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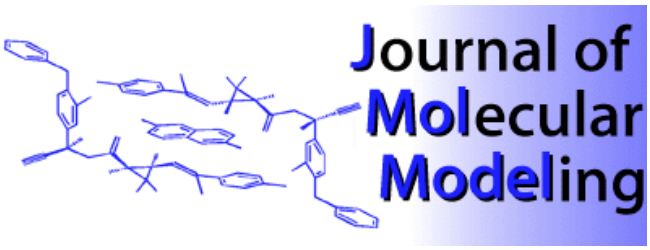


**FULL PAPER**

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# Some Thoughts about Bond Energies, Bond Lengths, and Force Constants

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**Abstract** The bond energy (BE) of a polyatomic molecule cannot be measured and, therefore, determination of BEs can only be done within a model using a set of assumptions. The bond strength is reflected by the intrinsic BE (IBE), which is related to the intrinsic atomization energy (IAE) and which represents the energy of dissociation under the provision that the degree of hybridization is maintained for all atoms of the molecule. IBE and BE differ in the case of CC and CH bonds by the promotion, the hybridization, and the charge reorganization energy of carbon. Since the latter terms differ from molecule to molecule, IBE and BE are not necessarily parallel and the use of BEs from thermochemical models can be misleading. The stretching force constant is a dynamical quantity and, therefore, it is related to the bond dissociation energy (BDE). Calculation and interpretation of stretching force constants for local internal coordinate modes are discussed and it is demonstrated that the best relationship between BDEs and stretching force constants is obtained within the model of adiabatic internal modes. The valence stretching force constants are less suitable since they are related to an artificial bond dissociation process with geometrical relaxation effects suppressed, which leads to an intrinsic BDE (IBDE). In the case of $AX_n$ molecules, symmetric coordinates can be used to get an appropriate stretching force constant that is related to the BE. However, in general stretching force constants determined for symmetry coordinates do not reflect the strength of a particular bond since the related dissociation processes are strongly influenced by the stability of the products formed.

**Keywords** Bond energy (BE), Intrinsic bond energy (IBE), Bond dissociation energy (BDE), Force constants, Adiabatic internal mode

## Introduction

A primary goal of molecular modeling is the prediction of structure, stability, and chemical reactivity of molecules that are difficult to investigate by experimental means. Today, there are many methods ranging from simple structure descriptions to molecular mechanics and quantum chemical approaches to fulfill this goal. Each of these models is based on simplifications and assumptions, which should facilitate the task of molecular modeling. Molecular modeling does provide new insights into the properties of molecules and molecular reactivity provided one considers appropriately the assumptions and simplifications made within the model used.

Despite the enormous potential and possibilities of molecular modeling with the help of advanced quantum chemi-

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*Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday in recognition of his pioneering work in the field of Theoretical Chemistry*

cal methods, there is still a need to understand the properties and behavior of molecules on the basis of simple models that require no sophisticated calculations. One wants to connect the properties of a molecule with those of atoms, bonds, or small functional groups so that the knowledge of these group properties makes it possible to describe whatever molecule may be constructed from atoms, bonds (diatomic groups) or functional groups. Central to many of these model approaches is the theory of the chemical bond. [1-4] One assumes that properties of a particular bond are conserved when this bond is transferred from one molecule to another. In this way, one expects to predict, for example, from the known length values of typical bonds structural features of new molecules or from bond energies the stability of molecules composed of these bonds. For this reason, typical bond lengths have been tabulated [5] and sophisticated additivity schemes set up to predict from bond energies (or group energies) heats of formation and other stability data. [6,7] While this approach seems to be straightforward and has been applied successfully in many cases, it bears some basic unsolved problems, as this article will show. The major problem is that the chemical bond is not an observable quantity and does only exist within a given model. Models of the chemical bond range from simple ball-and-stick descriptions to sophisticated and rather complicated quantum chemical relationships that can be applied only in the simplest cases of bonding. The most important models today are the MO model (a bond requires the occupation of a bonding MO), [2] the Ruedenberg model (electron delocalization in the bond leads to a lowering of kinetic energy), [8] and the electron density model (the bond is represented by a maximum path of electron density connecting the nuclei in question). [4,9]

Since the chemical bond is only a model quantity (something what many chemists do not realize), all bond properties can only be defined within a given model and are thus not measurable. This applies to the bond strength, the bond energy, the bond length, the bond stretching force constant, the bond stretching frequency, the bond dipole moment, and other bond properties. This may be difficult to see on first sight, in particular since some of these quantities are listed in chemistry textbooks. Therefore, we will consider the model character of these properties one by one.

### *Bond energy*

Commonly, the bond dissociation energy (BDE) is taken as a measure for bond energy (BE) and bond strength. Clearly, this is only correct in the case of a diatomic molecule. [10] As shown in Figure 1, the BDE covers two independent stability parameters, namely a) the BE and b) the stabilization or destabilization energy of the products formed in the disso-

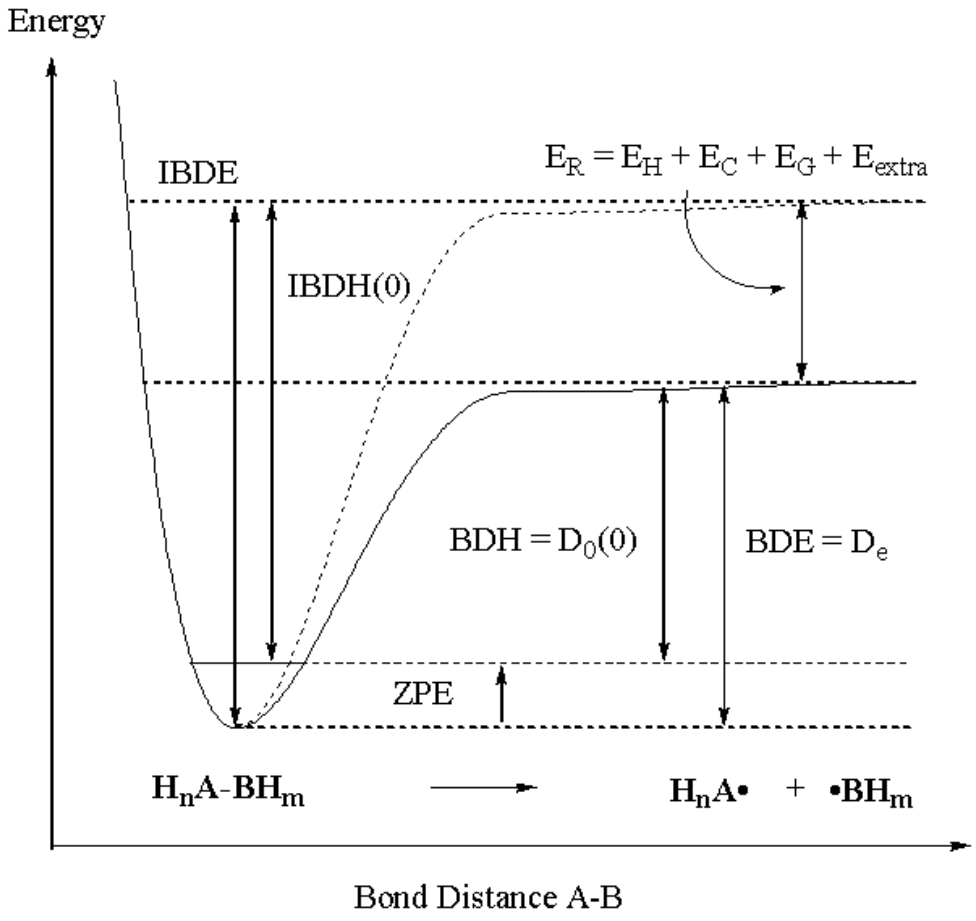


**Figure 1** *Definition of bond dissociation energy (BDE), bond dissociation enthalpy at 0 K (BDH), intrinsic BDE (IBDE), and intrinsic BDH (IBDH) for the bond A-B.* $E_R$ *denotes the reorganization energy, which is set free upon dissociation of bond* A-B *(see text)*

ciation process. There is no simple way to determine the (de)stabilization effects of the products by an independent experiment because the (de)stabilization energy is referenced with regard to an artificial state that the products would have if the same electronic features of the parent compound were retained. However, upon dissociation the dissociation products will relax geometrically, which is a consequence of rehybridzation effects in the fragments formed. In addition, the fragments may stabilize because new delocalization possibilities ($\pi$-delocalization in a conjugated system, hyperconjugation, three-electron delocalization, anomeric delocalization, etc.) may develop. Methods have been developed to predict these (de)stabilization effects to correct BDEs to BEs, however, these methods are again based on model descriptions and, therefore, do not really offer a straightforward determination of the BE. [1,3,11]

*Bond length*

Diffractionists measure averaged internuclear distances and distances between averaged nuclear positions, whereas spectroscopists derive internuclear distances from the analysis of the rotational constants of the ground state of a molecule (and its isotopomers to obtain sufficient information). Experimentally, it is not possible to determine the equilibrium bond length directly, which is of major interest for the discussion of the bond strength. However, for the sake of simplification we assume that the internuclear distances can be determined both experimentally and with the help of quantum chemical calculations. Two questions arise: 1) Suppose that one considers two atoms, for which the internuclear distance decreases. At what distance does a bond between the two atoms develop so that one can speak of a bond length? 2) Bonds can be bent as found in small rings. [4,12,13] What distance can be used as bond length since the internuclear distance is no longer equal to the bond length? This question is actually also relevant for acyclic molecules since there is indication for small molecules that the path of maximum electron density, which can be considered as an image of the chemical bond, [9,14] does not follow the internuclear distance. [9,12,13] – In view of these questions a strict definition of bond length seems to be more problematic than is generally assumed, particularly if one wants to use the bond length as a descriptive parameter for the determination of the bond strength.

