Generalization of the Badger Rule
Based on the Use of Adiabatic Vibrational Modes

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Abstract: In the last 90 years, hundreds of investigations have focused on establishing empirical relationships between bond length r and bond stretching frequency ω or bond stretching force constant k. An overview over the 67 most important investigations is presented where Badger-type relationships that emerge from these studies as the most successful ones are discussed in more detail. The existence of such relationships is rationalized with the help of a Morse model potential. In this connection, it is shown that the hard sphere size of a bonded atom has a strong impact on any bond length - stretching force constant relationship. In a diatomic molecule, hard sphere sizes increase with the number of electrons increasing from cations to neutral species, and then to anions. In polyatomic molecules, a multitude of different hard sphere situations is possible and the variation occurs more smoothly in dependence of the electron-donating or withdrawing ability of substituents, the magnitude and distribution of charge, the state multiplicity, the distribution of like and opposite spin, and the deviation of the bond electron density path from the internuclear connection line. Both calculated and experimental data for polyatomic molecules reveals that Badger-type relationships between r and k exist for each bond type AB. In the case of bonds AB and AC that are closely related, the overall features of $r = f(k)$ are similar and it is possible to define effective bond lengths that lead to more general Badger-type relationships. However, the latter are only valid within strictly defined limits and may no longer apply to charged or excited bond situations of the same bond AB. A general Badger-type rule will be preferentially one with an exponential dependence of r on k. If suitable effective bond lengths are derived for all bonding situations, a finite set of Badger-type relationships will result, which is applicable to all bonding situations AB with A from period i and B from period j thus coming close to the original concept of Badger for diatomic molecules. A prerequisite for any relationship connecting r with k is the use of local mode information. The major ways of obtaining this information via isolated stretching modes, overtones spectroscopy, frequency averaging, compliance force constants, or potential energy distribution (PED) analysis are discussed. The adiabatic internal coordinate modes (AICoMs) are described as theoretically well-founded local modes. Their properties and advantages are discussed.

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1. Introduction

Empirical relationships relating bond lengths with the corresponding bond stretching frequencies or bond stretching force constants were first derived in the 20ies of the last century (see Table 1.1 for a summary) and have been a topic of research in connection with the nature of the chemical bond ever since. [1-67] It is remarkable that in a time of easily accessible quantum chemical results there remains a need for empirically based estimates of either bond lengths or stretching frequencies. There are three primary reasons why such empirical rules and relationships are still valuable tools for modern research: 1) Established relationships between bond properties add to our understanding of the chemical bond, especially if they can be rationalized on a quantum mechanical basis because bonding between atoms is a quantum mechanical phenomenon. - 2) There are experimental situations in which it is relatively easy to measure one bond property but difficult to obtain other bond properties. For example, it is easier to measure the vibrational spectra of a compound than to carry out a structural analysis. This is especially true for solid materials that do not crystallize, molecules on a surface, or molecules in some form of aggregation. If quantum chemical calculations are only feasible for model systems rather than the actual targets of chemical research then vibrational spectroscopy may be the only tool for obtaining information that provides an insight into bond properties. - 3) In the realm of computational chemistry, there is also a need for empirical relationships. They may be used to determine suitable bonding force fields for molecular mechanics utilizing force constant - bond length relationships. For quantum chemical geometry optimizations, there is the need to set up a guess matrix of energy second derivatives (the Hessian matrix corresponding to the force constant matrix of a molecule), which is best done with the help of available geometry information and a suitable force constant - bond length relationship. For example, standard procedure to calculate the geometry of a molecule are based on an initial guess of the energy Hessian derived with the help of the Badger rule. [42,55] - It is due to reasons 1, 2, and 3 that there is ongoing research exploring the relationships between bond length r, bond stretching frequency ω or force constant k, bond order N, and bond dissociation energy D as is documented by a significant number of research papers on this topic (for recent work, see Ref.s [56-67]).

Table 1.1

Investigations focusing on relationships between bond properties such as r, k, ω, N, and D are summarized in Table 1.1. Originally, such relationships were established for diatomic molecules and later extended to polyatomic molecules. Attempts have been made to verify and rationalize these relationships via model potentials for diatomics as for example Morse potentials, modified Morse potentials, double-reciprocal potentials (see entry 13, Table 1.1), single-reciprocal exponential potentials (15, Table 1.1) or more complex forms of the potential (29, Table 1.1). These relationships eventually led to the formulation of universal diatomic potentials [68,69] that attempt to define energy and spectroscopic properties of a universal bond, which can be considered as the equivalent of "the hydrogen atom in atom spectroscopy." [70] Clearly, the derivation and rationalization of fundamental relationships between the various bond properties lead to a

better understanding of the chemical bond. Therefore, it is appropriate to sketch the major steps in this development stretching now over almost 90 years.

After preliminary work by Kratzer [1], Birge [2], and Mecke [3], Morse, [4] in 1929, was the first to derive an empirical relationship between bond length and bond stretching frequency (4, Table 1.1] for diatomic molecules. Badger criticized the Morse relationship as being too limited in its practical application. [6] In 1934, he proposed a new relationship (entry 6) for diatomic molecules that relates the stretching force constant k to an effective bond length R obtained as the difference between equilibrium bond length r_e and an empirical parameter d_{ij} characteristic of the distance of closest contact between the bonded atoms. The experimental data available to Badger suggested that d_{ij} is the same for all atoms of period i bonded to atoms of period j. In 1935, Badger [9] generalized the relationship between k_e and r_e to polyatomic molecules by introducing an additional parameter (entry 7: c_{ij} or c_{nm}), which also depends on the location of the bonded atoms in the periodic table. Despite numerous alternative relationships suggested by various authors (entries 8 - 30; interesting extensions by Huggins (11), Linnett (15), Gordy (20), Guggenheimer (22)), the Badger rule was widely used until the early 60ies. In 1961, Herschbach and Laurie [31] pointed out that the Badger rule was not providing reliable predictions for heavier elements. Therefore they suggested two major extensions of the Badger rule (see entry 31), one of which expresses the bond length r_e as a logarithmic function of the stretching force constant again using parameters that depend just on the periods i and j of the bonded atoms rather than the properties of these atoms themselves. The other extends Badger's rule also to cubic and quartic force constants thus confirming that both harmonic and fundamental stretching frequencies can be related to effective bond lengths. A cautious extension to polyatomic molecules was also discussed for bonds of similar type, i.e. which do not suffer "an abrupt change" [31] in their properties when compared in a series of molecules.

The extension of the Badger-Herschbach-Laurie equations to metal-metal bonds required extensive reparametrization as carried out by Harvey in 1996 (entry 54) or the use of more elaborate exponential functions (Miskowski et al., entry 47). In 2000, Cioslowski and co-workers [58] investigated the applicability of Badger-type equations to a test set of 108 diatomic molecules. They found that in a large number of cases the Badger rule does not lead to satisfactory predictions of stretching force constants and therefore cannot be considered a reliable tool for setting up the initial guess Hessian matrix in quantum chemical geometry optimizations. This result was contrasted by an investigation of Ohno and co-workers (entry 61), who could derive a simplified Badger-type equation by using effective bond lengths in the study of 74 CX bonds (X = C, Si, Ge, N, P, As, O, S, Se, F, Cl, Br) contained in polyatomic molecules. Kraka and Cremer [67] made a similar observation when investigating some 46 isoelectronic CO and CF^+ bonds. For the purpose of resolving these contradictory claims on the applicability of the Badger-Herschbach-Laurie equations between bond length and bond stretching force constant, there is the need to reinvestigate the physical basis of Badger-type relationships and to obtain a reliable assessment of their predictive value. We will approach this problem

in two steps by considering first diatomic and then polyatomic molecules. We will identify those physical effects that influence the length of a chemical bond and, by doing so, clarify whether a relationship between bond length and stretching force constant exists. Then, we will determine those vibrational properties that lead to a description of chemical bonds in polyatomic molecules. Clearly, these cannot be the normal modes measured in infrared or Raman spectroscopy because they are in most cases delocalized, i.e. they reflect the movement of larger structural units of the molecule (if not to say the whole molecule) rather than that of a specific bond within the molecule. In view of the limited usefulness of measured vibrational data, it is questionable whether an extension of the Badger rule to polyatomic molecules, as it was attempted in the past, can be successful on a larger scale. To solve this problem, we will discuss the difference between localized and delocalized vibrational modes, how the former can be derived from the latter, and how they lead to an extension of the Badger rule applicable to molecules.

2. Applicability of Badger-type Relationships in the case of Diatomic Molecules

A more general type of the Badger rule is given by Eq. (2.1) [41,71,87]

$$k_e(r_e - d)^p = c \tag{2.1}$$

where the quantity $(r_e - d)$ is the effective bond length R, d and c are constants depending on the nature of atoms A and B, and the exponent p can take values between 2 and 8 thus embedding the original Badger rule (Table 1.1: 6, 7, 9) with p = 3. Alternative relationships with $p = 2$ (Table 1.1: 1, 28, 29, 30), $p = 4$ (2, 3, 38), $p = 5$ (17), $p = 6$ (4, 5, 8, 12, 15, 16, 36, 39), or non-integer values of p between 2 and 6 (e.g. 21, 22, 25, 33, 34, 43) are summarized in Table 1.1. Apart from Eq. (2.1), relationships in form of a power series (35), a logarithmic (11, 23, 31, 33, 44) or exponential dependence (50, 53) of r_e on k_e or vice versa were also used as already mentioned in the introduction. Previous research could not clarify, which of the relationships (2.1) or their extensions in form of logarithmic or exponential functions is the most reliable and useful one.

In Figure 2.1, measured stretching force constants of 120 diatomic molecules in their ground state composed of atoms out of the first three rows of the periodic table and taken from the compilation of Huber and Herzberg [71] are plotted against the corresponding experimental bond lengths. The essence of the Badger rule becomes obvious from the diagram since it reveals that the data points cluster into 6 groups, each of which can be connected by a function according to Eq. (2.1). The six groups correspond to the six possible ij-combinations of periods (1-1, 2-1, 2-2, 3-1, 3-2, and 3-3). The corresponding bond lengths and stretching force constants are listed in Table 2.1.

Table 2.1 and Figure 2.1

In all cases, exponent p is a fractional quantity, which increases from 3.18 (1-1) to 7.44 (3-3) thus revealing a strong dependence on the the number of electron shells of A and B in molecule AB, i.e. on indices i, j, and i+j. Clearly, by choosing appropriate effective bond lengths with the help of close contact parameters it will be possible to merge the six curves of Figure 2.1 into one. This however could become problematic because of a large variation in the prefactor increasing from 2.8 to 602. Testing various sets of Badger parameters given in the literature confirms that it is not possible to obtain one generally applicable form of either the Badger rule, the Herschbach-Laurie variation or any of the other forms suggested in the literature (Table 1.1). There is the general trend that with the number of data points in a group scattering increases and the reliability of any Badger-type relationship to predict either bond length or force constant, once the other quantity has been determined, decreases. Closer inspection reveals that especially cations and anions deviate from the Badger-type relationships obtained in the least-squares sense. This is most obvious for the 1-1 group which consists of just 5 data points, four of which belong to cations (Figure 2.1, Table 2.1). Scattering is in this case so strong that the $k - r$ function given is no longer meaningful although it largely parallels those obtained for the 5 other groups.

Henry and Swanton [45,72] provided some evidence that suggests the existence of a relationship between the bond length $r_e(AB)$ of bond AB and its associated stretching force constant $k_e(AB)$. They used a modified Morse potential that fulfilled in the case of diatomic molecules the following conditions:

1) The potential energy V must approach infinity for $r \rightarrow 0$, which is not the case for the general form of the Morse potential. Therefore, a hard-sphere distance r_a is introduced, which leads to $V(r < r_a) = \infty$. 2) V measured relative to the separated atoms A and B must approach zero for $r \rightarrow \infty$. 3) V must approach the value of D_e for $r \rightarrow r_e$.

The potential (2.2) fulfills conditions 1), 2), and 3).

$$V(r > r_a) = D_e(1 - e^{-a_e(r-r_e)})^2 - D_e \tag{2.2a}$$

$$V(r_a) = V_a = D_e(1 - e^{-a_e(r_a-r_e)})^2 - D_e \tag{2.2b}$$

Henry and Swanton used Eq. (2.2) to derive relationship (2.3) between the harmonic frequency ω_e of a diatomic molecule and its bond length r_e: [72]

$$(r_e - r_a)\omega_e = 2\hbar(D_e/2\mu)^{1/2} ln[1 + (V_a/D_e + 1)^{1/2}] \tag{2.3}$$

Taking the derivative with regard to k_e leads to

$$\frac{\partial(r_e - r_a)}{\partial k_e} = \frac{\partial(r_e - r_a)}{\partial \omega_e}\frac{\partial \omega_e}{\partial k_e} = \frac{\omega_e}{2k_e}\frac{\partial(r_e - r_a)}{\partial \omega_e} \tag{2.4a}$$

$$\frac{\partial(r_e - r_a)}{\partial k_e} = \frac{(-V_a/\hbar)(2\mu x_e)^{1/2}}{k_e^2\{(4V_a x_e \mu/\hbar^2 k_e) + 1\}^{1/2}\{1 + [(4V_a x_e \mu/\hbar^2 k_e) + 1]\}^{1/2}} \tag{2.4b}$$

where μ is the reduced mass and x_e the anharmonicity constant. For the case that k_e is large, the derivative (2.4) varies with k_e^{-2}, whereas for a small value of the force constant variation takes place with k_e^{-1} and otherwise with k_e^{-p} for $1 < p < 2$. By this all possibilities of Eq. (2.1) are accounted for as becomes obvious when calculating the derivative of Eq. (2.1), which leads to

$$\frac{\partial(r_e - d)}{\partial k_e} = c \; k_e^{-(1+1/p)} \tag{2.5}$$

where the exponent is between -1 and -2 depending on the value of p. The Badger rule for diatomic molecules will be obtained if the hard sphere distance r_a and the associated potential V_a do not change within a period, which would also require that the bond dissociation energy D_e varies only slightly within a period of the periodic table. This however is generally not the case and therefore Badger-type rules will only hold for closely related bonding situations in the case of diatomic molecules.

Next we consider the physical effects determining the length of a chemical bond and its associated bond stretching force constant. The latter reflects the strength of the chemical bond, which in the general case is the result of a covalent contribution (depending on the overlap of the atomic orbitals forming the bonding and antibonding diatomic orbitals, their electron occupation, and the energy splitting between them) and an ionic (polar) contribution (depending on the electronegativity difference between A and B and the charge transfer resulting therefrom). Covalent and ionic contributions also impact bond length. However, contrary to the bond strength and the stretching force constant, the bond length depends on a third quantity which can be related to the size of the atomic core or, alternatively, its hard sphere size, which is related to the core size but also includes the effects of the valence electrons. It is this third quantity, which determines the magnitude of the Badger parameter d_{ij}. Badger's assumption that d_{ij} is constant for all bonds formed from period i atoms and period j atoms is not justified. The hard sphere size of an atom depends on its charge and, accordingly, will be smaller for the cation and larger for the anion compared to the size of the neutral atom. This fact is reflected in Figure 2.1 where some of the strongly scattered data points correspond to charged molecules. Smaller variations will also result if open and closed shell systems of the same bond type are compared. In general, positively or negatively charged AB bonds as well as excited states of a given molecule AB should involve atoms A and B with different hard sphere sizes than those of the neutral ground state of AB.

