arc connecting the bonds involved in the bending motion.

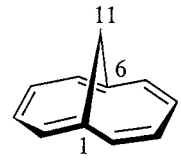
TABLE II

Internal parameters q_n and internal frequencies ω_n ($n = a$; adiabatic internal frequencies; n = BG: intrinsic frequencies; $n = c$: c-vector frequencies) calculated for (a) benzene (1a) and (b) 1,2-dideuterobenzene (1b) at the HF / 6-31G(d, p) level of theory.[a]

n		Parameter set					(a) $X = H$ (**1a**)			(b) $X = D$ (**1b**)		
X = H	X = D	A	B	C	D	q_n	ω_a	ω_{BG}	ω_c	ω_a	ω_{BG}	ω_c
1	1	C1	C2			1.386	1406	1370	1491	1406	1480	2196
2	2	C2	C3			1.386	1406	1370	1491	1406	1307	1729
3	3	C3	C4			1.386	1406	1370	1491	1406	1439	1671
4		C4	C5			1.386	1406	1370	1491			
5	4	C5	C6			1.386	1406	1370	1491	1406	1439	1671
6	5	C6	C1			1.386	1406	1370	1491	1406	1307	1729
7	6	C1	C2	C3		120.0	997	714	1110	997	725	4152
8	7	C2	C3	C4		120.0	997	714	1110	997	1328	2462
9		C3	C4	C5		120.0	997	714	1110			
10		C4	C5	C6		120.0	997	714	1110			
11	8	C5	C6	C1		120.0	997	714	1110	997	1328	2462
12	9	C6	C1	C2		120.0	997	714	1110	997	725	4152
13	10	C6	C1	C2	C3	0.0	653	422	913	653	422	913
14	11	C2	C3	C4	C5	0.0	653	422	913	653	422	913
15	12	C4	C5	C6	C1	0.0	653	422	913	653	422	913
16	13	X7	C1			1.076	3348	3346	3353	2458	2452	2462
17	14	X8	C2			1.076	3348	3346	3353	2458	2452	2462
18	15	H9	C3			1.076	3348	3346	3353	3348	3346	3353
19	16	H10	C4			1.076	3348	3346	3353	3348	3346	3353
20	17	H11	C5			1.076	3348	3346	3353	3348	3346	3353
21	18	H12	C6			1.076	3348	3346	3353	3348	3346	3353
22	19	X7	C1	C6		120.0	1403	1441	1498	1087	1086	1161
	20	D8	C2	C3		120.0				1087	1086	1161
23		H8	C2	C1		120.0	1403	1441	1498			
24	21	H9	C3	C2		120.0	1403	1441	1498	1403	1441	1498
25		H10	C4	C3		120.0	1403	1441	1498			
	22	H10	C4	C5		120.0				1403	1441	1498
26	23	H11	C5	C4		120.0	1403	1441	1498	1403	1441	1498
27		H12	C6	C5		120.0	1403	1441	1498			
	24	H12	C6	C1		120.0				1403	1441	1498
28	25	X7	C1	C2	C6	0	969	1051	1168	809	831	975
29	26	X8	C2	C3	C1	0	969	1051	1168	809	831	975
30	27	H9	C3	C4	C2	0	969	1051	1168	969	1051	1168
31	28	H10	C4	C5	C3	0	969	1051	1168	969	1051	1168
32	29	H11	C5	C6	C4	0	969	1051	1168	969	1051	1168
33	30	H12	C6	C1	C5	0	969	1051	1168	969	1051	1168

[a] Distances in Å, angles in degrees, frequencies in cm^{-1}. Nuclei A, B, C, and D are numbered according to Figure 2. Parameters 28–33 ($X = H$, **1a**) and 25–30 ($X = D$, **1b**) correspond to out-of-plane bending angles γ.

ternal bond angles, a set of symmetry-equivalent external bond angles, and a minimum of symmetry equivalent torsional angles [5]. Problems become obvious when one wants to investigate a cyclic molecule for which there exist different choices of the CC stretching motions as e.g., for 1,6-methano[10]annulene (**3**).