*Bond stretching force constant and bond stretching frequency*

Apart from diatomic molecules, the stretching modes of a molecule couple to some extent among each other (for example, when there are equivalent bonds) and, also, with other modes. As will be discussed in the next chapter in more detail, it is misleading to associate in the case of a polyatomic molecule one of the normal modes of the molecule with the stretching mode of a particular bond since normal modes are always delocalized. Hence, vibrational spectroscopy does not provide direct and unbiased information on the bond stretching force constant and bond stretching frequency of a particular bond of a polyatomic molecule. This can only be obtained with the help of a model of local vibrational modes as will be discussed in the next chapter.

*Bond dipole moment*

The bond dipole moment depends on the internuclear distance and the charges of the atoms linked by a bond. Although atomic charges can be calculated in many ways quantum chemically or determined with the help of measured infrared intensities, the definition of the atomic charge is only possible if the atom in a molecule is defined within a given model. Accordingly, there are many different definitions of the bond dipole moment always related to a particular model of the atom in a molecule and of the atomic charge.

Obviously, all properties of a bond can only be defined within a given model. Observable molecular properties, which are often related to bonds, depend actually on the whole molecule (its wave function or electron density) or the potential energy surface (PES) at and in the vicinity of that stationary point, which is occupied by the molecule in question. This is true for the BDE, which depends on the stability of the fragments generated in the dissociation process. And it is also true for bond stretching frequencies taken from measured infrared or Raman spectra since the vibrational modes associated with the frequency in question are not localized in the bond, but extend to other parts of the molecule. In view of this, the question has to be asked whether the bond strength can be described at least within a suitable model using bond properties determined within this model. This could be done within an orbital model, a density model of the bond or a dynamic model based on the PES of the molecule in question.

In this work, we will discuss the possibility of describing bond strength and bond energy with the help of the model of local bond stretching modes and their associated force constants and frequencies. For this purpose, we will distinguish between static bond properties such as bond length, bond dipole moment, bond order, etc. and dynamic bond properties such as stretching force constant, stretching frequency, etc. We will discuss the question whether the bond strength as a static quantity can be described with both static and dynamic bond properties. In chapter 2, we will first consider various possibilities of defining a bond stretching force constant. Then, we will make a choice as for the most useful definition of a bond stretching force constant. In chapter 3, we will critically review the definition of a bond energy. In particular, we will discuss those situations, in which the bond energy really reflects the strength of a chemical bond. Finally, in chapters 4 and 5, the relationships between bond strength, bond energies and bond stretching force constants are analyzed. As an application example, we will discuss the strength of the CC and CH bonds of cyclopropane in chapter 6.

## Bond stretching force constants

As noted above bond stretching force constant and bond stretching frequency are not observable quantities. Measurable are only molecular frequencies, which with the help of the normal mode analysis can be associated to the vibrational normal modes $\mathbf{l}_\mu$ of a *K*-atomic molecule using the basic equation of vibrational spectroscopy [15] expressed in terms of Cartesian displacement coordinates

$$\Delta\mathbf{x} = \mathbf{x} - \mathbf{x_e} \equiv \mathbf{x} = \left(x_1, y_1, z_1, \ldots, x_{3K}, y_{3K}, z_{3K}\right)^\dagger \quad (1)$$

or in terms of internal displacement coordinates

$$\Delta\mathbf{q} = \mathbf{q} - \mathbf{q_e} \equiv \mathbf{q} = \left(q_1, \ldots, q_{N_{Vib}}\right)^\dagger \quad (2)$$

as

$$\mathbf{fL} = \mathbf{ML}\Lambda \quad (3)$$

or

$$\mathbf{FD} = \mathbf{G}^{-1}\mathbf{D}\Lambda \quad (4)$$

In these equations **f** and **F** denote the force constant matrix expressed in Cartesian displacement coordinates and internal displacement coordinates, respectively; **M** is the mass matrix, **G** the Wilson matrix defined by Eqs. 5 and 6:

$$\mathbf{G} = \mathbf{B}\mathbf{M}^{-1}\mathbf{B}^\dagger \quad (5)$$

$$B_{ni} = \left(\frac{\partial q_n(\mathbf{x})}{\partial x_i}\right)_{\mathbf{x}=\mathbf{x_e}} \quad (6)$$

$\Lambda$ is the eigenvalue matrix (dimension 3K x 3K) with the $N_{vib} = 3K - M$ vibrational eigenvalues $\lambda\mu$ on the diagonal

$$\lambda_\mu = 4\pi^2 c^2 \left(\omega_\mu\right)^2 \text{ for } \mu = 1, \ldots, 3K - M = N_{Vib} \quad (7)$$

where $\omega_\mu$ is the harmonic vibrational frequency. The eigenvector matrix **L** contains $N_{Vib}$ normal mode eigenvectors $\mathbf{l}_\mu$ as column vectors. The remaining M eigenvalues and eigenvectors of ***L*** and $\Lambda$ (M = 5 for linear and M = 6 for nonlinear molecules) correspond to overall translation and rotation of the molecule. **D** contains the normal mode vectors $\mathbf{d}_\mu$ ($\mu$ = 1, ... , $N_{vib}$) given as column vectors and expressed in internal coordinates.

The relationship between force constant matrices **f** and **F** is given by

$$\mathbf{F}=\mathbf{C}^\dagger\mathbf{f}\mathbf{C} \quad (8)$$

since matrix **C** provides the connection between normal mode vectors $\mathbf{l}_\mu$ of matrix **L** and normal mode eigenvectors $\mathbf{d}_\mu$ of matrix **D** according to

$$\mathbf{l}_\mu = \mathbf{C}\mathbf{d}_\mu \quad (9)$$

Force constant matrix **F** no longer contains the translational and rotational solutions and, consequently, **D** gives the transformation from normal coordinates **Q** to internal coordinates **q**.

$$\mathbf{q} = \mathbf{DQ} \quad (10)$$

The vibrational Eqs. 3 and 4 show clearly that the normal modes associated with the normal mode frequencies $\omega_\mu$ are delocalized modes since each normal coordinate is a linear combination of internal coordinate displacements $q_n$. Accordingly, one can consider each normal mode as a linear combination of internal coordinate modes $\boldsymbol{v_n}$, which are associated each with a particular internal coordinate $q_n$. The degree of delocalization of a normal mode is primarily determined by the amount of coupling between the internal modes constituting the normal mode. In this way, the off-diagonal elements of the force constant matrix represent the coupling force constants. This becomes clear when we realize that the "***c***-vectors" of the transformation matrix ***C***, each of which is associated with a given internal coordinate, can be used as localized internal coordinate modes. [16,17] Hence, a normal mode would be strictly localized if

$$\left(\mathbf{d}_\mu\right)_n = \delta_{n\mu} \quad (11)$$

with $\delta_n$ being the Kronecker delta. Eq. 11 leads to

$$\mathbf{l}_\mu = \mathbf{c}_n \quad (12)$$

where it is assumed that $\mu = n$. Eq. 12 is only fulfilled if all displacements along vectors $\mathbf{c_n}$ and $\mathbf{c_m}$ (m ≠ n) do not couple and a diagonal force constant matrix **F** is obtained with all coupling force constants $F_{nm} = 0$. This can be expressed by saying that electronic coupling between the localized internal modes is zero. Second, there is always mass coupling (coupling due to the kinetic energy, kinematic coupling) between the ***c***-vectors because the *G* matrix of Eq. 4 is nondiagonal. Mass coupling can only be suppressed to some extent if, for example, the reduced mass of a diatomic fragment is dominated by the mass of one of the atoms as in the case of a CH bond. However, if the two masses are comparable neither Eq. 11 nor Eq. 12 is true. Often, vibrational spectroscopists assume diagonal character of the **G** matrix if there is a large mass difference between the atoms participating in the molecular motions since this assumption is the only basis to discuss measured frequencies in terms of internal mode frequencies.

In view of this discussion, it makes little sense to select a particular vibrational normal mode of a polyatomic molecule as stretching vibration of a particular bond and to use the associated stretching force constant $k_\mu$ as measure for the bond strength. Because of this, Konkoli and Cremer developed the theory of adiabatic internal modes (AIMs), which can be used to describe the dynamic properties of well-specified molecular fragments. [16] Each AIM of a molecule is associated with just one internal coordinate $q_n$, i.e. it is independent of all the other internal coordinates $q_m$ (m ≠ n). The construction of an AIM is based on the question how an internal coordinate mode $\boldsymbol{\nu_n}$ would vibrate if the associated internal coordinate were displaced by an amount $q_n^*$ in the way that the increase in the potential energy is minimal. To accomplish this goal, mode $\boldsymbol{\nu_n}$ which is lead by $q_n^*$ (leading parameter principle [16]), must be constrained to the molecular fragment associated with $q_n$, i.e. the rest of the molecule is allowed to relax upon applying a perturbation $q_n^*$. This is equivalent to minimizing the potential energy given in normal coordinates **Q** under the constraint that the internal coordinate displacement $q_n$ is kept constant:

$$V(\mathbf{Q}) = min. \tag{13a}$$

$$q_n = const. = q_n^* \tag{13b}$$

The potential energy V and the internal coordinate $q_n$ depend on the normal coordinates according to Eq. 14 (harmonic approximation) and Eq. 15.