In the set of diatomic molecules investigated in this work (Table 2.1), there are 20 molecules for which, beside the neutral state there is also a charged state. Some of them do not lead to a significant change in the hard sphere size because an electron is added to a lone pair (or π) orbital not involved in bonding (see, e.g. 15 and 16 in Table 2: HO and HO^-; also 10 and 11). Therefore, the variations found for a bond AB in polyatomic molecules cannot be reflected by the limited number of diatomic molecules investigated in this and previous studies. This would only be given if, beside the ground state molecules, a large body of data would also be available for charged and excited states. Therefore, it is necessary to extend the investigation

of the Badger rule to polyatomic molecules and verify the following two predictions based on the investigation of the diatomic molecules.

1) Badger-type relationships depending simply on period-characteristic parameters such as c_{ij} and d_{ij}, as is the case with diatomic molecules, are no longer applicable to polyatomic molecules. They split up in AB bond-specific relationships that are fulfilled for AB bonds with closely related electronic structure. AB-bonds with different hard sphere sizes will have to be described with other relationships.

2) In special cases, bond-specific Badger rules can collapse to a single rule. This is likely to occur for bond types that share a common atom, for example AB and AC, provided the electronic structures of these bonds are related in such a way that the hard sphere sizes of atoms B and C can be described with just one parameter. In the following chapters, we will investigate these predictions in detail. For this purpose, we have to clarify first how to determine bond stretching vibrations for polyatomic molecules that are localized in a bond and are not contaminated due to the coupling with other vibrational modes.

3. Dissection of a Polyatomic Molecule into a Collection of Quasi-diatomic Molecules: Local Vibrational Modes

Vibrational modes are in most cases delocalized within a molecule. The properties of these modes (frequencies or force constants) are not suitable for an investigation of Badger-type relationships. Instead, there is the need for local mode information that provides bond stretching frequencies or force constants, which are no longer contaminated by contributions from other vibrational modes. For the purpose of clarifying the relationship between delocalized normal and local internal coordinate modes, we present in the following the theory of the adiabatic internal coordinate modes (AICoMs) recently use to set up bond length - bond stretching force constant relationships by Kraka and Cremer. [67]

The standard method for calculating the vibrational spectra of polyatomic molecules with K atoms is based on two major approximations. [73,74] First, the Born-Oppenheimer approximation is used, which leads to the separation of the nuclear motion from the electronic motion and by this to the concept of the potential energy surface (PES). The assumption is made that the nuclei of the molecule move as classical particles on the PES. Secondly, the vicinity of the minimum occupied by the vibrating molecule in question is described by a Taylor expansion of $V(\mathbf{x})$

$$V(\mathbf{x}) = V(\mathbf{0}) + \sum_{i}^{3K}\left(\frac{\partial V}{\partial x_i}\right)_{\mathbf{0}} x_i + \frac{1}{2!}\sum_{i,j}^{3K}\left(\frac{\partial^2 3V}{\partial x_i \partial x_j}\right)_{\mathbf{0}} x_i x_j + \frac{1}{3!}\sum_{i,j,k}^{3K}\left(\frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k}\right)_{\mathbf{0}} x_i x_j x_k + \cdots \tag{3.1}$$

In Eq. (3.1), $\mathbf{x}$ describes the displacements of the nuclei from the equilibrium positions at the minimum of the PES in form of Cartesian displacement coordinates (i.e. $x = r - r_e$ in case of a diatomic molecule)

$$\mathbf{x} = (x_1, y_1, z_1, \ldots, x_{3K}, y_{3K}, z_{3K})^{\dagger} \tag{3.2}$$

The Taylor series is truncated after the quadratic term and since the first order term is zero at the minimum,

$$\left(\frac{\partial V}{\partial x_i}\right)_{\mathbf{0}} = 0 \qquad \text{for} \qquad i = 1, \cdots, 3K \tag{3.3}$$

one obtains Eq. (3.4)

$$V(\mathbf{x}) = \frac{1}{2}\sum_{i,j}^{3K}\left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_{\mathbf{0}} x_i x_j = \frac{1}{2}\sum_{i,j}^{3K}(f_{ij})_{\mathbf{0}}\ x_i x_j \tag{3.4}$$

which is the basis of the harmonic (mechanical) approximation for describing vibrational modes. In Eq. (3.4), the constants f_{ij} represent the force constants, which are collected in the Cartesian force constant matrix $\mathbf{f}$.

If the molecule behaves as a classical particle on the PES, Newton's second law applies:

$$K_{x,I} = m_I \frac{d^2 x_I}{dt^2} = \frac{d}{dt}(m_I \dot{x}_I) = \frac{d}{dt} p_{x,I} \tag{3.5}$$

where $K_{x,I}$ is the x-component of the force exerted on a nucleus I with mass m_I, t the time, $\dot{x}_I$ the velocity, and $p_{x,I}$ the corresponding momentum. Newton's second law can be expressed in terms of kinetic energy T and potential energy V

$$-\frac{\partial V}{\partial x_I} = \frac{d}{dt}\left(\frac{\partial T}{\partial \dot{x}_I}\right) \tag{3.6}$$

Using mass-weighted coordinates,

$$\xi_i = m_I^{1/2} \tag{3.7}$$

Eq. (3.6) can be simplified via (3.8) to (3.9) and (3.10)

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{\xi}_i}\right) + \frac{\partial V}{\partial \xi_i} = 0 \quad \text{for} \quad i = 1, \cdots, 3K \tag{3.8}$$

$$\frac{d}{dt}\dot{\xi}_i + \frac{1}{2}\frac{\partial}{\partial \xi_i}\sum_{j,k}^{3K} f_{jk}\xi_j\xi_k = 0 \tag{3.9}$$

$$\frac{d^2 \xi_i}{dt^2} + \sum_{j}^{3K} f_{ij}\xi_j = 0 \tag{3.10}$$

Eq.s (3.10) represent the vibrational equations, which can be solved by using standard mathematical procedures.

It is advantageous to revert back to Eq. (3.6) and to consider two simplifications. First, the representation of the harmonic potential is changed by a coordinate transformation, which leads from the bilinear form (3.4) to a linear form depending on a new set of coordinates, the so-called normal coordinates. Second, the vibrational equations resulting out of Eq. (3.6) are rewritten in matrix notation using the vector of Cartesian displacements $\mathbf{x}$, the mass matrix $\mathbf{M}$, and the force constant matrix $\mathbf{f}$. For example, the kinetic energy T of the vibrating molecule and the harmonic potential V are expressed in this notation as

$$T(\dot{\mathbf{x}}) = \frac{1}{2}\dot{\mathbf{x}}^{\dagger}\mathbf{M}\dot{\mathbf{x}} \tag{3.11}$$

$$V(\mathbf{x}) = \frac{1}{2}\mathbf{x}^{\dagger}\mathbf{f}\mathbf{x} \tag{3.12}$$

Using the matrix notation and the normal coordinates, the vibrational problem can be written in form of the pseudoeigenvalue problem

$$\mathbf{f}\mathbf{L} = \mathbf{M}\mathbf{L}\mathbf{\Lambda}, \tag{3.13}$$

in which $\mathbf{\Lambda}$ is the eigenvalue matrix with the $N_{Vib} = 3K - L$ vibrational eigenvalues λ_μ on the diagonal

$$\lambda_\mu = 4\pi^2 c^2 (\omega_\mu)^2 \quad \text{for} \quad \mu = 1, \cdots, 3K - L = N_{vib} \tag{3.14}$$

where ω_μ is the harmonic vibrational frequency. The eigenvector matrix $\mathbf{L}$ contains N_{Vib} normal mode eigenvectors $\mathbf{l}_\mu$ as column vectors. In $\mathbf{L}$ and $\mathbf{\Lambda}$, L eigenvectors and eigenvalues correspond to overall translation and rotation of the molecule ($L = 5$ for linear and $L = 6$ for non-linear molecules). These eigenvalues are equal to zero provided translational and rotational motions are completely independent of the vibrational modes. This is true for the translational motions, but not for the rotational motions, which couple with the vibrational motions because of cubic terms in the potential energy function (3.1). Consequently, one finds eigenvalues close to zero, which correspond to the overall rotation of the molecule. The columns that corresponds to translational and rotational modes are omitted from matrix $\mathbf{L}$.

Eq. (3.13) reveals that the mass matrix represents a metric, which has to be eliminated to convert Eq. (3.13) to an eigenvalue problem. This leads to using mass-weighted Cartesian displacement coordinates as shown in Eq.s (3.7) to (3.10). Normal coordinates $\mathbf{Q}$ are related to Cartesian coordinates according to

$$\mathbf{x} = \mathbf{L}\mathbf{Q} \tag{3.15}$$

The vibrational equations can also be formulated in an analogous way using internal displacement coordinates $\mathbf{q}$, which describe changes of internal coordinates (bond length, bond angle, dihedral angle, etc.) instead of changes in atomic positions as expressed by $\mathbf{x}$.

$$\mathbf{q} = (q_1, \ldots, q_{N_{Vib}})^{\dagger} \tag{3.16}$$

For the transformation from internal to Cartesian coordinates, L additional coordinates corresponding to external motions (rotations and translations) are derived, which possess eigenvalues λ_i close to or equal to zero. The transformation from Cartesian to internal coordinates is done with the matrix $\mathbf{C}$

$$\mathbf{C} = \mathbf{M}^{-1}\mathbf{B}^{\dagger}\mathbf{G}^{-1} \tag{3.17}$$

where $\mathbf{B}$ is defined by Eq. (3.18)

$$B_{ni} = \left(\frac{\partial q_n(\mathbf{x})}{\partial x}\right)_{\mathbf{x}=\mathbf{x}_e} \tag{3.18}$$

and $\mathbf{G}$ is the Wilson matrix. [75]

$$\mathbf{G} = \mathbf{B}\mathbf{M}^{-1}\mathbf{B}^{\dagger} \tag{3.19}$$

The dynamics of the nuclear motions can be made independent of translations and rotations and the vibrational problem is solved in the internal coordinates only. The internal kinetic energy is given by

$$T(\dot{\mathbf{q}}) = \frac{1}{2}\dot{\mathbf{q}}^{+}\mathbf{G}^{-1}\dot{\mathbf{q}} \tag{3.20}$$

and the potential energy is approximated in accordance with Eq. (3.4) by

$$V(\mathbf{q}) = \frac{1}{2}\mathbf{q}^{\dagger}\mathbf{F}\mathbf{q} \tag{3.21}$$

where $\mathbf{F}$ is the internal force constant matrix, given by

$$\mathbf{F} = \mathbf{C}^{\dagger}\mathbf{f}\mathbf{C} \tag{3.22}$$

The vibrational equation in internal coordinates is given in Eq. (3.23).

$$\mathbf{F}\mathbf{D} = \mathbf{G}^{-1}\mathbf{D}\mathbf{\Lambda} \tag{3.23}$$

where $\mathbf{D}$ contains the normal mode vectors $\mathbf{d}_{\mu}$ ($\mu = 1, \cdots, N_{vib}$) given as column vectors and expressed in internal coordinates. Eq. (3.22) no longer contains the translational and rotational solutions and, consequently, $\mathbf{D}$ directly gives the transformation from normal coordinates to internal coordinates.

$$\mathbf{q} = \mathbf{D}\mathbf{Q} \tag{3.24}$$

The relationship between eigenvectors $\mathbf{l}_{\mu}$ and eigenvectors $\mathbf{d}_{\mu}$ is provided by matrix $\mathbf{C}$ according to

$$\mathbf{l}_{\mu} = \mathbf{C}\mathbf{d}_{\mu} \tag{3.25}$$

The vibrational equations presented above show that the normal modes associated with the normal mode frequencies ω_{μ} are delocalized modes since each normal coordinate is a linear combination of internal coordinate displacements. In the following, it has to be discussed under which circumstances one can expect normal modes to be localized within a given molecular fragment associated with a specific internal coordinate.

3.1 Localized Vibrational Modes. The degree of delocalization of a normal mode is primarily determined by the amount of coupling between the internal modes contained in the normal mode. In this way, the off-diagonal elements of the force constant matrix represent the coupling force constants. This becomes clear when realizing that the "$\mathbf{c}$-vectors" of the transformation matrix $\mathbf{C}$, each of which are associated with a given internal coordinate, can be used as internal localized modes. [76] Hence, a normal mode would be strictly localized if

$$(\mathbf{d}_{\mu})_n = \delta_{n\mu} \tag{3.26}$$

with $\delta_{n\mu}$ being the Kronecker delta. Eq. (3.26) leads to

$$\mathbf{l}_\mu = \mathbf{c}_n \tag{3.27}$$

where it is assumed that $\mu = n$. Eq. (3.27) will only be fulfilled if all displacements along vectors $\mathbf{c}_n$ and $\mathbf{c}_m$ ($m \neq n$) do not couple and a diagonal force constant matrix $\mathbf{F}$ is obtained with all coupling force constants $F_{nm} = 0$. This implies that electronic coupling between the internal localized modes is zero. Second, there is always mass coupling (coupling due to the kinetic energy) between the $\mathbf{c}$-vectors because the $\mathbf{G}$ matrix of Eq. (3.23) is non-diagonal. Mass coupling can 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. (3.26) nor Eq. (3.27) are true. Often, vibrational spectroscopists assume diagonal character of the $\mathbf{G}$ matrix provided there is a large mass difference between the atoms participating in the molecular motions since this assumption provides the only basis to discuss measured frequencies in terms of local mode frequencies.

Apart from mass coupling (coupling due to the kinetic energy), which is always present, there is electronic coupling (coupling due to the potential energy) as indicated by finite off-diagonal elements of the force constant matrix expressed in internal coordinates. Coupling constants are particularly large in the case of bond-bond interactions as they occur in delocalized π systems or in strained cyclic or polycyclic ring compounds. One observes that stretching force constants are the largest constants in a molecular force field, and that these force constants also show the largest variation. Bending force constants are smaller than stretching force constants and torsional force constants are in turn smaller than bending force constants, at least as long as a torsional mode at a single bond is concerned. This qualitative ordering of the magnitude of the diagonal force constants provides an estimate of the coupling between stretching, bending, and torsional modes only if the stretching and torsional modes couple only weakly. [75,77,78]

The various forms of stretch-stretch couplings can be described in the following way. Possible is a) a coupling between symmetry equivalent stretching modes, b) coupling between stretching modes involving the same atom combinations, and c) coupling between stretching modes involving different atom combinations. Only case c) causes coupling when the internal force constant-reduced mass ratio of the different bond types are compatible, whereas cases a) and b) will always be present to some extent if there exist several bonds of the same type in a molecule. Case b) coupling will be small if the internal force constants of two bonds are very different as in the case of AB bonds of different bond order (e.g., C-C vs C≡C). One internal stretching mode can be decoupled from other stretching modes of the same type by a change in mass as a consequence of isotope substitution so that the force constant-mass ratio varies considerably.