(**3**)

TABLE III

Internal parameters q_n and internal frequencies ω_n ($n = a$; adiabatic internal frequencies; n = BG: intrinsic frequencies; $n = c$: c-vector frequencies) calculated for (a) cyclooctatetraene dication (2a) and (b) 1,2-dideuterocyclooctatetraene dication (2b) at the HF / 6-31G(d, p) level of theory.[a]

$X = H$	$X = D$	Parameter set					$X = H$ (**2a**)			$X = D$ (**2b**)		
n	n	A	B	C	D	q_n	ω_a	ω_{BG}	ω_c	ω_a	ω_{BG}	ω_c
1	1	C1	C2			1.400	1325	1293	1411	1325	1412	2099
2	2	C2	C3			1.400	1325	1293	1411	1325	1243	1732
3	3	C3	C4			1.400	1325	1293	1411	1325	1267	1534
4	4	C4	C5			1.400	1325	1293	1411	1325	1462	1670
5		C5	C6			1.400	1325	1293	1411			
6	5	C6	C7			1.400	1325	1293	1411	1325	1462	1670
7	6	C7	C8			1.400	1325	1293	1411	1325	1267	1534
8	7	C8	C1			1.400	1325	1293	1411	1325	1243	1732
9	8	C1	C2	C3		135.0	802	671	951	802	595	5741
10	9	C2	C3	C4		135.0	802	671	951	802	768	4284
11	10	C3	C4	C5		135.0	802	671	951	802	1120	2348
12		C4	C5	C6		135.0	802	671	951			
13		C5	C6	C7		135.0	802	671	951			
14	11	C6	C7	C8		135.0	802	671	951	802	1120	2348
15	12	C7	C8	C1		135.0	802	671	951	802	768	4284
16	13	C8	C1	C2		135.0	802	671	951	802	595	5741
17	14	C1	C2	C3	C4	0	248	−312	705	248	−684	3706
18	15	C2	C3	C4	C5	0	248	−312	705	248	−257	2178
19		C3	C4	C5	C6	0	248	−312	705			
20		C4	C5	C6	C7	0	248	−312	705			
21		C5	C6	C7	C8	0	248	−312	705			
22	16	C6	C7	C8	C1	0	248	−312	705	248	−257	2178
23	17	C7	C8	C1	C2	0	248	−312	705	248	−684	3706
24	18	C8	C1	C2	C3	0	248	−312	705	248	535	4448
25	19	X9	C1			1.077	3349	3347	3351	2459	2455	2460
26	20	X10	C2			1.077	3349	3347	3351	2459	2455	2460
27	21	H11	C3			1.077	3349	3347	3351	3349	3347	3351
28	22	H12	C4			1.077	3349	3347	3351	3349	3347	3351
29	23	H13	C5			1.077	3349	3347	3351	3349	3347	3351
30	24	H14	C6			1.077	3349	3347	3351	3349	3347	3351
31	25	H15	C7			1.077	3349	3347	3351	3349	3347	3351
32	26	H16	C8			1.077	3349	3347	3351	3349	3347	3351
33	27	X9	C1	C2		112.5	1473	1582	1664	1136	1175	1283
34		H10	C2	C3		112.5	1473	1582	1664			
	28	D10	C2	C1						1136	1175	1283
35		H11	C3	C4		112.5	1473	1582	1664			
	29	H11	C3	C2						1473	1582	1664
36		H12	C4	C5		112.5	1473	1582	1664			
	30	H12	C4	C3						1473	1582	1664
37		H13	C5	C6		112.5	1473	1582	1664			
	31	H13	C5	C4						1473	1582	1664
38	32	H14	C6	C7		112.5	1473	1582	1664	1473	1582	1664
39	33	H15	C7	C8		112.5	1473	1582	1664	1473	1582	1664
40	34	H16	C8	C1		112.5	1473	1582	1664	1473	1582	1664
41	35	X9	C1	C2	C8	0	607	1148	1282	523	945	1104
42	36	X10	C2	C3	C1	0	607	1148	1282	523	945	1104
43	37	H11	C3	C4	C2	0	607	1148	1282	607	1148	1282
44	38	H12	C4	C5	C3	0	607	1148	1282	607	1148	1282
45	39	H13	C5	C6	C4	0	607	1148	1282	607	1148	1282
46	40	H14	C6	C7	C5	0	607	1148	1282	607	1148	1282
47	41	H15	C7	C8	C6	0	607	1148	1282	607	1148	1282
48	42	H16	C8	C1	C7	0	607	1148	1282	607	1148	1282