$$V(\mathbf{Q}) = \frac{1}{2}\sum_{\mu=1}^{N_{Vib}} k_\mu Q_\mu^2 \tag{14}$$

$$q_n(\mathbf{Q}) = \sum_{\mu=1}^{N_{Vib}} D_{n\mu} Q_\mu \tag{15}$$

where $D_{n\mu}$ is an element of matrix **D**. Eq. 13 is solved with the help of a Lagrange multiplier λ,

$$\frac{\partial}{\partial Q_\mu}\left[V(\mathbf{Q}) - \lambda\left(q_n(\mathbf{Q}) - q_n^*\right)\right] = 0 \tag{16}$$

The solution of Eq. 16 for internal parameter $q_n$ and the μth normal coordinate is given by

$$Q_\mu^{(n)} = \frac{\dfrac{D_{n\mu}}{k_\mu}}{\displaystyle\sum_{\nu=1}^{N_{Vib}} \frac{D_{n\nu}^2}{k_\nu}} q_n^* \tag{17}$$

which means that the constraint to internal coordinate $q_n$ leads to a change in the normal coordinates. The adiabatic internal mode $\mathbf{a}_n^{\mathbf{Q}}$ for internal coordinate $q_n$ expressed in terms of normal coordinates takes the form of Eq. 18:

$$Q_\mu^n = \left(\mathbf{a}_n^{\mathbf{Q}}\right)_\mu q_n^* \tag{18}$$

The AIM $\mathbf{a}_n^{\mathbf{Q}}$ can be transformed to AIM $\mathbf{a}_n$ expressed in Cartesian coordinates with the help of the **L**-matrix.

$$\mathbf{a}_n = \mathbf{L}\mathbf{a}_n^{\mathbf{Q}} \tag{19}$$

Force constant, mass, and frequency of an AIM are defined by Eqs. 20, 21, and 22 [16,17]:

$$k_n^a = \mathbf{a}_n^\dagger \mathbf{f} \mathbf{a}_n \tag{20}$$

$$m_n^a = \frac{\left(\mathbf{b}_n^\dagger \mathbf{a}_n\right)^2}{\mathbf{b}_n^\dagger \mathbf{M}^{-1} \mathbf{b}_n} \tag{21}$$

$$\omega_n^a = \left(\frac{\mathbf{a}_n^\dagger \mathbf{f} \mathbf{a}_n}{G_{nn}}\right)^{1/2} = \left(\frac{k_n^a}{m_n^a}\right)^{1/2} \tag{22}$$

where vector $\mathbf{b_n}$ corresponds to the nth column of the **B** matrix and where

$$\mathbf{b}_n^\dagger \mathbf{a}_n = 1 \tag{23}$$

since the AIMs are properly normalized. The AIM mass can be recognized to be identical to element $1/G_{nn}$ associated with the ***G*** matrix and, accordingly, represents a generalization of the reduced mass for internal parameters associated with more than two atoms.

Utilizing the definition of AIMs, each bond of a molecule can be associated uniquely with a bond stretching force constant $k_n^a$ and frequency $\omega_n^a$, which together with bond length $q_n$ establish a set of bond parameters which may be related to the bond strength. AIM force constants and frequencies can be calculated with the help of quantum chemical methods or measured vibrational spectra. [18] Experimental AIM force constants and frequencies will be denoted as $k_n^{a,exp}$ and $\nu_n^{a,exp}$, respectively, to distinguish from calculated $k_n^a$ and $\omega_n^a$ values, which depend on the harmonic approximation and the quantum chemical method used for their calculation. In this work, we will primarily focus on experimental AIM properties to avoid a distracting discussion of the accuracy of the quantum chemical methods used. Nevertheless, we will also present calculated quantities to document agreement or disagreement between theory and experiment.

Another advantage of the AIM concept is that it can be applied to any set of internal parameters used for the description of the molecular geometry. Hence, one can also determine the AIMs for a set of symmetry coordinates $q_s$, which will become necessary if one wants to describe equivalent bonds of a molecule appropriately. The corresponding force

**Table 1** *Comparison of CH and CC stretching force constants calculated for some hydrocarbons at B3LYP/6-31G(d,p). [a]*

| Molecule | Bond | $r_e$ | $k_n^c$ | $k_s^c$ | $k_n^a$ | $k_s^a$ | $k_n^{c.exp}$ | $k_s^{c.exp}$ | $k_n^{a.exp}$ | $k_s^{a.exp}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $CH_4$ | C-H | 1.092 | 5.421 | 5.510 | 5.365 | 5.510 | 4.949 | 5.053 | 4.897 | 5.053 |
| $C_2H_6$ | C-C | 1.530 | 4.493 | 4.493 | 4.149 | 4.149 | 4.396 | 4.396 | 4.033 | 4.033 |
| | C-H | 1.095 | 5.265 | 5.351 | 5.214 | 5.312 | 4.835 | 5.041 | 4.787 | 5.004 |
| $C_3H_8$ | C-C | 1.531 | 4.411 | 4.552 | 4.075 | 4.284 | 4.323 | 4.461 | 3.967 | 4.176 |
| | C-H(c) | 1.098 | 5.137 | 5.191 | 5.093 | 5.142 | 4.736 | 4.715 | 4.695 | 4.670 |
| | C-H(ip) | 1.095 | 5.269 | 5.274 | 5.219 | 5.219 | 4.843 | 4.883 | 4.795 | 4.828 |
| | C-H(op) | 1.096 | 5.228 | 5.278 | 5.174 | 5.230 | 4.810 | 4.955 | 4.759 | 4.906 |
| c-$C_3H_6$ | C-C | 1.508 | 4.423 | 4.268 | 4.140 | 4.135 | 4.163 | 4.018 | 3.891 | 3.885 |
| | C-H | 1.086 | 5.568 | 5.599 | 5.540 | 5.562 | 5.143 | 5.215 | 5.117 | 5.181 |
| c-$C_6H_{12}$ | C-C | 1.537 | 4.429 | 4.570 | 3.920 | 4.414 | 4.364 | 4.511 | 3.808 | 4.340 |
| | C-H(ax) | 1.100 | 5.066 | 5.065 | 5.016 | 4.986 | 4.585 | 4.568 | 4.539 | 4.494 |
| | C-H(eq) | 1.097 | 5.155 | 5.182 | 5.115 | 5.148 | 4.710 | 4.788 | 4.672 | 4.756 |
| $C_2H_4$ | C=C | 1.330 | 10.107 | 10.107 | 9.911 | 9.911 | 9.207 | 9.207 | 8.976 | 8.976 |
| | C-H | 1.087 | 5.603 | 5.637 | 5.572 | 5.616 | 5.130 | 5.164 | 5.102 | 5.146 |
| $C_4H_6$ | C=C | 1.340 | 9.547 | 9.397 | 9.301 | 9.087 | 8.792 | 8.654 | 8.488 | 8.254 |
| | C-C | 1.457 | 5.396 | 5.396 | 5.153 | 5.153 | 5.168 | 5.168 | 4.885 | 4.885 |
| | C-H(to) | 1.085 | 5.664 | 5.666 | 5.636 | 5.637 | 5.149 | 5.128 | 5.123 | 5.101 |
| | C-H(ti) | 1.087 | 5.588 | 5.587 | 5.554 | 5.556 | 5.096 | 5.054 | 5.065 | 5.026 |
| | C-H(c) | 1.090 | 5.458 | 5.458 | 5.429 | 5.414 | 4.961 | 4.944 | 4.932 | 4.903 |
| $C_6H_6$ | C=C | 1.396 | 7.502 | 8.010 | 6.601 | 8.006 | 7.096 | 7.581 | 6.212 | 7.576 |
| | | | 7.282 | | | | 6.873 | | | |
| | C-H | 1.086 | 5.584 | 5.612 | 5.564 | 5.609 | 5.133 | 5.113 | 5.113 | 5.109 |
| $C_2H_2$ | C ° C | 1.205 | 17.647 | 17.647 | 17.645 | 17.645 | 15.824 | 15.824 | 15.820 | 15.820 |
| | C-H | 1.066 | 6.472 | 6.474 | 6.472 | 6.473 | 5.906 | 5.886 | 5.905 | 5.885 |

*[a] All force constants in mdyn Å$^{-1}$. Abbreviations have the following meanings: c, central $CH_2$ or CH group; ip, in-plane CH bond; op, out-of-plane CH bond; ax, axial CH bond; eq, equatorial CH bond; to, terminal CH bond, outwardly directed; ti, terminal CH bond, inwardly directed.*

constants will be identified by the symbol $k_s^a$ and $k_n^{a,exp}$ depending on whether they are calculated with a quantum chemical method or derived from experimental frequencies.

Vibrational spectroscopists prefer to discuss the bonds of a molecule in terms of the force constants $k_n^c$ of the valence force field of the molecule. As noted above these force constants are associated with vectors $c_n$ of matrix $\boldsymbol{C}$. Following the AIM approach, one can define local modes also for force constants $k_n^c$ and, in this way, associate a stretching frequency $\omega_n^c$ with a $\boldsymbol{c}$-vector mode. [16,17] Therefore, we will consider the possibility of describing chemical bonds with either $k_n^c$ or $k_n^a$. In total, eight different bond stretching force constants can be considered when the strength of a given bond should be described:

$$k_n^c,\ k_n^{c,\mathrm{exp}},\ k_s^c,\ k_s^{c,\mathrm{exp}},\ k_n^a,\ k_n^{a,\mathrm{exp}},\ k_s^a,\ k_s^{a,\mathrm{exp}} \qquad (24)$$

which are either directly obtained from a quantum chemical calculations or derived from measured vibrational frequencies [19] ($k^{exp}$) as described in ref [18]. In Table 1, these force constants are listed for a small set of selected hydrocarbons, which will be discussed in the following chapters. Calculated values were obtained with density functional theory (DFT) employing the B3LYP hybrid functional [20] and the 6-31G(d,p) basis set. [21] It is well-known that this approach provides rather reliable force constants and frequencies for most first row molecules, [22] in particular hydrocarbons, which will be exclusively considered in this work. There are some general trends in calculated or experimentally based stretching force constants, which can be summarized as follows.