Localization of vibrational normal modes occurs in favorable cases with small electronic and mass coupling effects between the internal motions. For example, for a triatomic molecule such as HOCl where one internal stretching (OH stretching) is largely decoupled from the other stretching mode (OCl stretching)

and the bending mode (HOCl bending). It is also reasonable to say that the bending vibration in HOCl is decoupled from both stretching modes, i. e. in HOCl there are three normal modes, each of which is a largely localized vibrational mode associated with one of the three internal parameters.

For a general polyatomic molecule, localization of a normal mode within a particular molecular fragment is uncommon. For example, in aldehydes or ketones the normal mode that is dominated by the C=O stretching vibration is measured as a strong band in the area 1600 - 1800 cm^{-1} where the exact position of the band depends on the bond strength but also on the fact that the corresponding normal mode is not localized in the C=O group. In formaldehyde, acetaldehyde, and acetone, the internal C=O stretching mode contributes 89%, 85%, and 84 % respectively, to the normal mode considered to represent C=O stretching.

The discussion shows the dilemma of using normal mode properties to unravel geometric or electronic details of a molecule without being able to separate effects associated with different molecular fragments so that reliable information is gained. Because of these reasons, AICoMs [79] were introduced to obtain local modes that are associated with a specific structural unit of a molecule without being contaminated by coupling with other vibrational modes.

3.2 The Adiabatic Internal Coordinate Modes (AICoMs). Each AICoM of a molecule is associated with just one internal coordinate q_n, i.e. it is independent of all other internal coordinates q_m $(m \neq n)$. The construction of an AICoM is based on how an internal coordinate mode $\mathbf{v}_n$ would vibrate if the associated internal coordinate were to be displaced by an amount q_n^* in the way that the increase in the potential energy becomes minimal. To accomplish this objective, mode $\mathbf{v}_n$ which is lead by q_n^* (leading parameter principle [79]), 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 $\mathbf{Q}$ under the constraint that the internal coordinate displacement q_n is kept constant (Eq. 3.28):

$$V(\mathbf{Q}) = min. \tag{3.28a}$$

$$q_n = const. = q_n^* \tag{3.28b}$$

The potential energy V and the internal coordinate q_n depend on the normal coordinates according to Eq. (3.29) and Eq. (3.30).

$$V(\mathbf{Q}) = \frac{1}{2} \sum_{\mu=1}^{N_{Vib}} k_\mu Q_\mu^2 \tag{3.29}$$

$$q_n(\mathbf{Q}) = \sum_{\mu=1}^{N_{Vib}} D_{n\mu} Q_\mu \tag{3.30}$$

(see 3.24) where k_μ is the force constant for normal mode $\mathbf{d}_\mu$ and $D_{n\mu}$ is an element of matrix $\mathbf{D}$ of Eq. (3.23). Eq. (3.28) is solved with the help of the method of Lagrange multipliers,

$$\frac{\partial}{\partial Q_\mu}[V(\mathbf{Q}) - \lambda(q_n(\mathbf{Q}) - q_n^\star)] = 0 \tag{3.31}$$

where λ is the Lagrange multiplier. Eq. (3.31) leads to (3.32) and (3.33):

$$\frac{\partial V(\mathbf{Q})}{\partial Q_\mu} - \frac{\partial \lambda}{\partial Q_\mu}(q_n(\mathbf{Q}) - q_n^\star) - \lambda \frac{\partial (q_n(\mathbf{Q}) - q_n^\star)}{\partial Q_\mu} = 0 \tag{3.32}$$

$$\frac{\partial V(\mathbf{Q})}{\partial Q_\mu} = \lambda(\frac{\partial q_n(\mathbf{Q})}{\partial Q_\mu} - \frac{\partial q_n^\star}{\partial Q_\mu}) \tag{3.33}$$

where in (3.33) it is considered that $q_n(\mathbf{Q}) = q_n^\star$ is a constant. When the expression (3.29) for $V(\mathbf{Q})$ and (3.30) for $q_n(\mathbf{Q})$ is inserted into (3.33), the result is

$$\frac{\partial}{\partial Q_\mu}\frac{1}{2}\sum_{\nu=1}^{N_{Vib}} k_\nu Q_\nu^2 = \lambda \frac{\partial}{\partial Q_\mu}\sum_{\rho=1}^{N_{Vib}} D_{n\rho} Q_\rho \tag{3.34}$$

which leads to

$$k_\mu Q_\mu = \lambda D_{n\mu} \tag{3.35}$$

The solution of Eq. (3.31) (which concerns internal parameter q_n) for the μth normal coordinate is

$$Q_\mu^{(n)} = \frac{D_{n\mu}}{k_\mu}\lambda \tag{3.36}$$

where the superscript (n) of Q denotes a solution obtained under constraint (3.28b) for q_n. There is one such solution for each normal coordinate. When these solutions are used to express the displaced internal parameter $q_n^\star$, one gets

$$q_n^\star = \sum_{\mu=1}^{N_{Vib}} D_{n\mu} Q_\mu^{(n)} = \sum_{\mu=1}^{N_{Vib}} \frac{D_{n\mu}^2}{k_\mu}\lambda \tag{3.37}$$

which leads to expression (3.38) for the Lagrange multiplier

$$\lambda = \frac{1}{\sum_{\mu=1}^{N_{Vib}} \frac{D_{n\mu}^2}{k_\mu}} q_n^\star \quad . \tag{3.38}$$

Eq. (3.36) can be rewritten as

$$Q_\mu^{(n)} = \frac{\frac{D_{n\mu}}{k_\mu}}{\sum_{\nu=1}^{N_{Vib}} \frac{D_{n\nu}^2}{k_\nu}} q_n^\star \quad , \tag{3.39}$$

which means that the constraint for internal coordinate q_n leads to a change in the normal coordinates. The adiabatic internal mode $\mathbf{a}_n^Q$ for internal coordinate q_n expressed in terms of normal coordinates follows from (3.40):

$$Q_\mu^{(n)} = (\mathbf{a}_n^Q)_\mu q_n^\star \tag{3.40}$$

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

$$\mathbf{a}_n = \mathbf{L}\ \mathbf{a}_n^Q \tag{3.41}$$

Hence, Eq.s (3.40) and (3.41) completely specify the form of an AICoM.

3.3 Properties of Adiabatic Internal Coordinate Modes. Once an AICoM vector is known one can define a force constant that corresponds to the AICoM motion.

$$k_n^a = \mathbf{a}_n^\dagger \mathbf{f} \mathbf{a}_n \tag{3.42}$$

For the purpose of deriving an AICoM frequency with the help of k_n^a, one has to define the mass m_n^a that is associated with the AICoM. The latter has to fulfill two criteria. First, the AICoM mass m_n^a has to be extractable from the functional form of the internal coordinate q_n. Second, m_n^a has to be directly connected to the vibrational motion $\mathbf{a}_n$ caused by a change in q_n. While the potential energy has already been used to derive the AICoM vectors, so far nothing has been said with regard to the kinetic energy T. It has been shown that upon a perturbation of the equilibrium geometry caused by a change of the leading parameter, $q_n^\star$, the atoms of the molecule move in such a way that the kinetic energy adopts a minimum and the generalized velocity $\dot{q}_n$ becomes identical with $\dot{q}_n^\star$. Again, this leads to a constrained minimization problem, the solution of which is found with the help of another Lagrange multiplier. [79] The results of the derivation are

$$T(\dot{q}_n^\star) = \frac{1}{2} m_n^a (\dot{q}_n^\star)^2 \tag{3.43}$$

and

$$m_n^a = \frac{(\mathbf{b}_n^\dagger \mathbf{a}_n)^2}{\mathbf{b}_n^\dagger \mathbf{M}^{-1} \mathbf{b}_n} \tag{3.44}$$

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

$$\mathbf{b}_n^\dagger \mathbf{a}_n = 1 \tag{3.45}$$

since the AICoMs are properly normalized. Hence, the AICoM mass can be recognized to be identical to a diagonal element G_{nn} of the **G** matrix, which is a generalization of the reduced mass to internal parameters connecting more than two atoms. This is an indirect proof that the constraints put on V and T to get the AICoMs are well-chosen. With the AICoM force constant and the AICoM mass, it is straightforward to obtain the AICoM frequency

$$\omega_n^a = \left(\mathbf{a}_n^+ \mathbf{f} \mathbf{a}_n\ \ G_{nn} \right)^{1/2} = \left(\frac{k_n^a}{m_n^a} \right)^{1/2} \tag{3.46}$$

The force constant, frequency, and mass associated with a given AICoM for internal coordinate q_n provide the most important properties for its characterization. This information can be used to investigate normal modes by considering them as being composed of AICoMs. If one knows the decomposition of a normal

mode in terms of AICoMs, then one can clarify whether the normal modes are more or less delocalized and what electronic or geometric information they contain.

3.4 Characterization of Normal Modes in Terms of AICoMs. A chemist investigates and understands molecular geometry and conformation in terms of internal coordinates rather than using Cartesian or normal coordinates. All molecular structure information is detailed by listing the corresponding internal coordinates. Therefore, it is justified to add to the static representation of a molecule provided by the internal coordinates, a dynamic representation provided by the AICoMs. Accordingly, the AICoMs can be used as the dynamic counterparts of the internal coordinates to describe the normal modes and by this the dynamic behavior of a molecule. The problem is that there are no rules to define an amplitude that specifies to what extent a particular adiabatic mode $\mathbf{a}_n$ is active in normal mode $\mathbf{l}_\mu$. Therefore, criteria were set up that should be fulfilled by a given definition of an amplitude $\mathcal{A}_{n\mu}$, to guarantee a physically meaningful *characterization of normal modes (CNM)* in terms of AICoMs. These criteria are 1) the symmetry criterion, 2) the stability criterion, and 3) the dynamic criterion.

1) The symmetry criterion expresses the necessity that symmetry equivalent adiabatic modes have to have the same amplitude in a normal mode provided the normal mode retains this symmetry.

2) The stability of results concerns the independence of the AICoM amplitudes from the choice of the internal coordinate set. The amplitudes should not change significantly for a normal mode if they are calculated with different redundant internal coordinate sets and the differences in the parameter sets only concerns coordinates irrelevant to the normal mode.

3) There must be a relationship between the amplitude $\mathcal{A}_{n\mu}$ of an AICoM contained in a normal mode to the difference $\Delta\omega_{n\mu} = \omega_n - \omega_\mu$ in the way that a small difference implies large amplitudes while large differences lead to very small amplitudes. In other words, the scattering of points $\mathcal{A}_{n\mu}$ versus $\Delta\omega_{n\mu} = \omega_n - \omega_\mu$ should be enveloped by a Lorentzian curve. If this is the case, one can say that the dynamical origin of the normal mode principle is fulfilled. (*Dynamical origin of normal mode concept*)

The amplitude that fulfills the three criteria and performs best is defined in Eq. (3.47)

$$A_{n\mu} = \frac{\langle \mathbf{l}_\mu \mid \mathbf{f} \mid \mathbf{a}_n \rangle^2}{\langle \mathbf{l}_\mu \mid \mathbf{f} \mid \mathbf{l}_\mu \rangle \langle \mathbf{a}_n \mid \mathbf{f} \mid \mathbf{a}_n \rangle} \tag{3.47}$$

Amplitude $A_{n\mu}$ of Eq. (3.47) can be considered as an absolute amplitude, but it is common practice to renormalize $A_{n\mu}$ and to express it in percentage:

$$A^{\%}_{n\mu} = \frac{A_{n\mu}}{\sum_m A_{m\mu}} 100 \tag{3.48}$$

It should be noted that the renormalized amplitudes of Eq.s (3.47) and (3.48) lead to a description of the normal modes as it is often performed with the help of the *Potential Energy Distribution (PED)* analysis. [80-83] However, the PED analysis suffers from several deficiencies that can lead to non-physical results as is demonstrated by the following example.

The PED and the CNM analysis with adiabatic amplitudes were carried out for bicyclobutane (Figure 3.1), for which the normal modes had been calculated at the B3LYP/6-31G(d,p) level of theory. For this purpose, a parameter set containing all CC and CH stretches, the non-bonded "$C\cdots C$ stretching" interaction (see Figure 3.1) for the description of the ring bending (puckering), and two HCC bends for each hydrogen (in total 24 parameters) was constructed. If one compares the results of the PED and the CNM analysis, a major difference in the description of the ring folding and the bridge stretching motion is observed.

Figure 3.1

Figure 3.1 shows that the adiabatic modes for the ring folding (C$\cdots$C stretching) and the CC_{bridge} stretching are localized in the corresponding molecular fragments. The movements of the hydrogen atoms follow that of the C atoms in the energetically optimal way without carrying out a coupled CH stretching motion. In Figure 3.1 this is indicated by dashed arrows giving the direction of the H atom movements. The CC_{bridge} stretching motion is similarly described by the **c**-vector motions even though the movement of the H atoms is now stronger since it has to comply with fixed CH bond distances, i.e. all relaxations in the geometry because of CC_{bridge} stretching are suppressed for those internal coordinates defined in the parameter set for bicyclobutane. However, **c**-vector motion for ring folding ($C\cdots C$ stretching) differs considerably from the corresponding AICoM in the way that the CH_2 carbons hardly move. Instead, the hydrogens at the bridging carbons strongly move keeping the CC_{bridge} distance and those CCH bending angles defined in the parameter set constant, while changing the angle HCC_{bridge} (not contained in the parameter set), which is of course a consequence of the construction of **c**-vector modes. Clearly, the folding motion is not correctly described and this has serious consequences for the PED analysis.

Both methods predict that for normal mode 1, the dominant contribution is the folding motion of the ring (C$\cdots$C stretching): It amounts to 34.8% according to the CNM analysis and to 48.3% according to the PED analysis. However, for the latter description ring folding is also dominant for normal mode 5. Actually, normal mode 5 consists of a vibration of the CC_{bridge} and C$\cdots$C fragments in the way that when the CC_{bridge} bond becomes longer, the C$\cdots$C distance becomes shorter, and the hydrogens follow the vibration of the carbon atoms to which they are attached. The CNM analysis based on adiabatic amplitudes describes mode 5 as being composed of 40.1% stretching of the CC bridge bond and 28.5% of ring folding as reflected by a vibration of the C$\cdots$C unit. Hence, mode 1 possesses more ring folding character whereas mode 5 is dominated by a vibration of the CC bridge. However, the PED amplitudes suggest a contribution of 60% of ring folding C$\cdots$C and 17.8% of CC_{bridge} stretching simply because the **c**-vectors provide a misleading

description of the folding motion as shown in Figure 3.1. Hence, the PED analysis suggests that there is more than one ring folding motion in bicyclobutane, which makes little sense and indicates that PED can lead to physically unreasonable descriptions due to the mechanical behavior of **c**-vectors. This is confirmed by the CNM analysis based on the AICoM amplitudes.