[a] Distances in Å, angles in degrees, frequencies in cm^{-1}. Nuclei A, B, C, and D are numbered according to Figure 3. Parameters 41–48 ($X = H$, **2a**) and 35–42 ($X = D$, **2b**) correspond to out-of-plane bending angles γ.

In this case, it would not be clear whether the C_1C_6 distance should be included in the set of internal parameters because depending on the substituents at C_{11} one observes C_1C_6 distances between 1.6 and 2.2 Å [16]. An appropriate choice would be that shown in Figure 2(b) for 1,2-dideuterobenzene (**1b**) for which the bond length C_4C_5 (corresponding to C_1C_6 in **3**) as well as the two associated internal CCC bond angles are not included in the parameter set. While it is hardly possible to predict whether a parameter set corresponding to that of **1a** or to that of **1b** leads to more reasonable intrinsic frequencies for **3**, one can check the situation for **1b** since one knows the exact answer in this case: *D*-substituents as in **1b** do not change the electronic structure of **1** and, therefore, all internal motions apart from those involving the *D* atoms have to remain unchanged:

$$\delta\omega = \omega_n(\mathbf{1a}) - \omega_n(\mathbf{1b}) = 0 \quad (\text{for } \phi_n \text{ not containing } D) \tag{38a}$$

$$\delta\omega = \omega_n(\mathbf{1b}) - \omega_m(\mathbf{1b}) = 0 \quad (\text{for } \phi_n \text{ and } \phi_m \text{ being symmetry-equivalent fragments}). \tag{38b}$$

Any deviation of $\delta\omega$ from zero reflects the dependence of ω_n on the parameter set chosen, where we define a characteristic $\delta\omega$ as the difference between maximum and minimum value of a set of internal frequencies calculated for related internal motions such as all CC stretching or all CCC bending motions [Eq. (38b)].

As shown in Table II(b), adiabatic frequencies ω_a are completely parameter set independent since all $\delta\omega$ values are equal to zero for each set of equivalent internal motions associated with the same internal parameters [ω_a(CC) = 1406 cm^{-1}, $\delta\omega_a$(CC) = 0, ω_a(CCC) = 997 cm^{-1}, $\delta\omega_a$(CCC) = 0, etc.]. This confirms that adiabatic internal motions reflect features of the electronic structure rather than the choice of the internal parameter set. In the case of **3**, it would not matter whether the C_1C_6 parameter would be considered in the analysis or not. For all possible parameter sets, a particular internal motion of **3** would always possess the same adiabatic frequency.

On the other hand, **c**-vector frequencies for CC stretching motions of **1b** calculated with the parameter set indicated in Figure 2(b) vary between 1671 and 2196 cm^{-1}, thus yielding a characteristic parameter set error of $\delta\omega_c$(CC) = 525 cm^{-1} [Table II(b)]. Apart from this, ω_c frequencies adopt unphysically large values for CC stretching motions [$\omega_c(C_1C_2)$ = 2196 cm^{-1}, Table II(b)] and CCC bending motions [$\omega_c(C_1C_2C_3)$ = 4152 cm^{-1}, $\delta\omega_c$(CCC) = 1690 cm^{-1}), which are considerably larger than the corresponding adiabatic or intrinsic frequencies [1406, 1480 and 997, 725 cm^{-1}; see Table II(b)]. As mentioned above, the **c**-vectors are defined by the constrain **BC** = **I**, which enforces an unphysical form of the **c**-vector for the C_1C_2 stretching motion as is shown in Figure 4. Stretching of C_1C_2 automatically involves a stretching of bond C_4C_5 [Fig. 4(a)] in the **c**-vector description, which almost doubles the stretching frequency. On the other hand, the adiabatic vector describing the C_1C_2 stretching motion is largely localized in the C_1C_2 fragment [Fig. 4(b)] and, therefore, provides a physically reasonable account of the stretching mode.