(1) Calculated stretching force constants are always larger than force constants derived from experimental spectra due to the harmonic approximation used for the calculation of the vibrational modes.

(2) AIM stretching force constants $k_n^a$ are mostly somewhat smaller than the $\boldsymbol{c}$-vector stretching force constants $k_n^c$, which has to do with the adiabatic relaxation of the molecular geometry when calculating the former.

(3) Use of symmetry coordinates leads in most cases (see Table 1) to a slight but significant increase of the stretching force constant. The exceptions of these trends can be explained when considering the molecular structure.

(4) Both AIM and $\boldsymbol{c}$-vector stretching force constants associated with bond lengths $q_n$ increase (decrease) for decreasing (increasing) magnitude of $q_n$. In general, this is no longer

true for stretching force constants calculated with symmetry coordinates $q_s$.

(5) The matrix of $k_n^c$ constants does not necessarily comply with the symmetry of the molecule (see, e.g., $C_6H_6$ in Table 1) while the matrix of AIM force constants does. Use of symmetry coordinates always enforces the symmetry of the molecule for the force constant matrix.

One cannot say *a priori*, which force constant is more appropriate for a description of bond strength. Therefore, we will discuss in chapter 4 the physical background of the various force constants in more detail. Before this, we will analyze in chapter 3, which energy term may best describe the bond strength. In this way, a basis for relating bond characteristic energy terms and stretching force constants or stretching frequencies will be established.

## How to determine the bond energy?

For a polyatomic molecule, BEs, contrary to BDEs, cannot be measured. The BDE is the reaction energy that leads to the cleavage of a particular bond A-B

$$H_nA-BH_m \rightarrow H_nA\bullet + \bullet BH_m \tag{25}$$

The experimental dissociation enthalpy $D_0$ at T K (T = 298 K) is given by

$$\begin{aligned} D_0(T) &= \Delta\Delta H_f^0(T) \\ &= \Delta H_f^0(T, H_nA\bullet) + \Delta H_f^0(T, \bullet BH_m) \\ &\quad - \Delta H_f^0(T, H_nA-BH_m) \end{aligned} \tag{26a}$$

and is related to the (non-measurable) dissociation energy $D_e^{exp}$ at equilibrium by

$$\begin{aligned} D_e^{exp} &= E(H_nA\bullet) + E(\bullet BH_m) - E(H_nA-BH_m) \\ &= D_0 - \Delta ZPE - \Delta THERM(T) - RT \end{aligned} \tag{26b}$$

where the zero-point energy difference

$$\begin{aligned} \Delta ZPE &= ZPE(H_nA\bullet) + ZPE(\bullet BH_m) \\ &\quad - ZPE(H_nA-BH_m) \end{aligned} \tag{27a}$$

and the difference in thermal corrections

$$\begin{aligned} \Delta THERM(T) &= THERM(T, H_nA\bullet) + THERM(T, \bullet BH_m) \\ &\quad - THERM(T, H_nA-BH_m) \end{aligned} \tag{27b}$$

(containing translational, rotational and vibrational contributions) depend on the vibrational frequencies of parent molecule and fragments. Hence, one has to distinguish between the bond dissociation enthalpy measured at temperature T and the BDE obtained from a quantum chemical calculation. Knowing all vibrational corrections, one can calculate from experimental $D_0(T)$ values the corresponding $D_e^{exp}$ values and compare them with directly calculated dissociation energies $D_e^{cal}$. Similarly, one has to distinguish between the BE and the bond enthalpy BH derived from measured atomization enthalpies at T K. However, in this work, we are more interested in the conceptual role of BE and BDE and, therefore, we will use these terms irrespective of the fact whether they are obtained from measurements at T K or from calculations.

The determination of BEs in thermochemistry is based on two assumptions (1) and (2), which define the model of thermochemical BEs.

(1) The atomization energy AE of a molecule, given by the sum of BDEs, is equal to the sum of BEs:

$$AE = \sum_i BDE_i^{all} = \sum_i BE_i^{all} \tag{28}$$

where the sum runs over all bonds *i* and where $BE_i \neq BDE_i$ in the general case of a polyatomic molecule.

(2) BEs of bonds of the same type are assumed to be equal.

Assumption (2) makes it possible to determine from the AE of methane the value of BE(CH) and, then, to use this value to determine from the AE of ethane the value of BE(CC) according to

$$AE(CH_4) = 4\,BE(CH) \tag{29a}$$

$$AE(C_2H_6) = BE(CC) + 6\,BE(CH) \tag{29b}$$

Clearly, assumption (2) represents a strong simplification since the differing CH bond lengths of methane and ethane (Table 1) indicate that the BE(CH) values of the two molecules are different. Differences will become even larger if one compares CH bonds in $CH_3$, $CH_2$, and CH groups in different molecules. Linear equation systems have been set up, calculating BE(CH) and BE(CC) as averages of the CH and CC bonds of a large variety of hydrocarbons. [3,6,7] In this way, useful bond additivity schemes for the rapid calculation of thermochemical data were obtained. However, it is clear that the BEs defined in this way provide no information on individual CH and CC bonds. Accordingly, these bond additivity schemes fail if an unusual CH or CC bond is considered.

Apart from these considerations, the basic question arises whether the AE can be used as a starting point for determining bond strength and BE. The AE is a dynamic quantity since it is the energy of the scaling (atomization) reaction, i.e. that reaction for which all bond lengths of the molecule are simultaneously lengthened and broken.

$$C_m H_m \rightarrow \sum_i^m C\left(\phi_{ij,j=1,4}\right) + \sum_k^n H\left(\phi_k\right) \quad (30)$$

One can calculate this process by scaling all bond lengths of the molecule with a factor *f* increasing from 1 to ∞. In this way, all bond angles and dihedral angles of the molecule are retained, i.e. the molecule does not change symmetry during the scaling reaction since its overall shape does not change. Furthermore, we impose that the scaling (atomization) reaction (Eq. 30) does not lead to a change in spin,spin coupling between electrons and the atoms keep the form of their orbitals during the scaling reaction. The latter point is best illustrated considering a representation of the molecular wave function in terms of hybrid orbitals $\phi_j$. The degree of hybridization (mixing of AOs) is determined by the molecular wave function at the equilibrium geometry of the molecule. For the atomization reaction, it is requested that the hybrid orbitals and the degree of hybridization is maintained. However, for reasons of charge balance there will be in any case a reorganization of charge between the partners of a bond according to their electronegativity difference.

The scaling (atomization) reaction (Eq. 30) defines the intrinsic atomization energy IAE which is given by the sum of intrinsic bond energies (IBE):

$$IAE = \sum_i IBE_i \quad (31)$$

*The IBE is a direct measure of the bond strength* since it refers to the actual situation in the molecule. The IBE is much larger than the BE (similar to IBDE and BDE, Figure 1) since the latter is defined by the reaction

$$C_m H_n \rightarrow m\,C\left(^3P\right) + n\,H\left(^1S\right) \quad (32)$$

The reaction energy for

$$C\left(^3P\right) \rightarrow C\left(\phi_{ij,j=1,4}\right) \quad (33)$$

is equal to the reorganization energy $E_R$ and involves three positive energy quantities:

$$E_R = E_P + E_H + E_C \quad (34)$$

where $E_P$ is the promotion energy needed to promote an electron from the 2s(C,$^3$P) orbital to the empty 2p(C,$^3$P) orbital, $E_H$ the hybridization energy needed to mix the 2s and 2p orbitals in the excited state ($^5$S or $^3$D) to obtain the four hybrid orbitals $\phi_j$, and $E_C$ the charge reorganization energy to populate the hybrid orbitals in such a way that the situation in the molecule is correctly reflected. In the case of methane, $E_P$ and $E_H$ for *C($^3$P)* atom were estimated to be about 100 and 62 kcal mol$^{-1}$, respectively. [23]

The term $E_C$ covers several energy contributions that are a consequence of charge reorganization caused by bonding: a) delocalization of the electrons over the bond region; b) contraction of the density along the bond axis due to orbital contraction; c) polarization of the electron density from the nonbonding toward the bond region; d) charge transfer from one atom to the other if there is an electronegativity difference $\Delta\chi$ between the atoms constituting the bond. In a saturated hydrocarbon, the promotion and hybridization energy of C will dominate $E_R$ of a C-H bond so that one can neglect all other terms. Accordingly, the value of $E_R$*(C-H)* can be estimated to be 162/4 =40.5 kcal mol$^{-1}$ for each bond in methane. Hence, the IBE(CH) of methane as a true measure for bond strength should be about 144 kcal mol$^{-1}$ (for the corresponding enthalpy at 298 K, one gets 140 kcal mol$^{-1}$) while the BE(CH) is just 104 kcal mol$^{-1}$ (bond enthalpy 99.2 kcal mol$^{-1}$).

Hybridization energy $E_H$ and charge reorganization energy $E_C$ are different for the C atom in ethane and, consequently, one cannot assume that the IBE(CH) in ethane is the same as in methane. Even with the approximation $E_R(H) \approx 0$, one needs to know how $E_R(C)$ is split up between CC and CH bonds, i.e. there are at least four unknown parameters needed to relate the AE of ethane to the strength of its CC and CH bonds: $E_R$*(C,CC)*, $E_R$*(C,CH)*, *BE(CC)*, and *BE(CH)*. It is easy to see that for each additional hydrocarbon the number of unknowns increases in the way that the number of unknowns is always much larger than the number of known quantities. This leads to the following conclusions:

1) The bond strength is given by the IBE. The determination of IBEs without any other information than experimental AEs is not possible.