The example given (many more examples are found for mono- and polycyclic molecules) reveals the deficiencies of the PED analysis, which primarily result from the use of **c**-vectors. The disadvantages of the latter have explicitly been discussed in the literature. [76] The CNM analysis based on the amplitude $\mathcal{A}_{n\mu}$ of Eq. (3.47) has been applied with success in various investigations. [84]

3.5 Advantages of AICoMs. AICoMs have the advantage that they are derived from a clear dynamic principle, namely the leading parameter principle, which points out that a single internal coordinate q_n (in general, a single internal parameter) defines the displacements of the nuclei from their equilibrium positions and, by this, leads the internal mode $\mathbf{a}_n$. The *leading parameter principle* [79] implies a new set of Euler-Lagrange equations because the generalized momenta for all other internal coordinates q_m $(m \neq n)$ become zero [79], which can be pictured in the way that all atomic masses outside the molecular fragment are considered as massless points. Hence, the derivation of the AICoMs follows the same procedure as the derivation of normal modes and it has been shown that the solutions of the Euler-Lagrange equations for the AICoMs are obtained by requiring that the potential energy V is minimized for a geometric perturbation under the constraint that the perturbation is defined by $q_n^\star$. [79]

The second advantage of the AICoMs is that their properties, namely adiabatic force constant, adiabatic mass, and adiabatic frequency are clearly defined and easy to calculate. The adiabatic mass is a generalization of the reduced mass for diatomic molecules and corresponds to G_{nn}^{-1}, which adds credibility to the physical basis of the AICoMs.

The third advantage of the AICoMs is that they lead to the CNM analysis of normal modes in a more sound and physically meaningful way than, for example, provided by the PED analysis. This is due to a clear definition of the amplitudes $A_{n\mu}$. [85] The CNM analysis provides an easy way of analyzing vibrational spectra and quantitatively specifying the degree of delocalization of each vibrational mode.

As a fourth point it has to be mentioned that the CNM analysis simplifies the correlation of the vibrational spectra of different molecules.

The fifth advantage of the AICoMs is that an AICoM intensity can be derived, which can be used to investigate the charge distribution within a molecule.

AICoMs are discussed in this work for the equilibrium geometry of a molecule. However, they can also be defined and applied to a reacting molecule. In this case, the AICoMs are based on generalized modes and are separately discussed in a one-dimensional subspace, the reaction path, and a 3K-(L+1)-dimensional

subspace orthogonal to the reaction path. As has been shown by Konkoli, Kraka, and Cremer [86,87], the AICoMs lead in this case to a wealth of information and help to describe the reaction mechanism in great detail.

An important advantage of the AICoMs is that they can also be derived from experimental vibrational spectra and establishing in this way a solid connection between theory and experiment. This is pointed out in the following.

Calculated AICoM frequencies and force constants suffer in the same way as the frequencies and force constants of normal vibrational modes from the deficiencies of the quantum chemical method used and the harmonic approximation employed in standard calculations of vibrational spectra. Even when applying efficient scaling procedures, there is no guarantee that ab initio frequencies accurately reproduce the fundamental frequencies of the experiment. In view of this, it seems to be much more useful to calculate the adiabatic frequencies in such a way that the experimental frequencies of the fundamental vibrations are exactly reproduced. In this way, each adiabatic internal frequency is the exact local mode counterpart of the measured vibrational frequency.

Since an experimental vibrational spectrum can only provide the frequencies of the fundamentals, it raises the question how the vibrational modes are to be obtained. In principal, this is achieved by setting up a force field from available experimental information and then using the theory described above. Alternatively, the force field can be calculated by correlation corrected ab initio or DFT methods. Combining the two sources of information, namely experimental frequencies and calculated normal modes, it is possible to determine that force constant matrix that in the harmonic approximation would reproduce fundamental frequencies exactly. Clearly, the force field obtained in this way is made up by *effective* force constants rather than pure quadratic force constants since the elements of the force field have absorbed all deficiencies of the quantum chemical calculation (correlation errors, basis set errors) and in addition cover also all anharmonicity effects, normally described by cubic and quartic force constants. The use of this force field in the AICoM calculation leads to adiabatic force constants and adiabatic frequencies, which directly correspond to the measured vibrational spectrum and, therefore, can be used for analysis of the vibrational spectrum and for the description of bond properties.

The theory needed to obtain experimentally based AICoM properties is described in standard books on vibrational spectroscopy and can be summarized in the following way [88]. If one considers the difference between experimental fundamental frequencies ω_μ^{exp} and calculated harmonic frequencies ω_μ as a relatively small error caused by a similarly small error in the force constant matrix, then one can assume the changes in the normal mode vectors to be negligible and use first order perturbation theory to set up the corrected vibrational secular equation (3.49)

$$\mathbf{D}(\mathbf{F}_0 + \mathbf{\Delta F})\mathbf{D}^\dagger = \mathbf{\Lambda} + \mathbf{\Delta \Lambda} \tag{3.49}$$

where $\mathbf{F}_0$, $\mathbf{D}$ and $\mathbf{\Lambda}$ correspond to the force constant matrix, the eigenvector matrix, and the eigenvalue matrix of the ab initio or DFT calculation. It holds that

$$\mathbf{D}^T\mathbf{F}_0\mathbf{D} = \mathbf{\Lambda} \tag{3.50}$$

because the eigenvectors $\mathbf{D}$ are normalized with regard to $\mathbf{G}$, i.e. $\mathbf{DD^T} = \mathbf{G}$. Accordingly, one can write the equation for the first order correction as

$$\mathbf{D}^T\mathbf{\Delta F D} = \mathbf{\Delta\Lambda} \tag{3.51}$$

from which the correction for the force constant matrix results as

$$\mathbf{\Delta F} = (\mathbf{D}^{-1})^\dagger\mathbf{\Delta\Lambda}(\mathbf{D})^{-1} = \mathbf{G}^{-1}\mathbf{D\Delta\Lambda D}^T\mathbf{G}^{-1} \tag{3.52}$$

Hence, diagonalization of the experimentally determined correction matrix $\mathbf{\Delta\Lambda}$ leads to $\mathbf{\Delta F}$ and the force constant matrix $\mathbf{F}_0 + \mathbf{\Delta F}$, which correctly reproduces experimental frequencies. Once the force constant matrix $\mathbf{F}_0 + \mathbf{\Delta F}$ is determined, one can apply the adiabatic mode analysis in the same way as it is applied to calculated vibrational spectra.

Eq. (3.49) can also be used if only part of a vibrational spectrum of a given molecule has been measured. Those frequencies, which have not been experimentally observed, can be taken from calculated spectra after appropriate scaling. In this way, experimental adiabatic frequencies can be determined for any molecule, for which sufficient infrared and/or Raman information is available.

4. Local Mode Properties Obtained from Experiment

As was shown in the previous section, mass and electronic coupling are both responsible for the delocalized nature of the normal vibrational modes. Apart from this, there is the problem of Fermi resonances. The transformation that leads to a separation of the quadratic terms in Eq. (3.4) does not separate the cubic and quartic terms of expansion (3.1). These anharmonic terms are responsible for the fact that an overtone or a combination band can mix with the fundamental of a vibrational mode. This phenomenon is called Fermi resonance and it plays an important role in vibrational spectroscopy. [77,78] For example, the CH stretching modes undergo Fermi resonances with the first overtone of the CH_3 and CH_2 bending modes (both CCH and HCH bending). This leads to a shift in the CH stretching frequency, which makes the determination of a localized CH stretching frequency rather uncertain. [41,89-94]

Actually, the CH stretching motion as well as other XH stretching motions might be considered as being ideally suited to represent localized modes. For example, the stretching of a terminal bond couples always less than the motion of a bond in a central position of the molecule. Secondly, the mass ratio of a heavy

atom X and H is optimal to reduce mass coupling. Finally, there are little electronic coupling effects between XH bonds with other bonds (with the exception of hyperconjugation and anomeric effects). If one compares the coupling between symmetry equivalent stretching modes with the coupling between stretching modes involving the same atom combinations, and the coupling between stretching modes involving different atom combinations, then the first will always be present in symmetric molecules and, therefore, it will be the most important coupling effect for CH bonds whereas the second and third effect have smaller importance. Considering also Fermi resonances, the chance of observing a localized CH or XH stretching motion in a molecule is much smaller than might be expected. However, in certain situations one can obtain local mode information nevertheless, which will be discussed in the following.

4.1 Isolated Stretching Modes. McKean considered the problem of deriving isolated CH stretching motions and provided a simple solution by replacing in a given molecule all H atoms but the target H by their D isotope thus yielding CD_2H and CDH groups. [41,89-94] The change in mass decouples the remaining CH stretching mode from all CD stretching modes and particularly those, which previously (as CH stretching modes) coupled strongly because of symmetry. In addition, one can make three other assumptions:

1) Due to isotope substitution, the CH stretching mode is largely isolated, which means that it is not only decoupled from the CD stretching vibrations but also from other stretching, bending, or torsional modes.

2) For the transition from asymmetrical/symmetrical CH_n vibrations to an isolated CH stretching mode all anharmonicity effects stay the same.

3) After D isotope substitution, all Fermi resonances for the CH stretching mode are suppressed.

As a result of 1) to 3), the CH stretching mode is largely localized and the corresponding mode frequency, i.e. the isolated stretching frequency $\omega_{iso(CH)}$, can be considered to accurately reflect the value of a local mode frequency.

McKean prepared a large number of isotopomers to measure isolated CH stretching frequencies and to investigate their dependence on geometric and electronic features of a given molecule. [41,89-94] He showed that in this way CH bonds can be used as sensitive antenna or probes testing the properties of molecules. While his first work was just focusing on CH bonds, he and his co-workers studied later also other XH bonds (X: Si, Ge). In addition, other authors used McKean's approach to describe local XH stretching modes. [95-97]

Investigations involving other than CH bonds revealed the large difficulties experiment faces when a generalization of McKean's approach is attempted. For the purpose of decoupling one internal stretching mode from other stretching modes of the same type, the change in mass by isotope substitution must be so large that it modifies the mass ratio significantly. Replacement of H by deuterium results in a doubling of the mass and a satisfactory suppression of coupling and Fermi resonances so that any residual coupling for

the isolated CH stretching modes is estimated to be less than 5 cm^{-1}. For a CC bond, one would obtain a very small effect if ^{12}C is replaced by ^{13}C or even ^{14}C since the change in the mass ratio is too small in these cases to play any significant role in the localization of the CC stretching motion. Hence, this example demonstrates that the isolated stretching frequencies are very useful quantities for the description of XH bonding in terms of local modes. However a generalization of this approach faces too many difficulties to play any important role in the description of general AB bonds or when trying to verify the applicability and limitations of the Badger rule. In this situation, theory has made an important contribution.

Isolated stretching modes can be calculated for a given molecule containing a CH_n group by simply replacing for the calculation of the **G** matrix the masses of the H atoms by those of the D isotopes but keeping for the isotopomer the force field of the parent molecule. In this way, harmonic isolated CH stretching modes ω_n^{iso} are calculated, which can easily be compared with both McKean's experimental ω_n^{iso} values for CH stretchings and the AICoM CH stretchings. B3LYP/6-31G(d,p) calculations produce isolated CH stretching frequencies, which correlate well ($R^2 = 0.985$ [57]) with McKean's experimental ones. Calculating also the corresponding AICoM CH-frequencies reveals that AICoMs are the theoretical equivalences of McKean's isolated stretching modes:

a) There is a linear relationship between isolated CH stretching frequencies and AICoM CH stretching frequencies with a correlation coefficient of 0.997. - b) Since the isolated CH stretching modes can also be calculated, the equivalence of AICoMs and isolated stretching modes can be quantified by the CNM analysis. With just a few exceptions discussed in the following, the overlap between AICoM and isolated modes is above 99% (in two cases 98%). - c) The isolated CH stretching modes are local modes that imply a relaxation of the electron density distribution upon perturbation of the CH equilibrium bond length. We find very similar relaxation effects for calculated stretching modes and AICoM stretching modes.

Exceptions are found for alkines for which a residual coupling between CH stretching and triple bond stretching is observed. Acetylenic hydrogens are not completely isolated from the C≡C stretching as reflected by an adiabatic overlap amplitude $A_{n\mu}$, which is smaller than 96% when the CH stretching AICoM of H-C≡X is compared with the normal mode representing an isolated CH stretching vibration. This explains why isolated CH frequencies ω_{CH}^{iso} at a triply bonded C deviate from the linear relation between CH(AICoM) and isolated CH stretching frequencies. [41] Coupling leads to an error of 45 cm^{-1} in the isolated CH stretching frequency of acetylene. Similar, but much smaller residual mass and electronic couplings probably exist for other CH couplings and explain the small scattering of isolated stretching frequencies (errors about 5 cm^{-1}) relative to the corresponding AICoM frequencies. Hence, one has to consider the residual coupling when one uses isolated stretching frequencies as a tool for structural analysis.

The fact that the isolated stretching frequencies can be replaced by AICoM stretching frequencies as their theoretical counterparts leads to a number of advantages: 1. The linear relationship between isolated

CH stretching frequencies and CH bond lengths found by McKean and used to predict unknown CH bond lengths with an accuracy of ± 0.001 Å once the isolated CH stretching frequency is measured, is confirmed for AICoM CH stretching frequencies [57] where both experimental or calculated values can be used. - 2. Contrary to the determination of isolating stretching frequencies, which so far could only be carried out for XH bonds [41,89-94], AICoM stretching frequencies can be easily determined for each bond of a molecule and McKean relationships can be established for all type of bonds. For example, it could be demonstrated that a quadratic relationship between AICoM CC stretching frequencies and the CC bond length exists. [57]

4.2 Local Mode Frequencies from Overtone Spectroscopy. Another way of obtaining information on localized XH stretching modes is to record overtone spectra of these vibrational modes. [98] Henry has pioneered this work by showing that the higher overtones of a XH mode can be reasonably well described with an anharmonic potential of a quasidiatomic molecule. [98,99] Higher overtones ($\Delta v \geq 3$) of XH stretching modes reveal considerable local mode character. For overtones with $\Delta v = 5, 6$ one observes mostly one band for each unique XH bond, even if there are several symmetry equivalent XH bonds in the molecule. In fundamental and lower overtone modes, there is always a splitting of the frequency into, e.g., a symmetric and an antisymmetric mode frequency of two symmetry equivalent XH stretching modes, but this splitting virtually disappears for overtones with $\Delta v \geq 5$. In general, the different linear combinations of symmetry equivalent XH stretchings become effectively degenerate for the higher overtones.