In the case of the intrinsic frequencies of BG, one also finds relatively large characteristic parameter set errors for **1b** [$\delta\omega_{BG}$(CC) = 174 cm^{-1}; $\delta\omega_{BG}$(CCC) = 603 cm^{-1}, Table II(b)]. Three out of five CC stretching frequencies are different indicating a dependence on the *D* atoms although these atoms do not change the electronic structure of **1**.

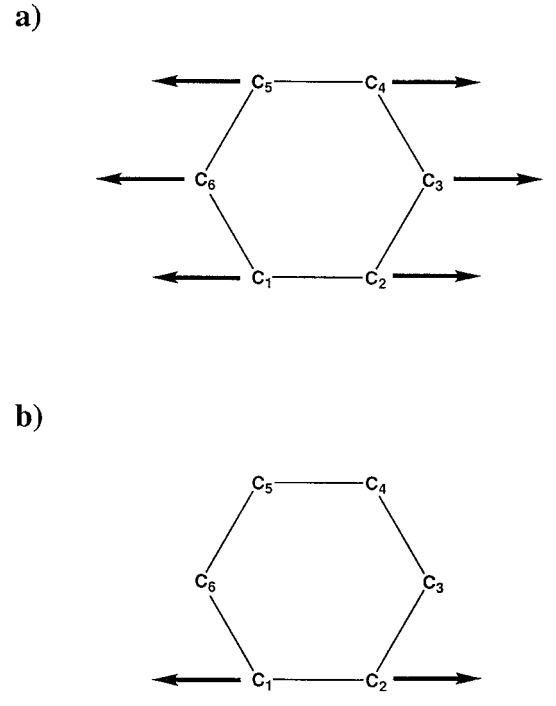


FIGURE 4. Graphical representation of (a) the **c**-vector stretching motion and (b) the adiabatic stretching motion of bond C1C2 in benzene. Displacements of atoms are indicated by arrows.

Clearly, **c**-vector frequencies and intrinsic frequencies do not lead to a physically or chemically reasonable description of the internal modes of **3** and, therefore, cannot be recommended. Of course, in the case of **1b**, one could reinstall the parameter set of **1a** [Fig. 2(a)] and get a reasonable account of internal modes. This is possible since the exact answer is known a priori, but, however, becomes impossible to solve in the case of substituents that change the electronic structure of **1**.

This is also revealed by the second example investigated in this connection, namely, the 1,2-dideuterocyclooctatetraenedication (**2b**) (Fig. 3), for which the D_{8h} symmetry of **2a** is lowered to C_{2v} and, again, a less symmetrical parameter set is used [Fig. 3(b)] to anticipate results for molecules with lower or no symmetry at all. Compared to **1**, the characteristic parameter set error of the intrinsic frequencies of the CC stretching motion increases to $\delta\omega_{BG}(\mathrm{CC}) = 219\ \mathrm{cm}^{-1}$ in the case of **2b** [see Table III(b)], which reflects some dependence on the number of CC bonds forming the ring. The parameter set error for the CCC bending motions is somewhat smaller for **2b** [$\delta\omega_{BG}(\mathrm{CCC}) = 525\ \mathrm{cm}^{-1}$] than for **1b**; however, it is still relatively large (63%) compared to an averaged intrinsic CCC bending frequency of 828 cm^{-1}.