2) The BEs reflect the bond strength only if the reorganization energies are about constant for bonds of the same type or change linearly with the bond strength.

3) Any simplifications and assumptions made to determine IBEs or BEs from a linear equation system with more unknowns than knowns make a detailed description of individual bonds impossible.

The thermochemical model of the BE, for example, is based on the assumption that all $E_R$ values of bonds of the same type are identical so that IBE and BE values differ just by constants so that the latter become a reliable measure for the bond strength. This assumption, however, makes it impossible to differentiate between the three different CH bonds of propane, although these must possess different BEs according to the corresponding CH bond lengths and CH stretching force constants listed in Table 1. Hence, the problem of getting reliable parameters of describing the bond strength can only be solved with the help of additional information typical for a given bond. This could be done by relating the bond length to the bond strength as has been done extensively in the literature. [24] On a qualitative basis, it is often argued that the shorter (longer) bond is always the stronger (weaker) bond, however this argument must be considered with care as for example in the case of bent bonds. [25]

From a theoretical point of view, the bond strength should depend on two quantities, namely a) the overlap between the AOs forming the bonding MOs and b) the polarity of the bond as caused by the electronegativity difference between

the atoms connected by the bond. The overlap decreases with an exponential dependence on the bond length and the electronegativity difference between the bonded atoms determines the effective charges at the atoms, which in turn are responsible for the attraction of the bond density to the nuclei by an 1/r-potential. The more polar a bond is the stronger is the resulting bond shortening. [26,27] BE schemes or related schemes based on bond order or other bond strength parameters have been suggested which are based on overlap and/or bond polarity [3,26-32], but so far a generally applicable model is not known. Also, one has attempted to directly calculate BEs from molecular energies [28] or molecular electron density distributions, [30,32] yet only limited applicability has been achieved. All these approaches use static quantities for the determination of the bond strength while the thermochemical BE is actually a dynamic quantity since it depends on the dynamic behavior of the molecule in the atomization reaction as determined by the features of the potential energy surface (PES) in the direction of atomization. Therefore, we will investigate in the next chapter whether this dynamic quantity can be better described with dynamic quantities associated with the vibrational motions of a molecule.

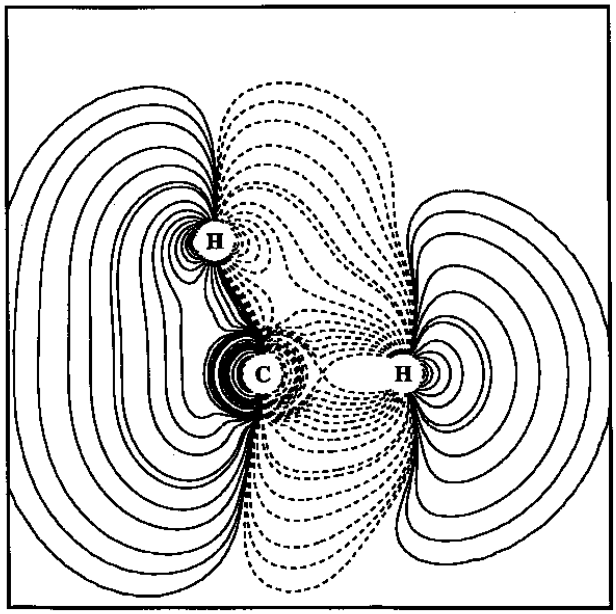


**Figure 2** *Contour line diagram of the difference electron density distribution obtained for a* **c***-vector stretching vibration of a CH bond in $CH_4$ shown in the plane of a $CH_2$ group (B3LYP/6-31G(d,p) calculations). The lower H atom and the C atom are moving by 0.02 Å from their equilibrium positions thus elongating the bond. Solid (dashed) contour lines indicate an increase (decrease) in the electron density because of CH elongation*

## Is the bond stretching force constant related to the bond strength?

The force constant $k_n$ provides a measure for the curvature of the PES in a given direction defined by the internal coordinate $q_n$ associated with $k_n$. In the case that $q_n$ is a bond length, it is assumed that the force constant is related to the bond strength. Since the curvature of the PES in the direction of a bond dissociation process can be described with either $k_n^c$ or $k_n^a$ it has to be clarified, which of these force constants is better suited to describe the bond strength. We will answer this question by analyzing the changes in the electron density distribution of the molecule during a ***c***-vector vibration and an AIM vibration. This would actually require a set of snapshots taken during a vibrational mode, however practice shows that it is sufficient to analyze just one snapshot taken for a small but finite elongation of the bond in the course of a bond stretching vibration.

In Figure 2, a contour line diagram of the difference electron density distribution obtained for a ***c***-vector stretching vibration of a CH bond in $CH_4$ is shown in the plane containing one C and two H atoms. Because of the movement of the H nucleus, the electron density distribution in the region of the CH bond is changed in the way that the H nucleus carries negative charge with it. The result is an increase of electron density beyond its previous equilibrium position, a similar increase behind the C atom, and a decrease of the electron density in the bond region (see Figure 2). Calculations show that the changes are not localized in the bond region, but extend to the other CH bonds. Hence, stretching of the CH bonds leads to an increase in front of the H and behind the $CH_3$ group where the density is taken from the bond region.

In a description with the ***c***-vectors all other CH bonds are frozen to their equilibrium values and, therefore, the electron density attached to these bonds has little chance to adjust to the new geometry with the elongated bond. This has two important consequences. First, the CH stretching force constant of the first bond, which reflects the energy change needed for a movement of the H nucleus out of its equilibrium position and the ease, by which the electron density distribution relaxes to this perturbation, will actually be larger than it would be if the other CH bonds and the electron density attached to them would relax and partially compensate the increase in the energy due to bond elongation. Secondly, stretching of a second CH bond is coupled to the first stretching by a positive stretch-stretch coupling constant. This simply means that stretching of the second bond is somewhat more difficult because of the elongation of the first bond.

Qualitatively, the same changes in the electron density occur for a CH stretching AIM. However, there are significant differences, which become only visible if the changes in the electron density caused by an AIM are compared with those cause by a ***c***-vector motion, i.e. by analyzing the difference-difference electron density distribution shown in Figure 3. The CH stretching AIM relaxes upon elongation of the CH1 bond the positions of the other H nuclei, which means that the electron density can adjust to the new situation.

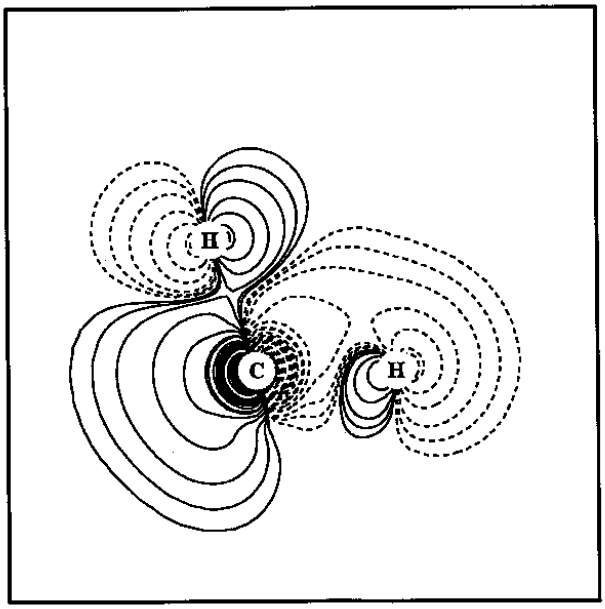


**Figure 3** *Comparison of the difference electron density distribution obtained for an AIM stretching vibration of a CH bond in $CH_4$ and the corresponding* **c***-vector vibration in form of a difference electron density distribution. Contour lines are shown in the plane of a $CH_2$ group (B3LYP/6-31G(d,p) calculations). The lower H atom and the C atom are moving by 0.02 Å from their equilibrium positions thus elongating the bond. Solid (dashed) contour lines indicate an increase (decrease) in the electron density cause by the AIM vibration relative to that caused by the* ***c****-vector vibration*

Upon bond elongation caused by an AIM, the other CH bonds move slightly in the opposite direction than the C atom thus approaching slightly a planar methyl radical with in-plane HCH angles of 120° and an HC···H angle of 90° as it would be formed in the dissociation reaction: $CH_4 \rightarrow \bullet CH_3 + \bullet H$. Because of these slight adjustments, the decrease of the bond density becomes smaller, less density is built up in front of the moving H, but more behind the C. In the extreme, these changes would lead to the pπ charge distribution of the methyl radical. Since the H atoms of the $CH_3$ group also move there is a slight build up of density in the moving direction and a decrease of density in the opposite direction (see Figure 3).

The adjustment of the electron density distribution to the new geometry is reflected in the adiabatic CH stretching force constant, which is smaller than that calculated for the ***c***-vector modes (see Table 1). Also, the stretch-stretch coupling constant becomes negative (see Table 2) indicating that after relaxation of geometry and density upon CH bond elongation stretching of a second CH bond becomes somewhat easier.