Since the overtone intensity decreases for each higher overtone level, conventional spectroscopy can not be used for overtones with Δv larger than 4. In gas phase investigations, the higher overtones are recorded by intracavity dye laser photoacustic spectroscopy, which uses sophisticated techniques to enhance the signal-to-noise ratio in the overtone spectra. [98] The local XH stretching modes are highly anharmonic. The very presence of overtones indicates that XH modes are anharmonic where the anharmonicity increases the higher the overtone is.

Table 4.1

The local mode behavior of the fifth overtone ($v = 6$) of CH stretching modes can be verified by comparison with the corresponding AICoM frequency. In Table 4.1, frequencies for the fifth overtone of CH stretchings of alkane, alkenes, and aromatic molecules are listed. [100-102] The values for thiophene are taken from liquid phase spectra whereas all other spectra were measured for the gas phase at room temperature. For isoxazole, there are only two overtone frequencies for the fifth overtone, which suggests that the difference between the overtones of the stretching motions of the C(4)H and C(5)H-bond are too small to be detected in the spectra. Similarly for toluene, the overtone spectra can not resolve any difference between the overtones of the meta and para CH stretchings.

Figure 4.1

In Figure 4.1, AICoM frequencies $\omega_n^a(CH)$ are correlated with frequencies taken from overtone spectroscopy (see Table 4.1). There is a linear relationship between the two quantities (correlation coefficient $R^2 = 0.990$), which again confirms that AICoMs are suitable local vibrational modes that are related to the local modes of overtone spectroscopy.

The use of overtone spectroscopy as a means of obtaining information on local vibrational modes and their properties is limited to terminal bonds, of which so far only XH (X = C, N, O, S, etc. [103,104]) bonds were investigated. Although coupling due to the potential energy (electronic coupling) is significant only for delocalized bonds, there is always coupling between local modes due to the kinetic energy (mass coupling). This coupling will be weak in the overtone spectra if the mass ratio between the two atoms of the bond considered is small as in the case of XH bonds. The investigation of isotopomers improves the situation, but these improvements are limited to XH bonds where the D,H mass ratio is favorable. Hence, a generalization of the local mode description by overtone spectroscopy is not possible.

4.3 Local Mode Information via an Averaging of Frequencies: Intrinsic Frequencies. Spectroscopists have often tried to assess the properties of local modes by simple averaging methods. For example, if two CH stretching modes in a CH_2 group interact to give a symmetric and an antisymmetric stretching mode, one can estimate the frequency of the corresponding local CH mode by taking the arithmetic mean of the frequencies of the symmetric and antisymmetric CH stretching vibration. A theoretical approach based on this idea was suggested by Boatz and Gordon [105], who derived the intrinsic frequencies ω_n^{BG} as representatives of local mode frequencies associated with an internal coordinate q_n.

$$(\omega_n^{BG})^2 = \sum_{\mu=1}^{N_{Vib}} \sum_{m=1}^{N_{Parm}} P_{nm}^{\mu} \omega_{\mu}^2 \tag{4.1}$$

where P_{nm}^{μ} leads to the PED amplitudes [105] and N_{Parm} defines the number of internal parameters used in the set of internal coordinates. N_{Parm} will be equal to N_{Vib} if a non-redundant parameter set is used, however, in general N_{Parm} can be larger than N_{Vib} for the calculation of the intrinsic frequencies.

Eq. (4.1) reveals that the intrinsic frequencies ω_n^{BG} are constructed as an average of those normal mode frequencies that have non-zero PED amplitudes for the internal parameters q_n. This averaging approach leads to problems when trying to obtain reliable local mode information, which becomes obvious when comparing intrinsic modes with AICoMs.

1) The intrinsic frequency is a frequency without a vibrational mode. This has to do with the fact that the derivation of ω_n^{BG} does not explicitly revert to a dynamic principle. AICoM frequencies correspond to AICoM vectors, which in turn are based on the leading parameter principle (the dynamic principle [79]) and the modified Euler-Lagrange equations for the vibrational problem expressed in terms of local modes. 2) The intrinsic frequencies are parameter set dependent whereas the AICoM frequencies are completely independent

of the size and the composition of the set of internal coordinates used for the description of the molecular geometry. 3) Intrinsic frequencies can become negative for a true equilibrium geometry, which is not the case for AICoMs. 4) Intrinsic frequencies reflect the molecular symmetry only when redundant coordinate sets are used. AICoM frequencies comply with the molecular symmetry, no matter whether redundant or non-redundant parameter sets are used to describe the internal vibrations. 5) For the intrinsic frequencies electronic and mass effects are not correctly separated, which is a problem when discussing electronic effects in terms of intrinsic frequencies. However, for the AICoM frequencies electronic and mass effect are clearly separated. 6) As a consequence of 5), intrinsic frequencies do not just lack an *intrinsic mode* but also an *intrinsic force constant*, which are both defined for AICoMs.

Table 4.2

For the purpose of showing some of the deficiencies of the intrinsic frequencies, in Table 4.2 intrinsic and AICoM frequencies for methane are listed employing HF/6-31G(d,p) theory and using eight incomplete (non-redundant) parameter sets (1 to 8 internal coordinates), one complete, non-redundant parameter set (3K-L = 9 internal coordinates) and one overcomplete, redundant parameter set with 10 internal coordinates. From Table 4.2, it can be seen that the intrinsic frequencies adopt different values for different numbers of coordinates in the parameter set. Even worse, for a given parameter set the intrinsic frequencies can take different values for symmetry equivalent stretching and bending modes. Even for the complete, non-redundant parameter set with 9 parameters, the intrinsic frequencies for the bending motions are different. When this is remedied in the way suggested by Boatz and Gordon, [105] the bending frequencies ω_n^{BG} become identical. Upon increasing the parameter set, the intrinsic frequencies decrease toward the values of the redundant set.

For the AICoM frequencies of methane just two values are obtained, namely 3255 cm^{-1} for CH stretchings and 1560 cm^{-1} for HCH bendings, no matter how many coordinates are used in the parameter set (see Table 4.2). It is obvious that the intrinsic frequencies of the redundant parameter set are the only one that should be compared with the AICoM frequencies and used for the discussion of electronic structure. However, it is by no means clear how intrinsic frequencies of similar reliability are obtained for a larger molecule with no symmetry at all. We have found in this work that for normal acyclic molecules using complete, non-redundant basis sets the intrinsic frequencies of stretching modes may agree well with the adiabatic frequencies. Problems arise with bending frequencies and even more with torsional frequencies, which can become negative.

4.4 Compliance Force Constants.

A way of obtaining local mode information, although it does not appear so on first sight, is provided by the use of compliance force constants. The latter are obtained when expressing the potential energy of a

molecule in terms of generalized displacement forces rather than internal displacement coordinates (see Eq. 3.21): [106,107]

$$V(\mathbf{g}) = \frac{1}{2}\mathbf{g}_q\mathbf{C}\mathbf{g} \tag{4.2}$$

where the elements of the compliance matrix $\mathbf{C}$ are given as the partial second derivatives of the potential energy V with regard to forces $f_i = -g_i$ and $f_j = -g_j$:

$$C_{ij} = \frac{\partial^2 V}{\partial f_i \partial f_j} \tag{4.3}$$

The gradient vector $\mathbf{g}_q$ of Eq. (4.2) can be obtained by differentiation of Eq. (3.21):

$$\mathbf{g}_q = \mathbf{F}\mathbf{q} \tag{4.4}$$

thus yielding

$$V(\mathbf{g}) = \frac{1}{2}\mathbf{q}^\dagger\mathbf{F}^\dagger\mathbf{C}\mathbf{F}\mathbf{q} \tag{4.5}$$

Comparing Eq. (4.5) with Eq. (3.21) clarifies that the compliance matrix $\mathbf{C}$ is identical with the inverse of the force constant matrix:

$$\mathbf{C} = \mathbf{F}^{-1} \tag{4.6}$$

From Eq. (4.4) one sees that

$$\mathbf{q} = \mathbf{F}^{-1}\mathbf{g} \tag{4.6}$$

Hence, the diagonal compliance force constant C_{ii} gives the displacement of internal coordinate q_i under the impact of a unit force while all other forces are allowed to relax. [107] This leads to the fact that off-diagonal elements of $\mathbf{C}$ are largely reduced. Although the compliance force constants are force constants without a vibrational mode, there seems to be some relationship to adiabatic force constants and by this also to the local modes associated with the adiabatic force constants.

The compliance force constants are largely independent of the internal coordinate set used. In a similar way as the adiabatic force constants describe the strength of a bond, the compliance force constants measure its weakness (the larger $C(AB)$ the weaker is bond AB, the smaller $C(AB)$ the stronger bond AB). Compliance force constants have been used to describe the gallium, gallium triple bond, [108] the strength of the NN and CO bond in NNH^+ and COH^+, respectively [109] or H-bonding in Watson-Crick base pairs. [110]

It will be interesting to derive the relationship between adiabatic and compliance force constants and to investigate whether both force constants can be used in a confirmative or even complementary way when describing chemical bonding.

5. Badger-type Relationships for Polyatomic Molecules

The vibrational spectra of 51 polyatomic molecules with a total of 170 different bonds were analyzed for the purpose of determining adiabatic and **c**-vector vibrational modes. Exclusively, those molecules were considered for which measured vibrational data is available so that either directly or with the approach described in Section 3.5 experimental AICoMs and **c**-vector modes could be determined and compared with the corresponding modes calculated at the B3LYP/6-31G(d,p) level of theory. This objective of the current analysis limited the molecules investigated exclusively to neutral closed-shell systems with normal bonding situations. This has to be considered when discussing the generalization of the Badger rule to polyatomic molecules.

The analysis of the stretching force constants and frequencies provided new insights into the usefulness of AICoMs. Calculated and experimental adiabatic frequencies correlate with a correlation coefficient R^2 of 0.997. The harmonic AICoM frequencies can be scaled down to experimental AICoM frequencies using a factor of 0.963. Similarly, calculated AICoM stretching force constants, if multiplied by 0.928, satisfactorily agree with experimental AICoM stretching force constants. Hence, it will be possible to base future studies on calculated adiabatic stretching modes. The correlation of AICoM stretching frequencies and force constants with the corresponding **c**-modes values led to a somewhat lower correlation coefficient R^2 of 0.988. The analysis of the data revealed that **c**-mode stretching force constants are always somewhat larger than AICoM force constants where the difference $k^c - k^a$ can be considered as a measure for the degree of mode coupling of the bond stretching vibration. For CH stretching force constants deviations are between 0.05 to 0.10 mdyne/Å, whereas for CC stretching force constants deviations increase to 0.2 - 0.3 mdyne/Å. If carbon is bonded to a hetero atom, a further increase in the deviation from AICoM force constants is found. However, deviations decrease when comparing CX single bonds with double and triple bonds. Adiabatic and **c**-vector force constants for triple bonds do hardly differ.

Not surprisingly, deviations as large as 1.9 mdyne/Å are found for CC and CX bonds in conjugated 5- and 6-membered rings. In general, strained cyclic and polycyclic systems lead to a relatively large coupling effect of bond stretching motions with other stretching and bending motions. These observations clearly show that **c**-mode vibrations mostly used in vibrational analysis are not suited to study bond properties. It remains to be clarified why studies based on these modes could lead to Badger-type relationships. A typical example is the study of Ohno and co-workers who could derive a Badger-type relationship for 74 different CX bonds using **c**-vector vibrational modes. [61] The CX double and triple bonds investigated outnumbered the CX single bonds by a factor 2, i.e. only a relatively small number of single bonds were considered. Also, the number of cases with X belonging to the third or the fourth period was large. Thirdly, all molecules with divalent Si or Ge were excluded from the test set as was also the case for triply bonded Si and Ge. Hence, the set of investigated molecules did not contain any "problem" cases and **c**-vector stretching force constants, although contaminated by coupling contributions, seemed to verify the Badger rule.

In Figure 5.1, the AICoM stretching force constants of 51 polyatomic molecules are given in dependence of the corresponding bond lengths. Hence, Figure 5.1 is based on the description of each polyatomic molecule as a collection of N quasi-diatomics where N is the number of bonds in the molecule. In so far it is not surprising that the diagrams in Figure 5.1 are closely related to those obtained for diatomic molecules (Figure 2.1). However, one essential difference between the Badger-type diagrams for diatomics and those for polyatomics becomes obvious: In the case of the latter molecules, there is one $k_e - r_e$ curve for each type of bond, i.e. the curves for OH, NH, CH, and BH bonds are all different, even though they seem to be closely related. This also holds for the relationships describing CC, CN, or CO bonds. We note that this observation is in agreement with the prediction made in chapter 2 and suggests that for each bond type AB specified by atoms A and B and the electronic state of the polyatomic molecule an individual curve can be expected. The curves are grouped according to A(period i)-B(period j) combinations, however do not coincide.

We have used various ways of fitting the data in Figure 5.1: The original Badger formula was tested, i.e $(k^a_{AB})^{-1/3}$ was plotted against r_e, but also other possible relationships were tested, which led to $(k^a_{AB})^{-1/p}$ with p = 2, 4, 5, or 6 in the general form of (5.1):

$$k^{-\frac{1}{p}} = ar_e + b \qquad p = 2 - 6 \tag{5.1}$$

The results of these tests can be summarized as follows:

1) Badger's rule is fulfilled for individual bonds of polyatomic molecules provided that they are described by the AICoM concept and all bonds considered possess similar electronic features. The correlation coefficient are between 0.98, 0.99 or even higher. However, if cations, anions, or open shell cases are included, the scattering of data points will increase as seen in the case of the diatomics.

2) According to the calculated correlation coefficients, there is hardly any difference whether p = 3, 4, 5 or 6 is used in relationship (5.1). One can avoid relationships of form (5.1) by using the exponential form (5.2) previously suggested already by other authors (entries 31,33,47,50,53 in Table 1.1):

$$k^a_n = ae^{-br_e}. \tag{5.2}$$

The exponential dependence of the adiabatic force constant on the calculated bond length in Eq. (5.2) accounts for all possibilities provided by Eq. (5.1).

By defining an effective bond length, the curves of Figure 5.1 can be merged in one XH and one CX curve (see, for example Figure 5.2). This provides evidence that a universal Badger-type relationship can be derived on the basis of hard sphere adjustment parameters d_{AB} characteristic of A and B, their charge, and spin situation rather than just the location of A and B in periods i and j. Work is in progress to determine these parameters.

6. Conclusions

A universal relationship between bond length $r(AB)$ and bond stretching force constant $k(AB)$ valid for both diatomic and polyatomic molecules can only be derived if two major prerequisites are fulfilled. 1) The bond stretching force constant must correspond to a local stretching mode that is characteristic of the bond AB only. A generally applicable way of deriving local modes is provided by the adiabatic internal coordinate mode concept. As described in this work, AICoMs can be determined for all bonds of a molecule using either calculated or experimental vibrational mode frequencies. AICoMs have been verified in this work as suitable local modes by comparing them with McKean's isolated XH stretching modes and the local CH modes from overtone spectroscopy. They differ from **c**-vector modes because the latter are contaminated by the coupling with other vibrational modes. The averaging of vibrational frequencies to obtain local mode information is also not suitable because it can lead to physically not meaningful local mode frequencies.