There are molecules for which one can test different nonredundant parameter sets complying with the four rules of BG and still obtain relatively large deviations in calculated intrinsic frequencies. As an example, we consider benzocyclobutadiene (**4**) (Fig. 5), for which we have tested four different parameter sets. The common parameters of these sets are given in Figure 5 (in normal print) while the differences between them are caused by the choice of the additional bond length parameter r (set 1), bond length parameter w_1 (set 2), parameter w_2 (set 3), or, alternatively, all three of them at same time (set 4). The calculated BG intrinsic fre-

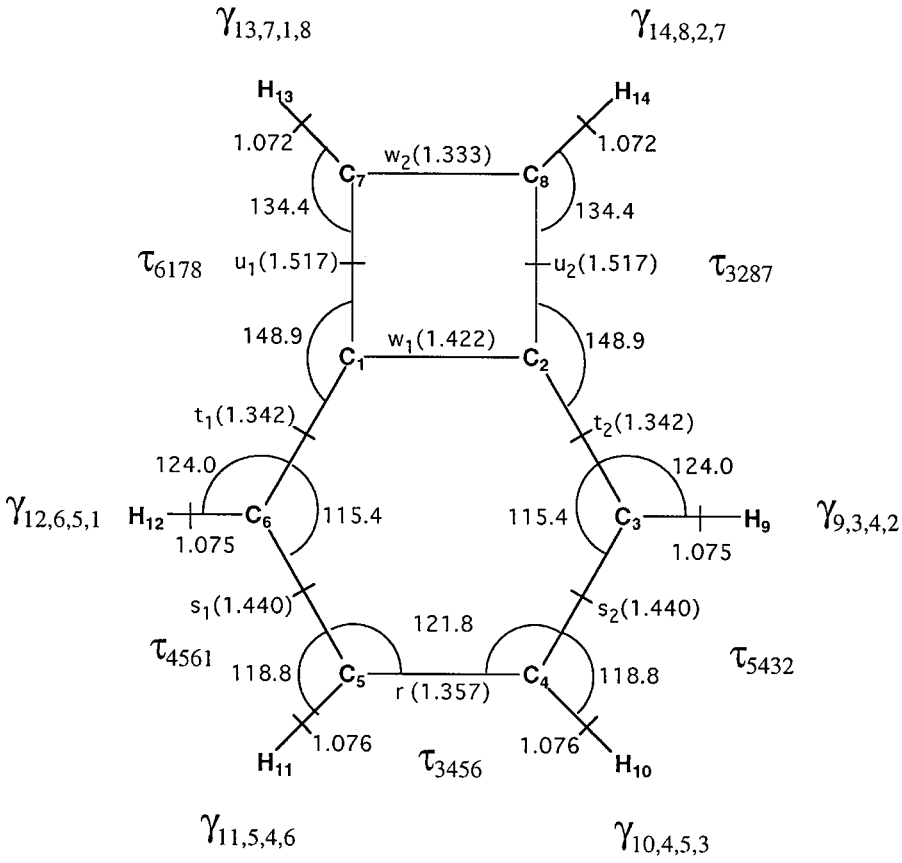


FIGURE 5. Parameter sets and HF / 6-31G(d, p) equilibrium geometry of benzocyclobutadiene (**4**). Numbering of atoms and the notation of parameters (torsional angles τ and out-of-plane bending angles γ) is explicitly given. Bond lengths and bond angles covered in the parameter set are indicated by a perpendicular line through the bond line and an arc connecting the bonds involved in the bending motion.

quencies (Table IV) for the CC stretching motions (s_1, s_2, t_1, t_2; see Fig. 5) change considerably in dependence of the choice of r, w_1, w_2. For example, by replacing r by w_1, the intrinsic frequency of the motion associated with s_1 and s_2 changes by $\delta\omega(s) = 150\ \text{cm}^{-1}$ from 1135 to 1285 cm^{-1} (Table IV). At the same time, the intrinsic frequency corresponding to parameters t_1 and t_2 decreases from 1710 to 1639 cm^{-1}, leading to $\delta\omega(t) = 71\ \text{cm}^{-1}$. Replacement of w_1 by w_2 does not lead to a significant change in intrinsic frequencies, while the intrinsic frequencies of the internal motions associated with parameters u_1 and u_2 do not change at all. Clearly, it is difficult to predict these changes and to indicate which parameter set leads to the most reasonable description of **4**.