In general, one observes for the AIMs of a molecule that the norm of coupling force constants decreases in (absolute) magnitude relative to the norm of the corresponding valence force constants associated with the ***c***-vector modes. This means that the relaxation of the AIMs decreases coupling in the AIM force field since the AIMs are more natural than the ***c***-vector modes. In particular, relatively large bend-bend coupling constants of cyclic molecules are strongly reduced in the AIM force field. At the same time, coupling is more spread in the molecule. For example, for the force field associated with the ***c***-vector modes of $CH_4$ there will be no stretch-bend coupling if the bending motion does not involve the elongated CH bond although density and geometry relaxation should also affect these bending motions. The AIMs describe this situation correctly thus leading also to small coupling values for those interactions which are zero in the ***c***-vector force field. However, in total couplings are still reduced (Table 2).

It is noteworthy that the ***c***-vector force field does not comply with the symmetry of the molecule $CH_4$, which is obvious for the valence force constants (different HCH bending force constants) and the coupling constants (3 different values for stretch-bends instead of 2; 3 different values for bend-bend couplings instead of 2). However, the AIM force field complies with the symmetry of the molecule and possesses the right number of different coupling constants. Similar discrepancies are found for larger molecules, which are particularly serious in the case of highly symmetrical molecules and molecules with strong coupling of internal coordinate forces. Of course, the force field complies with the molecular symmetry when symmetry coordinates (see chapter 5) are chosen for the calculation of the normal modes.

The analysis of the changes in the electron density distribution accompanying a vibrational mode can be carried out for each type of internal mode. It reveals that the AIMs comply better to the reality of a localized CH stretching motion than the ***c***-vector motion based on a totally rigid $CH_3$ group and an elongated CH bond. In a simplified way, *the AIMs can be considered as vibrational modes covering geometry and electron density relaxation effects while the* ***c****-vector modes are vibrations without geometry and major electron density relaxation effects. Hence the AIMs are the more natural vibrational modes and, therefore should be much more useful for the description of the dynamics of molecules.* For example, the AIM contrary to the ***c***-vector mode represents the true starting point of the bond dissociation reaction and, therefore, the adiabatic CH stretching force constant provides a more realistic description of the curvature of the PES of $CH_4$ in the direction of the CH bond elongation. The ***c***-vector force constant overestimates curvature of the PES since they refer to an artificial process without significant relaxation effects (see below).

If the geometry of a molecule is optimized, each parameter will be calculated under the provision that all other geometrical parameters are relaxed. This will also be done if the potential energy function for the dissociation of one CH bond of the methane molecule is calculated. *The AIM of the CH stretching motion is the vibration, which relaxes all other geometrical coordinates and hence it describes the onset of the CH dissociation reaction.* We conclude that the AIM stretching force constant $k_n^a$ is related to the BDE of one CH bond rather than its BE. Only if IBE, BE, and BDE all be-

**Table 2** *Adiabatic force field and valence force field for $CH_4$ (B3LYP/6-31G(d,p)) [a]*

| | CH1 | CH2 | CH3 | CH4 | H2CH1 | H3CH1 | H4CH1 | H2CH3 | H3CH4 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5.36 | -0.05 | -0.05 | -0.05 | -0.09 | -0.09 | -0.09 | 0.09 | 0.09 | CH1 |
| | | 5.36 | -0.05 | -0.05 | -0.09 | 0.09 | 0.09 | -0.09 | 0.09 | CH2 |
| CH1 | 5.42 | | 5.36 | -0.05 | 0.09 | -0.09 | 0.09 | -0.09 | -0.09 | CH3 |
| CH2 | 0.03 | 5.42 | | 5.36 | 0.09 | 0.09 | -0.09 | 0.09 | -0.09 | CH4 |
| CH3 | 0.03 | 0.03 | 5.42 | | 0.67 | -0.13 | -0.13 | -0.13 | -0.16 | H2CH1 |
| CH4 | 0.03 | 0.03 | 0.03 | 5.42 | | 0.67 | -0.13 | -0.13 | -0.13 | H3CH1 |
| H2CH1 | 0.14 | 0.00 | 0.00 | -0.14 | 1.13 | | 0.67 | -0.16 | -0.13 | H4CH1 |
| H3CH1 | 0.14 | -0.14 | 0.14 | -0.14 | 0.54 | 1.09 | | 0.67 | -0.13 | H2CH3 |
| H4CH1 | 0.14 | -0.14 | 0.00 | 0.00 | 0.57 | 0.54 | 1.13 | | 0.67 | H3CH4 |
| H2CH3 | 0.00 | 0.00 | 0.14 | -0.14 | 0.57 | 0.54 | 0.59 | 1.13 | | |
| H3CH4 | 0.00 | -0.14 | 0.14 | 0.00 | 0.59 | 0.54 | 0.57 | 0.57 | 1.13 | |

*[a] AIM force constant matrix is given in the upper right triangle and the* **c***-vector force constant matrix in the lower left triangle. Stretching force constants in mdyn Å$^{-1}$, stretch-bend interaction force constants in mdyn rad$^{-1}$, bending and bend-bend force constants in mdyn Å rad$^{-2}$*

have parallel, which implies that reorganization energies $E_R$ in bond dissociation and atomization reactions are identical or similar (as for diatomic molecules), can the AIM stretching force constant be used to describe the bond strength.

The force constant $k_n^c$ is also a dynamic quantity, which is not related to a chemical process. It covers the major electronic changes of the onset of a bond dissociation process, however not the important effects of geometrical and electronic relaxations. In so far, $k_n^c$ should be related to the intrinsic BDE (IBDE), which is that energy quantity, which would be obtained if all relaxation and rehybridization effects could be suppressed in the bond dissociation reaction. In view of the definition of the IBE, we define the IBDE by Eq. 35 (see also Figure 1)

$$IBDE = BDE + E_R \tag{35a}$$

$$E_R = E_H + E_C + E_G + E_{extra} \tag{35b}$$

where $E_G$ covers the energy needed for freezing the geometries of the fragments of the bond dissociation and $E_{extra}$ denotes the energy, which would be gained by delocalization of the unpaired electrons generated by bond cleavage (if one of the fragments possesses a conjugated system, provides the possibility of hyperconjugation or anomeric delocalization, etc.). In cases, in which the fragments are formed in an excited state and relax to the ground state, one has to add to Eq. 35 a promotion energy $E_P$ identical to the excitation energy between the two states.

In the same way as the sum of all BDE values obtained in a stepwise atomization of a molecule is identical to the sum of BEs and the AE, the sum of all IBDE is equal to the sum of all IBE and the IAE.

$$IAE = \sum_i IBDE_i = \sum_i IBE_i \tag{36}$$

where in general $IBDE > BDE$, $IAE > AE$ and $IBDE_i \neq IBE_i$. While the AIM stretching force constant $k_n^a$ is related to the BDE, the force constant $k_n^c$, which does not cover any geometry relaxation, can be associated with the *IBDE* of a bond. However, one would stretch the connection between *IBDE* and $k_n^c$ too far to expect that the ratios between the two force constants provide any insight on the relative magnitudes of IBDE and BDE. Since IBDE values of the bonds of polyatomic molecules are not known, little use can be made with $k_n^c$ values taken from a valence force field. On the other hand, AIM stretching force constants $k_n^a$ have been found to be useful quantities when discussing measured BDE values. Larsson and Cremer demonstrated that there is a linear relationship between $k_n^a$ and $D_e(CH)$. Deviations from this relationship give insight on extra-stabilization effects in radicals R• formed by dissociation of R-H. [11]

## Bond stretching force constant for symmetry coordinates

One could argue that the stretching modes so far discussed are related to one-bond dissociation reactions and, therefore, cannot be related to the BE, which is defined in a statistical way within the thermochemical model of bond strength. It is well-known that the four BDEs of methane all differ (products of different stability are formed in the four-step process leading to atomization) and that only their average can be used as BE. In the same spirit, one should ask, e.g., for the average of the CH stretching force constants for $CH_4$, $CH_3$, $CH_2$, and CH. This, however, would require a clumsy way of calculating a suitable CH stretching force constant related to the BE that could easily be flawed since different species such as closed-shell systems, radicals, and carbenes would have to be adequately described with one particular method.

It is far more easy to define symmetry coordinates in the way that the totally symmetric stretching mode is associated with a stretching force constant $k_s$, which describes the synchronous stretching of all equivalent bonds. In the case of molecules $AX_n$, this leads to the symmetry coordinate

$$s_1 = \frac{1}{n^{\frac{1}{2}}} \sum_j^n r_j \qquad (37)$$

where $r_j$ defines the *AX* bond length and $r_j = r_{j+1}$ for all j.

In Table 1, the AIM and ***c***-vector stretching force constants for symmetry coordinates are listed. Apart from a few exceptions, these force constants are larger than the corresponding force constants $k_n$. For methane, the $k_s^a(CH)$ value is 5.510 mdyn Å$^{-1}$ while the corresponding $k_n^a(CH)$ value is just 5.365 mdyn Å$^{-1}$. Since synchronous stretching of all CH bonds in methane leads to atomization, the values of $k_s^a(CH)$ and $k_s^c(CH)$ are identical. If the symmetric stretching mode for all equivalent bonds does not lead to atomization, then $k_s^c$ is usually larger than $k_s^a$ for the same reasons as discussed in connection with $k_n^c$ and $k_n^a$.