2) In view of the increasing size of an atom A or B with the number of its electrons, a universal bond length - force constant relationship must be based on effective bond lengths, which are corrected for the different hard sphere sizes of A and B. This work has shown that correction parameters cannot uniformly be defined for all atoms of a period i and all atoms of a second period j. Instead, they have to consider the charge and spin multiplicity of bond AB (or the molecule containing bond AB). In addition, one has to consider that in strained molecules such as cyclopropane the actual bond path is significantly longer than the internuclear distance because (concave or convex) bond bending. Because of this, the stretching force constant turns out to be smaller (indicating a weaker bond) then the length of the bond might suggest.

The results obtained in this work indicate that different bonding situations (single, double, triple bonded AB) of closed-shell molecules can be described with just one hard sphere parameter. Test calculations for cations and anions (not described in this publication) suggest that the number of parameters for a given bond AB will not be larger than 3 or 4 because in this way, cationic, anionic, closed and open shell situations can be described for a large body of molecules containing bond AB. Work is in progress to determine hard sphere parameters for bonds formed by atoms of the first three periods in a systematic way. This work will lead to a universal Badger-type relationship that will facilitate the derivation of suitable initial guesses of the Hessian matrix in quantum chemical geometry optimizations, the construction of force fields, and the prediction of bond lengths from measured vibrational data in surface studies, for molecular aggregates, and catalysis. Reversely, calculated bond lengths can be used to predict via the stretching force constant the strength of the bond.

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Tables

Table 2.1. Experimental bond lengths r and bond stretching force constants k of diatomic molecules AB. [a]

No	Molecule	r (Å)	k ($mdyne\mathring{A}^{-1}$)	No	Molecule	r (Å)	k ($mdyne\mathring{A}^{-1}$)
1	H_2 ($^1\sum_g^+$)	0.741	5.75	61	SiH ($^2\Pi_i$)	1.520	2.39
2	H_2+ ($^2\sum_g^+$)	1.052	1.60	62	SiH^- ($^3\sum^-$)	1.474	2.71
3	He_2+ ($^2\sum_u^+$)	1.081	3.40	63	SiH^+ ($^1\sum^+$)	1.504	2.67

4	$He_2 2+$ $(^1\sum_g^+)$	0.704	12.80	64	PH $(^3\sum^-)$	1.422	3.22
5	$HeH+$ $(^1\sum^+)$	0.774	4.94	65	PH^- $(^2\Pi_i)$	1.407	2.86
6	LiH $(^1\sum^+)$	1.596	1.03	66	PH^+ $(^2\Pi_r)$	1.435	3.04
7	BeH $(^2\sum^+)$	1.343	2.27	67	SH $(^2\Pi_i)$	1.341	2.43
8	BeH^+ $(^1\sum^+)$	1.312	2.64	68	HCl $(^1\sum^+)$	1.275	5.16
9	BH $(^1\sum^+)$	1.232	3.05	69	HCl^+ $(^2\Pi_i)$	1.315	4.13
10	CH $(^2\Pi_r)$	1.120	4.48	70	$LiNa$ $(^1\sum)$	2.810	0.21
11	CH^- $(^3\sum^-)$	1.089	4.48	71	NaO $(^2\Pi$	2.050	1.54
12	CH^+ $(^1\sum^+)$	1.131	4.11	72	NaF $(^1\sum^+)$	1.926	1.76
13	NH $(^3\sum^-)$	1.036	5.97	73	MgO $(^1\sum^+)$	1.749	3.48
14	NH^+ $(^2\Pi_g)$	1.070	4.73	74	MgF $(^2\sum^+)$	1.750	3.16
15	OH $(^2\Pi_i)$	0.970	7.80	75	AlN $(^3\Pi_i)$	1.768	3.03
16	OH^- $(^1\sum^+)$	0.970	7.65	76	AlO $(^2\sum^+)$	1.618	5.67
17	OH^+ $(^3\sum^-)$	1.029	5.41	77	AlF $(^1\sum^+)$	1.654	4.23
18	HF $(^1\sum^+)$	0.917	9.66	78	Si_2 $(^3\sum^-)$	2.246	2.15
19	HF^+ $(^2\Pi_i)$	1.001	5.38	79	SiN $(^2\sum^+)$	1.571	7.29
20	NeH^+ $(^1\sum^+)$	0.989	4.81	80	SiO $(^1\sum^+)$	1.510	9.24
21	$HeNe^+$ $(^1\sum^+)$	1.300	3.36	81	SiF $(^2\Pi_i)$	1.601	4.90
22	Li_2 $(^1\sum_g^+)$	2.67	0.26	82	CP $(^2\sum^+)$	1.562	7.83
23	LiO $(^2\Pi_i)$	1.695	2.08	83	PN $(^1\sum^+)$	1.491	10.16
24	LiF $(^1\sum^+)$	1.564	2.50	84	PO $(^2\Pi_r)$	1.476	9.45
25	BeO $(^2\sum^+)$	1.331	7.51	85	PO^- $(^3\sum^-)$	1.540	6.21
26	BeF $(^2\sum^+)$	1.361	5.60	86	PF $(^3\sum^-)$	1.590	4.97
27	B_2 $(^3\sum_g^-)$	1.590	3.38	87	PF^+ $(^2\Pi_r)$	1.500	7.70
28	BN $(^3\Pi)$	1.281	8.33	88	NS $(^2\Pi_r)$	1.494	8,52
29	BO $(^2\sum^+)$	1.205	13.66	89	NS^+ $(^1\sum^+)$	1.440	11.49
30	BO^+ $(^1\sum)$	1.205	12.27	90	BeS $(^1\sum^+)$	1.742	4.13
31	BF $(^1\sum^+)$	1.263	8.07	91	BS $(^2\sum^+)$	1.609	6.72
32	C_2 $(^1\sum_g^+)$	1.243	12.16	92	CS $(^2\sum^+)$	1.535	8.49
33	C_2^- $(^2\sum_g^+)$	1.268	11.21	93	CS^+ $(^2\sum^+)$	1.495	9.85
34	C_2^+ $(^2\Pi_u)$	1.301	6.44	94	SO $(^3\sum^-)$	1.481	8.30
35	CN $(^2\sum^+)$	1.172	16.29	95	SO^+ $(^2\Pi_r)$	1.424	11.62
36	CN^+ $(^1\sum)$	1.173	15.74	96	$LiCl$ $(^1\sum^+)$	2.021	1.42
37	CO $(^1\sum^+)$	1.115	19.80	97	$LiCl^-$ $(^2\sum^+)$	2.180	0.79
38	CO^+ $(^2\sum^+)$	1.115	19.80	98	$BeCl$ $(^2\sum^+)$	1.797	3.03
39	CF $(^1\sum^+)$	1.272	7.42	99	BCl $(^1\sum^+)$	1.716	3.47
40	N_2 $(^1\sum_g^+)$	1.098	22.95	100	CCl $(^2\Pi_{1/2})$	1.645	3.95
41	N_2^- $(^2\Pi_g)$	1.193	15.98	101	NCl $(^3\sum^-)$	1.614	4.03
42	N_2^+ $(^2\sum_g^+)$	1.116	20.09	102	ClO $(^2\Pi_i)$	1.570	4.71
43	N_2^{2+} $(^1\sum_g^+)$	1.132	15.85	103	ClF $(^2\Pi_r)$	1.638	4.48
44	NO $(^2\Pi_r)$	1.151	15.95	104	$BeAr^+$ $(^2\sum^+)$	2.085	0.59
45	NO^- $(^3\sum^-)$	1.063	8.17	105	Na_2 $(^1\sum^+)$	3.079	0.17
46	NO^+ $(^1\sum^+)$	1.116	24.84	106	$NaCl$ $(^1\sum^+)$	2.361	1.09
47	NF $(^3\sum^-)$	1.317	6.19	107	Mg_2 $(^1\sum_g^+)$	3.890	0.02
48	O_2 $(^3\sum^-)$	1.208	11.76	108	MgS $(^1\sum^+)$	2.142	2.26
49	O_2^- $(^2\Pi_{g,i})$	1.350	5.60	109	$MgCl$ $(^2\sum^+)$	2.119	1.79
50	O_2^+ $(^2\Pi_g)$	1.116	17.09	110	Al_2 $(^3\sum_g^-)$	2.466	0.97
51	F_2 $(^1\sum_g^+)$	1.412	4.70	111	AlS $(^2\sum^+)$	2.029	3.28
52	F_2^- $(^2\sum_u^+)$	1.880	1.46	112	$AlCl$ $(^1\sum^+)$	2.130	2.08
53	F_2^+ $(^2\Pi_{g,i})$	1.322	6.45	113	$SiCl$ $(^2\Pi_r)$	2.058	2.63
54	FO $(^2\Pi)$	1.326	5.41	114	SiS $(^1\sum^+)$	1.929	4.94
55	Ne_2^+ $(^2\sum_u^+)$	1.750	1.53	115	P_2^+ $(^2\Pi_{u3/2})$	1.986	4.12
56	NaH $(^1\sum^+)$	1.887	0.78	116	PS $(^2\Pi_r)$	1.900	5.06
57	MgH $(^2\sum^+)$	1.730	1.27	117	S_2 $(^3\sum_g^-)$	1.889	4.96

58	MgH^+ ($^1\sum^+$)	1.652	1.65	118	S_2^+ ($^2\Pi_{g,r}$)	1.825	5.88
59	AlH ($^1\sum^+$)	1.648	1.62	119	Cl_2 ($^1\sum_g^+$)	1.988	3.23
60	AlH^+ ($^2\sum^+$)	1.602	1.50	120	Cl_2^+ ($^2\Pi_{3/2g}$)	1.891	429

[a] Experimental values from Ref. [71]. Molecules AB are listed according to A(period i)-B(period j) combinations in the order 1-1, 2-1, 2-2, 3-1, 3-2, 3-3.

Table 4.1. Comparison of measured overtone frequencies for CH stretching ($\Delta v = 6$) with the corresponding B3LYP/6-31G(d,p) AICoM frequencies for various organic molecules. [a]

Molecule	bond	ω_n^a	$\Delta v = 6$
Methane		3129	16150
Fluoromethane		3074	15972
Chloromethane		3152	16216
Ethane		3085	15824
Ethene		3188	16550
Ethyne		3437	18430
Propane	CH_3, ip	3085	15845
	CH_3, op	3074	15746
	CH_2	3047	15562
Cyclopropane		3180	16504
Benzene		3186	16550
Furan	C(O)-H	3285	17223
	C(C)-H	3261	17121
Isoxazole	C(O)-H	3273	17143[b]
	C(C)-H	3284	17143[b]
	C(N)-H	3248	16911[b]
Thiophene	C(S)-H	3260	16890[c]
	C(C)-H	3218	16700[c]
Propene	=C-H(trans)	3195	16569
	=C-H(cis)	3175	16395
	H-(Me)C=	3138	16236
	CH_3, ip	3099	15895
	CH_3, op	3055	15681
n-Butane	CH_3, ip	3086	15829
	CH_3, op	3074	15751
	CH_2	3036	15473
Isobutene	CH_2	3186	16474
	CH_3, ip	3107	15978
	CH_3, op	3050	15628
Isobutane	CH	3015	15305
	CH_3, ip	3065	15683
	CH_3, op	3079	15804
Toluene	C(ortho)-H	3170	16430
	C(meta)-H	3184	16543
	C(para)-H	3188	16543
	CH_3, ip	3055	
	CH_3, op	3062	

[a,b,c] Measured frequencies from Ref.s [100] - [102]. ip and op denote in-plane and out-of-plane hydrogen atoms. All frequencies in cm^{-1}.

Table 4.2 Intrinsic frequencies ω_n^{BG} and AICoM frequencies ω_n^a in cm^{-1} given for 10 different parameter sets of CH_4 as calculated at the HF/6-31G(d,p) level of theory. [a]

	1	2	3	4	5	6	7	8	9	10
ω_n^{BG}										
CH_1	3461	3452	3421	3322	3306	3286	3261	3261	3261	3261
CH_2		3452	3421	3322	3306	3293	3276	3272	3261	3261
CH_3			3421	3322	3306	3293	3276	3272	3261	3261
CH_4				3322	3306	3286	3276	3261	3261	3261
H_2CH_1					1570	1563	1551	1529	1577	1419
H_3CH_1						1563	1551	1529	1460	1419
H_4CH_1							1551	1577	1577	1419
H_2CH_3								1577	1577	1419
H_3CH_4									1577	1419
H_4CH_2										1419
ω_n^a										
all CH	3255	3255	3255	3255	3255	3255	3255	3255	3255	3255
all HCH					1560	1560	1560	1560	1560	1560

[a] The composition of parameter sets 1 - 10 (topline) is obtained by adding internal coordinates in the first column, i.e. parameter set 1 contains just the CH1 bond length, parameter set 2 the bond lengths CH1 and CH2, etc.

Figure Captions

Figure 2.1. Experimental bond stretching force constants k in mdyne/Å are given in dependence of the bond length r in Å for diatomic molecules AB where atoms A and B belong to the first three periods. Symbol $k[i-j]$ denotes that an atom A from period i is bonded to atom B from period j.

Figure 3.1. Two internal vibrational modes of bicyclobutane as described by adiabatic (left) and **c**-vector modes (right). Top: Folding motion of the ring (C$\cdots$C). Bottom: Stretching of the bridge bond CC_{bridge}. Atom movements are indicated by solid arrows (strong movements) or dashed arrows (weak movements). Very small displacements are not shown for the sake of clarity. (B3LYP/6-31G(d,p) calculations)

Figure 4.1. Correlation of measured overtone frequencies $\Delta v = 6$ for CH stretching modes with the corresponding calculated adiabatic CH stretching frequencies. For details, see Table 4.1.

Figurre 5.1. Adiabatic stretching force constants given in dependence of equilibrium bond lengths both calculated at the B3LYP/6-31G(d,p) level of theory for polyatomic molecules.

Figurre 5.2. Merging of CX Badger-type relationships from Figure 5.1 by introducing an effective bond length R.

Table 1.1. Relationships between spectroscopic and geometrical constants of a bond in diatomic, quasidiatomic, and polyatomic molecules.