To avoid these problems of obtaining reliable intrinsic frequencies, one can use parameter set 4 containing two additional redundant parameters. This automatically leads to a decrease in frequency values associated with parameters r, w_1, w_2 (from 1609, 1382, and 1717 cm^{-1} to 1492, 1241, 1667 cm^{-1}, Table IV) resulting in $\delta\omega$ values of 117, 141, and 50 cm^{-1}, respectively. Clearly, these changes just caused by a variation of the parameter set used make it difficult to relate intrinsic frequency values to other fragment properties such as bond lengths or bond energies in the case of diatomic fragments.

INTERNAL FREQUENCIES OF TORSIONAL MOTIONS

Adiabatic and **c**-vector frequencies associated with torsional parameters τ [Fig. 3(a)], which describe the out-of-plane motions of the C atoms of **2**, are all positive [248 and 705 cm^{-1}; Table III(a)] in line with the fact that **2** in its equilibrium geometry adopts a planar form. On the other hand, the eight torsional intrinsic frequencies are negative [Table III(a)] despite the fact that the choice of the torsional parameters complies with the rules suggested by BG (minimum number of symmetry equivalent torsional angles) [5]. As a matter of fact, it is impossible to select a set of symmetry-equivalent torsional angles that leads to positive values for the torsional intrinsic frequencies. This is shown in Table V where all possible sets of symmetry equivalent torsional parameters and their associated intrinsic frequencies are listed.

Similar problems with the intrinsic frequencies of torsional motions occur in the case of **4** despite the fact that the minimum number of symmetry-equivalent torsional angles required by the BG rules is chosen (Fig. 5). The torsional intrinsic frequencies associated with parameters τ_{3456}, τ_{4561}, τ_{5432}, τ_{6178}, and τ_{3287} are equal to 676, 981, 981, -763, and -716 cm^{-1}, respectively. However, by adding the torsional angles τ_{1782} and τ_{6123}, which actually is in conflict with the fourth BG rule [5], one obtains positive torsional frequencies of 376, 329, 329, 328, 328, 545, and 610 cm^{-1}. These examples show that the intrinsic frequencies lead to incorrect descriptions which suggest for both **2** and **4** nonplanar geometries. These problems are not encountered in the case of adiabatic frequencies, which are all positive in the case of the torsional motions of **2** and **4**.

Conclusions

A detailed comparison of adiabatic internal frequencies, intrinsic internal frequencies, and **c**-vector internal frequencies reveals advantages of ω_a and disadvantages of $\omega_{n,BG}$ and ω_c.

TABLE IV

Internal stretching frequencies $\omega_{n,BG}$ and ω_a of the carbon framework of benzocyclobutadiene calculated at the HF/6-31G(d,p) level of theory for different parameter sets (see text).[a]

	Set 1 $\omega_{n,BG}$	Set 2 $\omega_{n,BG}$	Set 3 $\omega_{n,BG}$	Set 4 $\omega_{n,BG}$	Sets 1–4 ω_a
r	1609	—	—	1492	1547
$w1$	—	1382	—	1241	1332
$w2$	—	—	1717	1667	1720
$s1, s2$	1135	1285	1285	1200	1254
$t1, t2$	1710	1639	1639	1660	1607
$u1, u2$	1154	1154	1154	1154	1120

[a] Frequencies in cm^{-1}. Parameters are defined in Figure 5.

TABLE V

Intrinsic frequencies of BG calculated for the internal torsional motions of the cyclooctatetraene-dication at the HF / 6-31G(*d*, *p*) level of theory; all possible combinations of five to maximally eight torsional parameters are considered.[a]

Parameter	Frequencies										
τ_{1234}	−312	−257	−394		−375		−357		−389	−368	−362
τ_{2345}	−312	−684	−395	−375		−379		−385	−389	−357	−332
τ_{3456}	−312	535									−321
τ_{4567}	−312	−684	−395	−482	−345	−415	−357	−395	−354	−357	−302
τ_{5678}	−312	−257		−161	−497	−383	−438	−328	−337	−368	−321
τ_{6781}	−312		−395	−497	−283		−266	−325	−337	−357	−332
τ_{7812}	−312			−367		−383	−266	−328	−354		−362
τ_{8123}	−312		−395		−440	−415	−438	−395		−357	

[a] Frequencies in cm^{-1}. Torsional parameters are defined in Figure 2.