Inspection of the force constants of Table 1 reveals that the increase in $k_s$ is related to the number n of equivalent bonds in the way that a higher number n seems to lead to a higher $k_s$ value. This can be explained by remembering that stretching force constants are dynamic quantities, which are associated with a particular bond dissociation process. In the case of methane, the corresponding dissociation process leads to atomization and, by this, excludes any differences between $k_s^a$ and $k_s^c$ because of geometrical relaxation effects or extra-stabilization effects of the fragments formed. One could argue that the first BDE (actually enthalpy) of methane is 104.9 kcal mol$^{-1}$ [33] while the bond energy (related to the symmetric mode of stretching the four CH bonds of methane at the same time) is just 99 kcal mol$^{-1}$ and, accordingly, stretching force constant $k_n$ should be larger than stretching force constant $k_s$. However, symmetric stretching in methane is related to four times the IBE rather than the BE and the former (≈162 kcal mol$^{-1}$, see above) is much higher than the latter. Hence, the stretching force constants calculated with symmetry coordinates demonstrate two important aspects:

a) The stretching force constants are dynamic quantities associated with a particular dissociation process defined by the coordinate used.

b) In the case of stretching force constants calculated with symmetry coordinates, the associated dissociation process (atomization or fragmentation) has to be analyzed to clarify whether the stretching force constant is related to the IBE (atomization) or IBDE ($k_s^c$) and BDE ($k_s^a$) of a specific fragmentation process.

While both atomization reaction and one-bond dissociation processes are of direct chemical interest, most fragmentation processes associated with particular symmetry coordinates *s* and group stretching force constants $k_s$ are not of immediate interest and are also somewhat difficult to interpret since they strongly depend on the stability of the fragments formed as can be demonstrated by the following example.

The three different CH bonds of propane ($CH_2$, in-plane $CH_3$, out-of-plane $CH_3$, see Table 1) are compared with regard to their bond strength using bond lengths and bond stretching force constants $k_n$ and $k_s$. The bond lengths of Table 1 suggest that the in-plane CH bond of the methyl group is somewhat stronger than the out-of-plane CH bonds, which in turn are stronger than the CH bonds of the methylene group. This is confirmed by the AIM and ***c***-vector stretching force constants $k_n$ (Table 1). However, the $k_s$ values obtained with symmetry coordinates suggest that the bond strength of the out-of-plane CH bonds is larger than that of the in-plane CH strength bonds, which is contrary to the trends in bond lengths and force constants. One can resolve this contradiction by considering that there are four out-of-plane CH bonds and just two in-plane CH bonds in propane. Hence, the dissociation process (Eq. 38)

$$CH_3 - CH_2 - CH_3 \rightarrow \bullet CH_2 - CH_2CH_2 \bullet \qquad (38)$$

$$CH_3 - CH_2 - CH_3 \rightarrow \colon CH - CH_2 - CH \colon \qquad (39)$$

associated with the symmetry coordinate for the two in-plane CH bonds leads to the creation of radical centers at C1 and C3 while the dissociation process associated with the symmetry coordinate for the four out-of-plane CH bonds (Eq. 39) generates carbene centers at C1 and C3. Clearly, a carbene is more unstable than a radical, which means that the second process is characterized by a much higher endothermic reaction energy, which should be reflected by the curvature of the PES in the direction of the reaction coordinate of Eq. 39. Accordingly, $k_s$ *(CH,op)* > $k_s$*(CH,ip)* (Table 1), i.e. the $k_s$ stretching force constants can no longer be related to an individual CH bond since the associated dissociation reactions use reference molecules of strongly differing stability. This example shows clearly that one has to analyze the associated stretching coordinate and dissociation process and consider carefully whether the product stability may influence in any way the curvature of the PES and, by this, the stretching force constant before one draws any conclusions for the bond strength of a particular bond based on the corresponding stretching force constant $k_s$.

The discussion shows that apart from the special case of $AX_n$ molecules, there are no symmetry coordinates that can be related to the atomization (scaling) reaction of the molecule and, in general, group stretching force constants $k_s$ cannot be related to either IBE or BE. Contrary to general belief, the choice of symmetry coordinates does not provide better insight into the strength of the bonds of a general polyatomic molecule. On the contrary, one has to warn not to misinterpret stretching force constants $k_s$ as reflecting the bond strength of particular bonds.

## Stability of cyclopropane

Cyclopropane (**1**) possesses a surprisingly high stability in view of the fact that the strain of the three-membered ring

should be 70 kcal mol$^{-1}$ or even larger [25] while in reality it is just 27 kcal mol$^{-1}$. Different explanations have been given for the extra-stability of cyclopropane. [13,25,30,34] Schleyer [34] argued that the CH bonds in **1** are comparable with those of ethene (**2**) according to bond lengths (1.086 vs. 1.087 Å, Table 1, for a recent discussion, see ref [35]), degree of hybridization (in both cases sp$^2$-s CH bonds), and known CH BDE values (106.3 and 111.2 kcal mol$^{-1}$ [36]). Actually, the stretching force constants of Table 1 seem to suggest that the CH bond in **1** is even stronger than that in ethene: $k_n^{a,exp}$*(CH,**1**)* = 5.117 mdyn Å$^{-1}$ and $k_n^{a,exp}$*(CH,**2**)*= 5.102 mdyn Å$^{-1}$; $k_n^{c,exp}$*(CH,**1**)* = 5.143 mdyn Å$^{-1}$ and $k_n^{c,exp}$*(CH,**2**)* = 5.130 mdyn Å$^{-1}$. A recent CCSD(T) analysis of the equilibrium geometry of **1** derived from ED measurements of Kuchitsu and co-workers [37] confirms that the length of the CH bond in **1** (1.078) is 0.003 Å shorter than that of **2** (1.081 Å). [35] However, there is still a contradiction between experimental AIM stretching force constants and measured BDEs. Larsson and Cremer [11] showed that this contradiction can be resolved if one considers the hyperconjugative stabilization possibilities of a single electron in the cyclopropyl radical and in the vinyl radical, which should be larger in the first case (2 $CH_2$ groups for hyperconjugation) than in the second case. Hence, an idealized BDE value of **1**, [11] which does not cover this extra-stabilization effect of the cyclopropyl radical is 0.5 kcal mol$^{-1}$ larger than the corresponding value of **2** ($D_e^{ideal}$: 118.7 (**1**), 118.2 kcal mol$^{-1}$ (**2**), [11]). Accordingly, both bond length, stretching force constants $k_n$, and corrected BDE values $D_e^{ideal}$ [11] suggest that the CH bond of **1** is slightly stronger than the CH bond of **2**, which would mean an enormous stabilization effect for the cyclopropane ring resulting from six relatively strong CH bonds and overcompensating the weakening of the CC bonds caused by bond bending. Is this interpretation correct?

Employing symmetry coordinates, the ratio between the CH stretching force constants of **1** and **2** is even increased in favor of **1** (5.181 vs 5.146 and 5.215 vs. 5.164 mdyn Å$^{-1}$, see Table 1). This, however, is not surprising since the stretching force constants $k_s$*(CC)* and $k_s$*(CH)* are associated with formal dissociation reactions (Figure 4, reactions (5) and (6)) that lead in the case of **1** to a very labile cyclic multi-carbene but in the case of **2** to the ground state of $C_2$. Clearly, the use of $k_s$ values for a comparison of the CH bond strength in **1** and **2** is of little use and should be discarded. Similar criticism is appropriate for the one-bond stretching force constants $k_n$ since they are related to the BDE of reactions (1) and (3) of Figure 4 rather than to BE(CH) or IBE(CH) values. A small test will demonstrate this.

To assess the strength of CH and CC bond in **1** one can compare **1** with both **2** and cyclohexane (**3**) via reactions (8) and (9) of Figure 4, where (9) defines the diagonal conventional strain energy (CSE) of the three-membered ring. [38] There are seven unknowns (BE(CC) and BE(CH) in molecules **1** - **3**), but just three known quantities, namely the experimental AEs of the three molecules compared.

$$AE(\mathbf{1}) = 3BE(CC,\mathbf{1}) + 6BE(CH,\mathbf{1}) \quad (40a)$$

$$AE(\mathbf{2}) = 1BE(CC,\mathbf{2}) + 4BE(CH,\mathbf{2}) \quad (40b)$$

$$AE(\mathbf{3}) = 6BE(CC,\mathbf{3}) + 6BE(CH_{ax},\mathbf{3}) + 6BE(CH_{eq},\mathbf{3}) \quad (40c)$$

The remaining four quantities needed to determine all BE(CC) and BE(CH) values could be added by using the following relationships:

$$\frac{k_n^{a,\exp}(CH,\mathbf{1})}{k_n^{a,\exp}(CH,\mathbf{2})} = \frac{BE(CH,\mathbf{1})}{BE(CH,\mathbf{2})} \quad (40d)$$

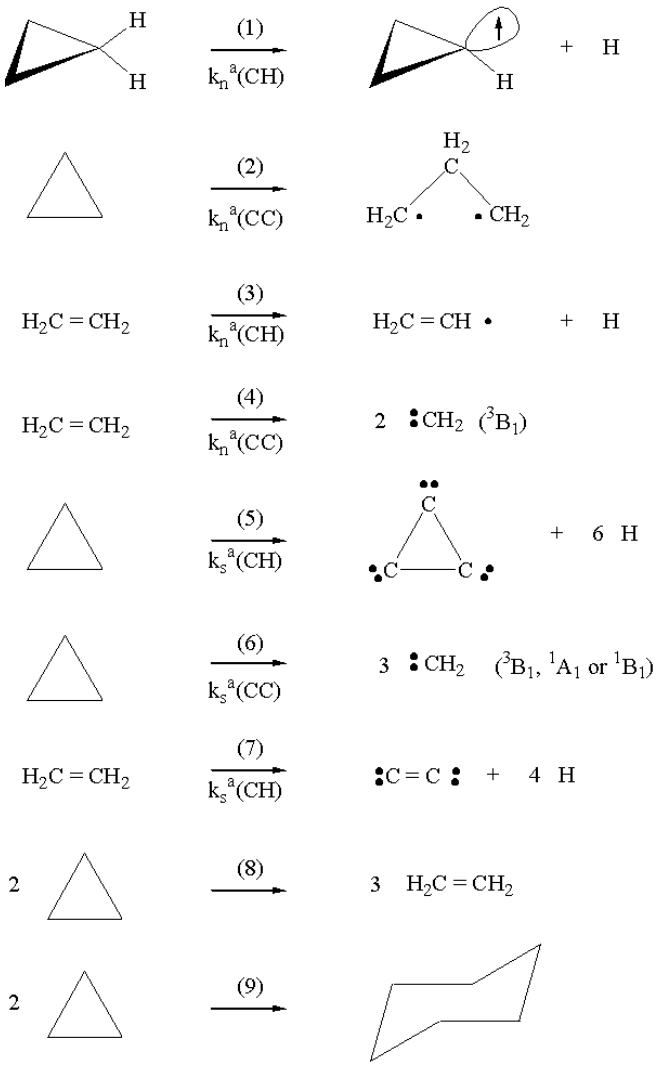


**Figure 4** *Dissociation reactions (1) – (7) of cyclopropane (**1**) and ethene (**2**). For each reaction, association with the proper stretching force constant is indicated. Reaction (8) compares **1** with **2**. The energy of reaction (9) defines the diagonal ring strain energy of **1***