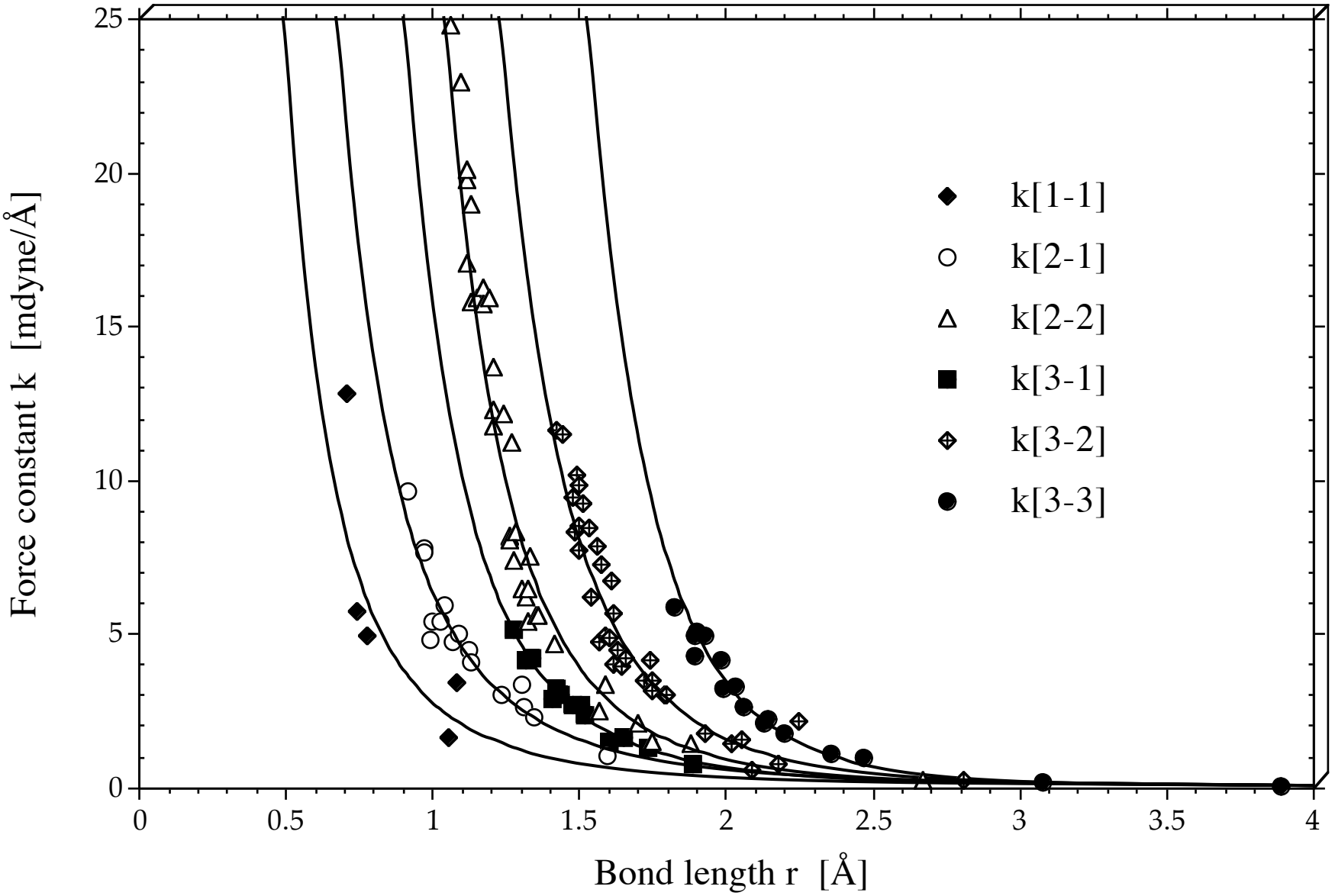
No	Year	Authors	Equation	Molecules	Comment	Ref.
1	1920	A. Kratzer	$\omega_e^2 I = const.$ $k_e r_e^2 = const.$	D	I: moment of inertia, valid for hydrogen halides	1
2	1925	R. T. Birge	$\omega_e r_e^2 = const.$	D	different electronic states of a given D	2
3	1925	R. Mecke	$\omega_e r_e^2 = const.$	D	different electronic states of a given D	3
4	1929	P. M. Morse	$\omega_e r_e^3 = const.$	D	different D of similar kind	4
5	1934	C. H. D. Clark	$r_e^2 = c_{nm}(\mu/nk_e)^{1/3}$ $\omega_e r_e^3 n^{1/2} = const.$	D	μ: reduced mass; m,n: group numbers for hydrides and non-hydrides	5
6	1934	R. M. Badger	$k_e(r_e - d_{ij})^3 = const.$	D	d_{ij} is typical of AB with A in period i and B in period j; $r_e - d_{ij}$: effective bond length	6
7	1935	R. M. Badger	$r_e = (c_{nm}/k)^{1/3} + d_{nm}$	D	constants typical of AB with A in group m and B in group n	7
8	1935	H. S. Allen, A. K. Longair	$r_e^2 = c_{ij}/k_e^{1/3}$ $k_e r_e^6 = const.$	D	constant typical of AB from a given period	8
9	1935	R. M. Badger	same as 7	QD	bonds in small symmetric polyatomic molecules	9
10	1935	M. L. Huggins	eq.s for D_e, r_e, ω_e, k_e	D	derived from modified Morse potential	10
11	1936	M. L. Huggins	$r_e = a - b\ log(ck_e)$	D	constants derived for periods, rule 6 explained	11
12	1938	G. B. B. M. Sutherland	$k_e r_e^6 n^{3/2} = const.$	D	related to 5	12
13	1940	G. B. B. M. Sutherland	$D_e = kr_e^2/nm$ $k_e = ma(n-m)r_e^{-(m+2)}$	D	$V = -ar^{-m} + br^{-n}$ (double-reciprocal V)	13
14	1940	R.A. Newing	$r_e = r_e(\omega_e, x_e, D_e, \mu)$	D	quantum mechanical arguments for existence of relationships	14
15	1940	J. W. Linnett	$k_e r_e^6 = const.$	D	testing of $V = -ar^{-m} - be^{-nr}$	15
16	1941	C.D. Clark, K.R. Webb	$k_e r_e^6 n = const.$ $k_e(r_e - d_{ij})^3 n^{1/2} = \text{const.}$	D	valid for molecules with similar μ modification of Badger rule; n as in 5	16
17	1942	J. W. Linnett	$k_e r_e^5 = const.$	D	same V as in 15	17
18	1944	C.K. Wu, C.T. Yang	$k_e = ar_e^{-(m+2)} + br_e^{-(m+1)}$	D	constants typical of period	18
19	1945	J. W. Linnett	$k_e r_e^{7.6} = const.$	P	for molecules with NH bond; for CH bonds 15 is better	19
20	1946	W. Gordy	$k_e = aN(x_A x_B/r_e^2)^{3/4}$	D	N: bond order, x_A, x_B: electronegativity of A, B	20

21	1946	K. M. Guggenheimer	$k = aN(z_A z_B)^{1/2} r_e^{-b}$	P, **c**-mode	N: bond order, z_A, z_B: valence electrons	21
22	1950	K. M. Guggenheimer		P (AX_n) **c**-mode	b = 2.46; 1.84; 2.06; etc. typical of bond polarity	22
23	1947	C.K. Wu, Chao	$logk_e = ar_e + b$	D	simplified version of 11	23
24	1950	G. Herzberg	various formulas	D	discussion of empirical rules, r_e and k_e changes over periods are shown for HX and OX bonds	24
25	1951	G. Lovera	$k_e = a(r_e + 1)^{-3.75}$	P, **c**-mode	molecules of groups 4b - 6b	25
26	1953	H. Siebert	$k_{CX} = aZ_X/n_X^3$ $r_X = a(n_X^3/Z_X)$ $N = a(k_N/k_1) + b$	P (XMe_n)	Z_X: atomic number; n_X principal quantum number of valence electrons for X; formula for k_{XY} r_X: covalent radius of X; N: bond order	26
27	1955	E.R. Lippincott, R.Schroeder	general formulas	D	use of a modified Morse potential	27
28	1957	H.O. Jenkins	$k_e = ar_e^{-2} - b$	D	homonuclear D	28
29	1958	Y. P. Varshni	eq.s for k_e, D_e, X_e	D	derived from $V = -a(r-d)^{-m} + b(r-d)^{-n}$	29
30	1958	Y. P. Varshni	$k_e(r_e - d)^p = const$ $r_e = ak_e^{-1/2} + b$	D	review; p = 2 turns out to be best	30
31	1961	D. R. Hershbach, V. W. Laurie	$k_e = 10^{-(r_e - a_{ij})/b_{ij}}$ $r_e = d_{ij} + (a_{ij} - d_{ij})k_e^{-1/3}$	D	constants derived for 7 formulas for cubic and quartic force constants	31
32	1964	H. S. Johnston	$r_e = a_{ij} - b_{ij} log(k)$	P, **c**-mode	Taken from 31	32
33	1964	J.A. Ladd,W.J. Orville-Thomas, B. C. Cox	$k = ar^{-b}$ or $log(k) = -b\ log(r) + c$	P, **c**-mode	$k = 35.5r^{-5.79}$ for CO bonds	33
34	1966	J.A. Ladd,W.J. Orville-Thomas	$k = ar^{-b}$	P, **c**-mode	$k = 34.4r^{-5.97}$ for NO bonds	34
35	1966	M. J. S. Dewar, G. J. Gleicher	$k = ar_e^{-2} + br_e^{-4} + cr_e^{-6}$	P, **c**-mode	assumed; used in PPP for calculating CN, CO, NN bond energies	35
36	1966	J. C. Decius	$k = ar^{-6}$	P, **c**-mode	$k = 38.5r^{-6}$ for NN bonds (GS and ES of P)	36
37	1966	J. Goubeau	review of formulas	P, **c**-mode	comparison of Badger, Gordy, and Siebert formulas	37
38	1968	R. F. Borkman, R. G. Parr	$r_e^2\omega = const.$	D	use of virial theorem; quantum mechanical analysis k related to overlap population, r_e, D_e, and AO kinetic energies	38
39	1968	R. S. Roy	$r_e^6 = a\ \ m_1 m_2\ \ n^{-2}\ \ k^{-1}$	D	n: group number; m_1, m_2: atomic masses; a is considered as universal constant	39
40	1970	J. Stals	k-r formulas reviewed	P, **c**-mode	material on CC, CN, CO, NN, NO, OO bonds	40
41	1978	D.C. McKean	$r(CH) = a\omega(CH) + b$	P isolated ω	isolated stretching frequencies as bond descriptors	41
42	1984	H. B. Schlegel	Badger rule 6	P, **c**-mode	ab initio calculations; use of **c**-vectors prediction of Hessian for geometry optimization	42

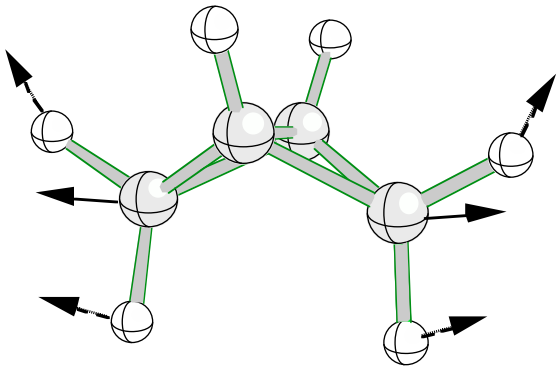
43	1987	D.M. Byler, H. Susi W. C. Damert	33 tested	P, **c**-mode	$k = 37.3r^{-5.35}$ for CN bonds	43
44	1987	H. B. Bürgi, J. D. Dunitz	$r = a - bln(k)$	P, **c**-mode	rationalized with modified Morse potential used in connection with reaction rates	44
45	1987	D. J. Swanton, B. R. Henry	$k_e(r_e - d_{ij})^n = c_{ij}$	D, P	justification of Badger-type rules with modified Morse potential; local mode approximation for overtones	45
46	1987	A.A. Zavitsas	$k = a\mu(D - b)$	P, **c**-mode	for CC and other bonds tested	46
47	1987	V.M. Miskowski et al.	$r = a + be^{-k/c}$	P, **c**-mode	for for M-M bonds in transition metal compounds	47
48	1989	J. C. Weisshaar	Badger rule 6	D	3rd row diatomics	48
49	1990	P. K. Mallick et al.	test of 31	P	extended to frequency shifts and bond length changes	49
50	1992	T. H. Fischer, J. Almlöf	$k_{AB} = ae^{-b(r_{AB}-r_{ref})}$	P	assumed; estimates of Hessian for geometry optimization	50
51	1992	A. Rutkowski, et al.	$-\Delta r_e(rel) \propto \Delta k(rel)$	D	relativistic changes in r_e and k	51
52	1993	R. G. Pearson	$k_e r_e = aN(x_a x_b) + b$		N: bond order; x: electronegativity	52
53	1995	R. Lindh et al.	$k_{AB} = ae^{-b(r_{AB}-r_{ref})^2}$	P	assumed; estimates of Hessian for geometry optimization	53
54	1996	P.D. Harvey	$r = aln(k) + b$	P, **c**-mode	Reparametrization of 31 for M-M bonds in transition metals	54
55	1997	J. M. Wittbrodt, H. B. Schlegel	Badger rule 6 $k_{AB} = a/(r_{AB} - b)^3$	P, **c**-mode	estimates of Hessian for geometry optimization, relationships for b established	55
56	1999	M. Stichler, D. Menzel	$\omega = a'(r - b)^{-3/2}$	P, **c**-mode	Badger rule tested for NO on Ru-surface	56
57	1999	J. A. Larsson, D. Cremer	$r = a\ \omega + b$ $r = a\ \omega^2 + b\omega + c$	P, **a**-mode	41 tested for 66 CH bonds extension to 40 CC bonds requires quadaratic relationship	57
58	2000	J. Cioslowski et al.	$k = A(r - b)^{-c}$	D	Badger-type rules are not universal shown for 108 diatomics	58
59	2001	P. Schwerdtfeger et al.	test of 31	P, **c**-mode	applied to Cu-Cu bonds	59
60	2003	J. Jules, J.R. Lombardi	test of 6, 31	D	N, r, and k related for M-M bond in metal dimers	60
61	2004	K. Ohno et al.	$k = aR^{-3}$	P, **c**-mode	for 74 molecules with CX bonds R: effective bond length	61
62	2006	T. Green et al.	$r = c_{ij}\omega^{-2/3} + d_{ij}$	P, **c**-mode	Badger rule applied to FeO bonds	62,63
64	2008	Y. W. Lin et al.	$r = c_{ij}\omega^{-2/3} + d_{ij}$	P, **c**-mode	Badger rule tested for CO interacting with amino acids	63
65	2008	U. Das, K. Raghavachari	$r = a\omega + b$	P,	isolated stretching frequencies	64

66	2008	T.H. Morton et al.	$\omega = a(r-b)^{-3/2}$	isolated ω P,**a**-mode	used to predict r(PH) for molecules on surface CF^+ bonds	65
67	2009	E. Kraka, D. Cremer	r,ω,k,n,BDE related generalized Badger	P, **a**-mode	relationships for for CO and CF^+ bonds	66

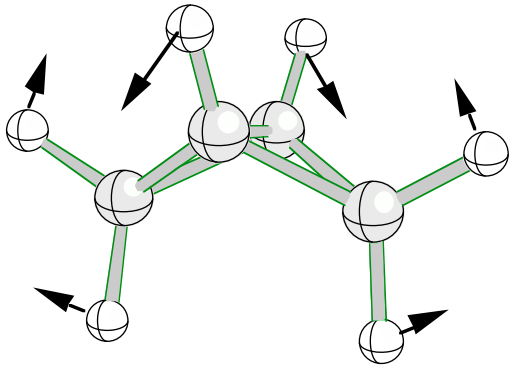
[a] A bond AB of a D: diatomic, QD: quasidiatomic, P: polyatomic molecule is considered where A is located in period i or group m and B in period j or group n of the periodic table. The derivation of force constants for polyatomic molecules has been based on **c**-modes, adiabatic-modes, isolated stretching modes, local modes from overtone spectroscopy, or simply assumed. D_e: bond dissociation energy; r_e: equilibrium bond length; ω_e: equilibrium bond stretching frequency; k_e: equilibrium bond stretching force constant; N: bond order; x_e: equilibrium anharmonicity constant; μ: reduced mass.