1. Contrary to adiabatic internal frequencies, intrinsic frequencies are based on an averaging procedure rather than a dynamic principle. As a consequence, intrinsic frequencies cannot fully reflect the physics of vibrational motions.
2. Intrinsic frequencies $\omega_{n,BG}$ depend strongly on the parameter set used to describe the geometry of the molecule. For example, by increasing the size of the parameter set, intrinsic frequencies decrease in magnitude. Adiabatic frequencies are completely independent of the choice of the parameter set.
3. Intrinsic frequencies can become negative because the amplitudes $A_{n\mu}$ defining $\omega_{n,BG}$ in Eq. (9) can be negative. As shown for the equilibrium geometry of molecules **2** and **4**, this leads to false information on the potential energy surface in question. In all these cases, adiabatic frequencies are positive in agreement with the fact that equilibrium geometries are investigated.
4. To make sure that intrinsic frequencies associated with symmetry-equivalent parameters adopt the same values, certain rules have to be applied which lead to redundant parameter sets and to an artificial reduction of the values of intrinsic frequencies. Adiabatic frequencies contain the same value for both redundant and nonredundant parameter sets.
5. Using the GF formulation of intrinsic frequencies [Eq. (32)–(34)], we have demonstrated that for these internal frequencies electronic and mass effects are not separated properly thus spoiling the description of electronic effects with the help of intrinsic frequencies. For the adiabatic frequencies, electronic and mass effects are strictly separated, which makes these frequencies perfectly suited for the description of the electronic structure of molecules.
6. Despite these deficiencies, intrinsic frequencies can be useful for acyclic molecules with low symmetry, for which the problems discussed above are not apparent. In these cases, intrinsic frequencies are certainly better than **c**-vector frequencies, which suffer from the fact that (a) they depend on the constrain $\mathbf{BC} = \mathbf{I}$ and (b) they are not localized in the molecular fragment ϕ_n that they should describe. The examples given (see Tables I–III) clearly suggest that one should refrain from using these frequencies.
7. In article I [1], we considered various possibilities of defining adiabatic internal masses, which led to internal frequencies ω_a, Ω_a, Ω_c, etc. The discussion of the internal frequencies of ethene and *cis*-1,2-dichloroethene (Table I and Fig. 1) clearly reveals that Ω frequencies are not useful since they are defined without using a fragment characteristic mass and, therefore, mass effects disguise electronic effects in these internal frequencies. In C_2H_4, Ω_c(CC) changes by 766 cm^{-1} when two H atoms are replaced by Cl atoms even though the CC bond does not change largely with regard to its electronic nature and bond length.

The comparison of internal frequencies carried out in this work clearly shows that the adiabatic internal frequencies represent the best choice of describing molecular fragments and assigning typical frequencies to any two-, three-, or *n*-atom unit. This leads to a new basis for describing chemical bonds in polyatomic molecules, which was previously not possible. The superiority of adiabatic frequencies compared to intrinsic frequencies will become even more obvious if one thinks about the calculation of characteristic frequencies for internal motions such as scissoring, rocking, twisting, or wagging of functional AH_n groups. Calculation of the intrinsic frequencies leads to large parameter set errors $\delta\omega$ that hardly provide a basis for characterization of these modes.

It will be a topic of further work to investigate in which situations it is of advantage to apply adiabatic modes. Possible are the analysis of vibrational spectra in terms of adiabatic modes, the description of structural units using the properties of adiabatic modes, the determination of molecular geometries with the help of vibrational spectroscopy, and the description of reaction mechanism. Some of these topics will be discussed in the following articles of this series [9, 17].

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