**Table 3** *Overview over static and dynamic quantities that can be related to the bond strength [a]*

**A) Static Properties** — Starting point: Electron density or properties derived therefrom

| Quantity | Associated model quantity | | Bond strength directly related? |
|---|---|---|---|
| bond length | Σ covalent radii + change ($\Delta\chi$) + change(environment)<br>*Comment*: bent bonds, stretched bonds, etc. lead to problems | | (yes) |
| bond density | a) overlap part | overlap of AOs<br>bond order<br>density at critical point<br>density in zero-flux-surface | no<br>(only if b) does not play a role) |
| | b) polarity part | $\chi$-difference<br>charge difference<br>bond dipolemoment | no |
| | a) + b) | | yes |

**B) Dynamic Properties** — Starting point: Potential energy surface (PES)

| Stretching force constants | Associated reaction process | Energy term | Conventional name | Bond strength directly related? |
|---|---|---|---|---|
| $k_n^a$ | one-bond dissociation with relaxation | $D_e$ or $D_0(T)$ | BDE | no |
| $k_n^c$ | one-bond dissociation without relaxation | $D_e + E_R$ | IBDE | no |
| | *Comment*: any BDE depends on product stability (BDEs may be qualitatively useful if just one type of bond is considered) | | | |
| $k_s^a$ | group fragmentation with relaxation | $\Delta_R E$ | group BDE | no |
| $k_s^c$ | group fragmentation without relaxation | $\Delta_R E + \Sigma E_R$ | not specified | no |
| | *Comment*: product stability depends on number of equivalent bonds | | | |
| $k_s^a$ | atomization for $AX_n$, general with relaxation | $\Delta_a E$ | $AE = n\ BE_i$ | no |
| | *Comment*: If $E_R$ can be considered to be constant | | | (yes) |
| $k_s^c$ | atomization for $AX_n$, general without relaxation | $\Delta_a E + \Sigma E_R$ | $IAE = n\ IBE_i$ | yes |
| $k_s^a = k_s^c$ | atomization for $AX_n$, high sym relaxation not relevant | $\Delta_a E + \Sigma E_R$ | $IAE = n\ IBE_i$ | yes |

*[a] Meaning of terms used: $\chi$-difference or $\Delta\chi$, difference in electronegativities; BDE, bond dissociation energy; IBDE, intrinsic bond dissociation energy; $\Delta_R E$, reaction energy of the fragmentation process; AE, atomization energy; IAE, intrinsic atomization energy; $\Delta_a E$, energy of the atomization reaction; $E_R$, reorganization energy covering all relaxation effects. The specification* high sym *for $AX_n$ molecules denotes the existence of a $C_n$ or $S_n$ symmetry element (for n = 2: $C_\infty$)*

$$\frac{k_n^{a,\exp}(CH,\mathbf{1})}{k_n^{a,\exp}(CH,\mathbf{3})} = \frac{BE(CH,\mathbf{1})}{BE(CH,\mathbf{3})} \quad (40e)$$

$$\frac{k_n^{a,\exp}(CH_{ax},\mathbf{3})}{k_n^{a,\exp}(CH_{eq},\mathbf{3})} = \frac{BE(CH_{ax},\mathbf{3})}{BE(CH_{eq},\mathbf{3})} \quad (40f)$$

$$\frac{k_n^{a,\exp}(CC,\mathbf{1})}{k_n^{a,\exp}(CC,\mathbf{2})} = \frac{BE(CC,\mathbf{1})}{BE(CC,\mathbf{2})} \quad (40g)$$

Using the force constant values of Table 1 and solving Eqs. 40a-g for the unknown BE(CC) and BE(CH) values leads to unreasonable bond energies not in line with general chemical understanding. This clearly demonstrates that neither ex-

perimental BDE nor AIM (or ***c***-vector) stretching force constants provide a reliable insight into the bond strength of the CH and CC bonds of **1**. There is no reason to assume that the reorganization energies for the one-bond dissociation and the atomization reaction are the same for the three molecules considered. The stretching force constants of Table 1 can only support the observation that the CH bond in **1** is unusually strong, but they cannot be used to quantify this effect or even to verify that it must be larger in **1** than in **2** (in this regard, also the CH bond length is not a reliable parameter).

Cremer and Gauss [30] used the bond density as a static quantity to describe the bond strength. Bader's method of virial partitioning [9] of the molecular space leads to zero-flux surfaces of the electron density distribution, which envelope the atomic subspaces and cut through the bonds thus specifying which part of the electron density is associated with what atom. Integration over the electron density of a zero-flux surface provides a measure of the bond strength which can be used to compare different bonds. Actually, this approach covers just that part of the bond strength related to the overlap between AOs in a bonding MO (vide infra) but does not cover that part of the bond strength related to the polarity of the bond. Cremer and Gauss [30] assumed that the electronegativity difference between C and H is small enough to be neglected, thus avoiding a determination of bond strengthening caused by bond polarity. Although this assumption can be considered to be reasonable, it may lead to an underestimation of the BE(CH) value and an overestimation of the BE(CC) value (106.6 and 71 kcal $mol^{-1}$ [30]). Another source of possible error is the fact that the CC bonds are curved and, therefore, the maximum of the electron density in the CC zero-flux surface is shifted away from the CC internuclear connection line, thus decreasing the electron-nuclei attraction energy. Again, neglect of such an effect might lead to an exaggeration of the BE(CC) value. Hence, the BE values calculated by Cremer and Gauss [30] cannot be considered to be very reliable. They suggest however that BE(CH) and $D_e^{exp}$(CH) for **1** (106.6 and 113.9 kcal $mol^{-1}$ at 0 K without ZPE contributions [11,30]) are different, thus excluding that the unusual stability of **1** is caused exclusively by CH bond strengthening. Future work, probably along the lines suggested by Cremer and Gauss, has to provide a quantitative basis for rationalizing the stability of **1**.

## Conclusions

The problem of defining the strength of a chemical bond has been approached from the basis of vibrational spectroscopy. Stretching force constants calculated with standard quantum chemical methods and programs [39,40] for local internal coordinate modes provide an important contribution to the description of molecular stability and reactivity. The following conclusions can be drawn from the discussion of calculated stretching force constants.

1) A description of bonds in terms of bond stretching force constants is best accomplished with the help of a local mode description.

2) Comparison of two different local mode descriptions of bond stretching shows that the adiabatic stretching modes are better than the ***c***-vector stretching modes. This is a result of the physical significance of the former and the artificial definition of the latter.

3) Bond stretching force constants can be used to describe the chemical reactivity of a molecule. For example, the adiabatic stretching force constants are related to the BDEs. They can be used to determine ideal BDE, which provide a measure for extra-stabilization effects in the radical produced. This verifies that a vibration can be considered as the onset of a chemical reaction using the coordinate associated with the vibration as reaction coordinate.

4) Contrary to general belief, bond stretching force constants $k_n$ do not reflect the strength of the bond or are related to the BE in a quantitative sense and often even not in a qualitative sense. They will fulfill this task only if IBDEs change parallel to BDEs and the latter parallel to BEs. This can only be possible for a group of closely related molecules with similar bonds, but has to be checked in each case by additional information on the strength of the bonds considered.

5) Use of symmetry coordinates raises the value of an adiabatic force constant in dependence on the number of equivalent atoms. This is understandable in view of the related dissociation process and has to be considered when using $k_s$ stretching force constants for a comparative discussion of bond strength. Only in the case of molecules $AX_n$, $k_s$ values can be directly related to the IBE (see Table 3).

6) The BE is best determined with the help of a static quantity. This could be the molecular energy provided a partitioning scheme is set up with the help of an additional quantity such as bond length. However, there are indications that the bond distances do not always change parallel to bond strength. Also, the bond distance is misleading in cases of bent bonds.

7) The best assessment of the BE should be based on an analysis of the electron density distribution. The electron density of the zero-flux surface should be related to bond strength and BE. However, the strength of the chemical bond depends on at least two factors:

a) Orbital overlap in the bonding MO as reflected, e.g., by bond order, bond density, etc.

b) Polarity (ionic character) of the bond. This is related to the total charges of the atoms connected and to the charge distribution along the MED.

In Table 3, the conclusions of this work are summarized. The calculation of BE and IBE values with the help of scaling reactions presents a challenge to quantum chemistry. It is known that even sophisticated *ab initio* calculations lead to results of moderate accuracy. Future developments are necessary to solve the problem of quantitatively determining the bond strength within a suitable model.

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