Force constant k [mdyne/Å]
Bond length r [Å]
k[1-1]
k[2-1]
k[2-2]
k[3-1]
k[3-2]
k[3-3]
0
5
10
15
20
25
0
0.5
1
1.5
2
2.5
3
3.5
4

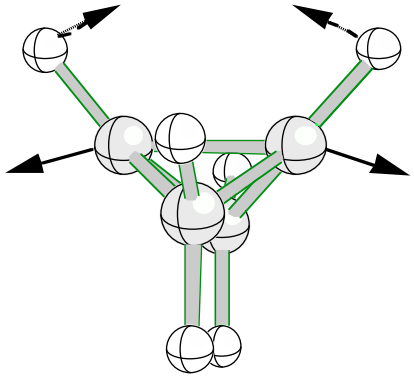
C···C, adiabatic mode



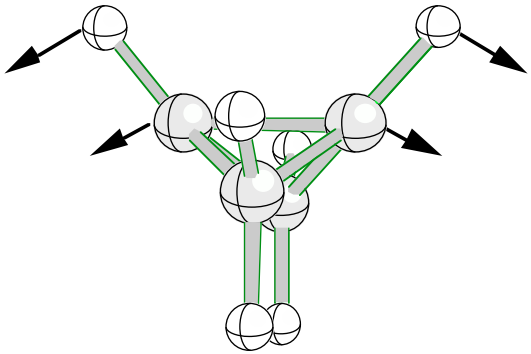
C···C, c-vector mode

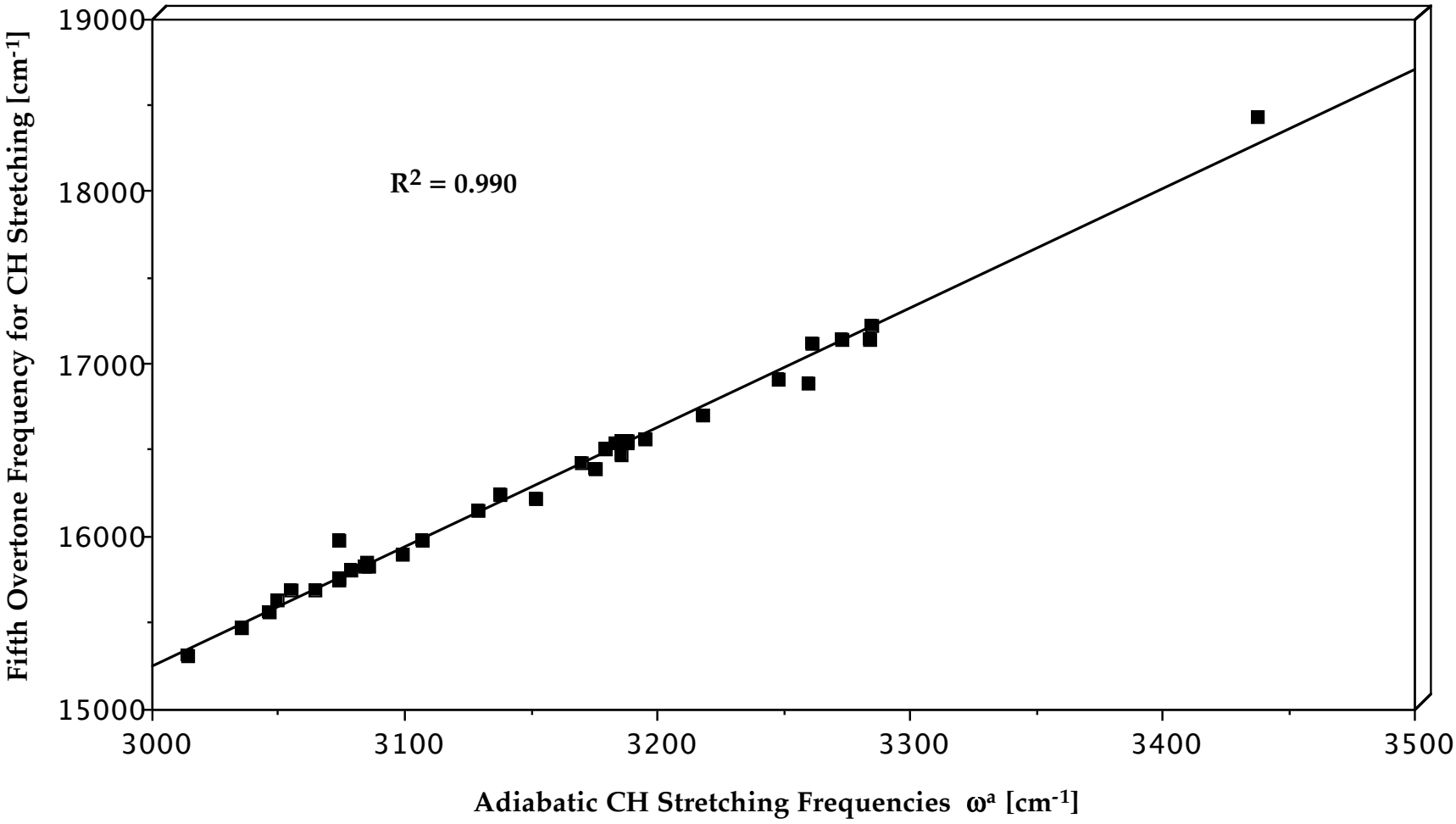


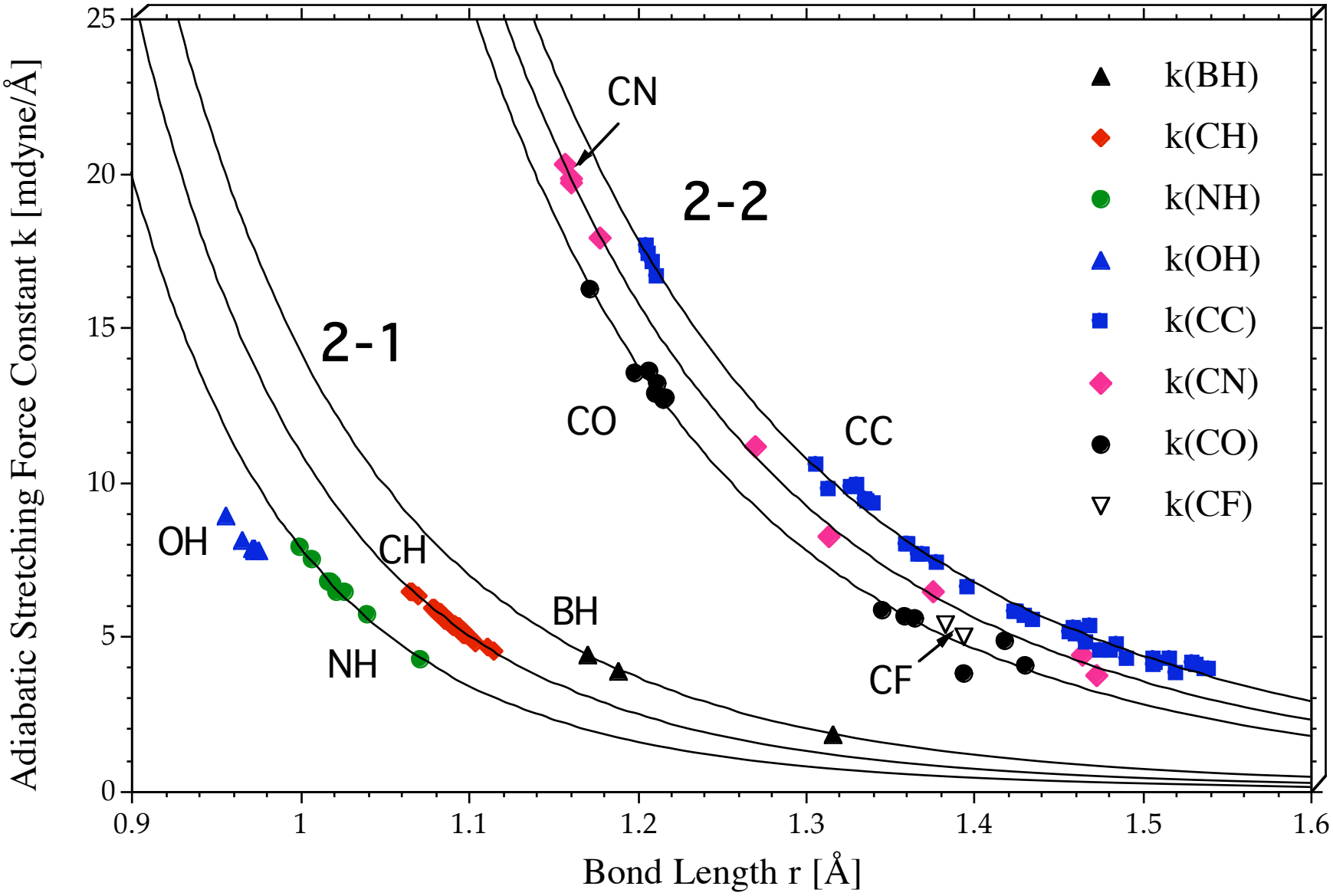
CC_{bridge}, adiabatic mode

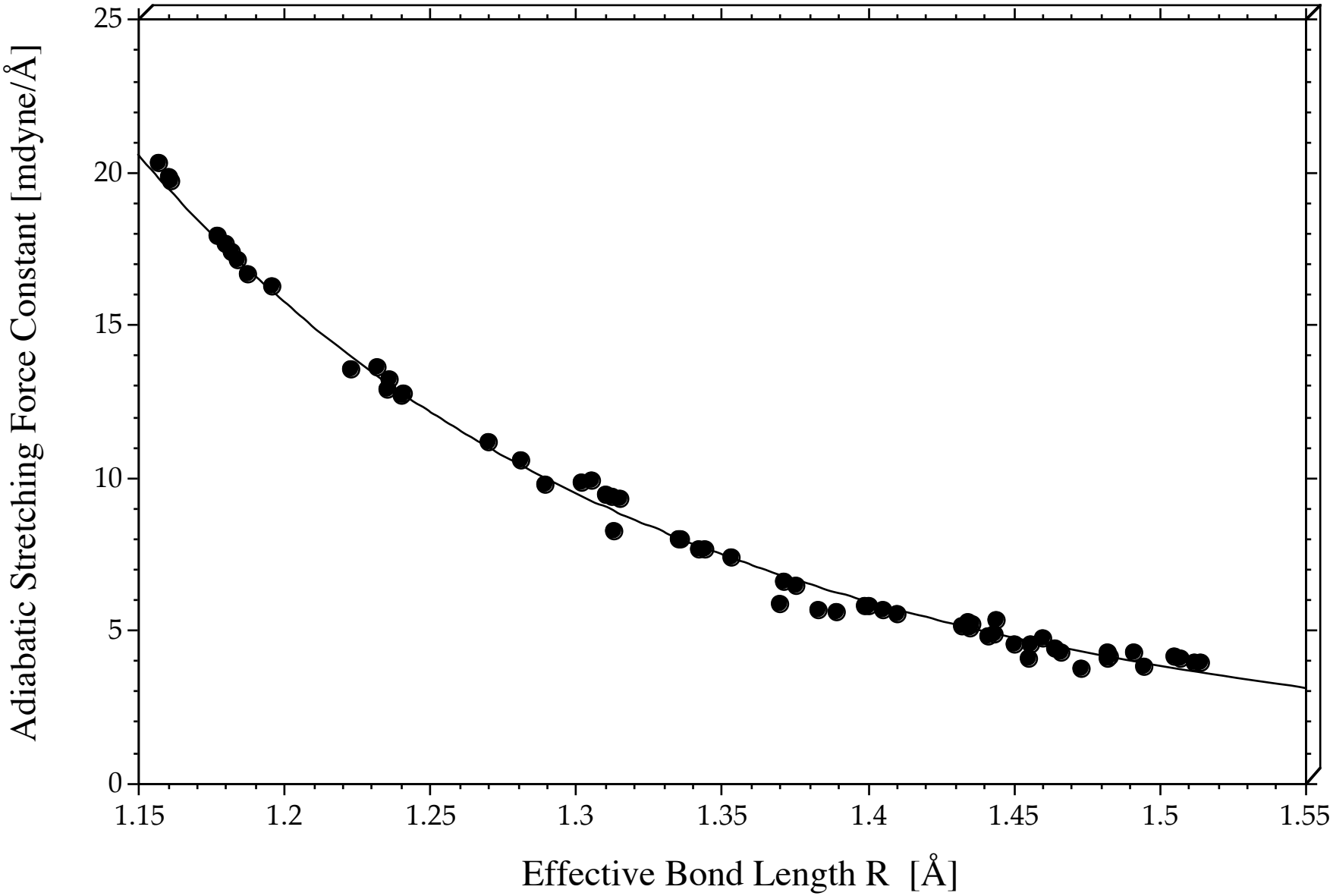


CC_{bridge}, c-vector mode




19000
18000
17000
16000
15000
3000
3100
3200
3300
3400
3500
R2 = 0.990
Fifth Overtone Frequency for CH Stretching [cm-1]
Adiabatic CH Stretching Frequencies ωa [cm-1]


Adiabatic Stretching Force Constant k [mdyne/Å]
Bond Length r [Å]
0
5
10
15
20
25
0.9
1
1.1
1.2
1.3
1.4
1.5
1.6
2-1
2-2
OH
CH
NH
BH
CO
CN
CC
CF
k(BH)
k(CH)
k(NH)
k(OH)
k(CC)
k(CN)
k(CO)
k(CF)


Adiabatic Stretching Force Constant [mdyne/Å]
25
20
15
10
5
0
1.15
1.2
1.25
1.3
1.35
1.4
1.45
1.5
1.55
Effective Bond Length R [Å]