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Theoretical verification and extension of the McKean relationship between bond lengths and stretching frequencies

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Dedicated to Professor Lawrence S. Bartell in recognition of his pioneering studies of molecular structure

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Abstract

Vibrational spectra contain explicit information on the electronic structure and the bonding situation of a molecule, which can be obtained by transforming the vibrational normal modes of a molecule into appropriate internal coordinate modes, which are localized in a fragment of the molecule and which are associated to that internal coordinate that describes the molecular fragment in question. It is shown that the adiabatic internal modes derived recently (Int. J. Quant. Chem., 67 (1998) 1) are the theoretical counterparts of McKean's isolated CH stretching modes (Chem. Soc. Rev., 7 (1978) 399). Adiabatic CH stretching frequencies obtained from experimental vibrational spectra can be used to determine CH bond lengths with high accuracy. Contrary to the concept of isolated stretching frequencies a generalization to any bond of a molecule is possible as is demonstrated for the CC stretching frequencies. While normal mode frequencies do not provide a basis to determine CC bond lengths and CC bond strengths, this is possible with the help of the adiabatic CC stretching frequencies. Measured vibrational spectra are used to describe different types of CC bonds in a quantitative way. For CH bonds, it is also shown that adiabatic stretching frequency leads to the definition of an ideal dissociation energy, which contrary to the experimentally determined dissociation energy is a direct measure of the bond strength. The difference between measured and ideal dissociation energies gives information on stabilization or destabilization of the radicals formed in a dissociation process.

Keywords: Bond stretching frequency; Adiabatic vibrational mode; Bond strength; Bond dissociation energy; Bond length

1. Introduction

One of the major goals in chemistry is the investigation and understanding of the chemical bond [1–4]. Bond lengths, bond stretching frequencies, vicinal NMR spin–spin coupling constants, and bond dissociation energies obtained from appropriate experiments are used to describe and discuss the strength of the chemical bond. The bond strength is best described by the bond energy, however both bond strength and bond energy are model quantities defined for a particular model of the chemical bond. Neither bond strength nor bond energy can directly be measured for polyatomic molecules and, accordingly, one has to revert to other molecular properties to get insight into the strength of the chemical bond. Clearly, measured properties such as bond dissociation energies or bond lengths can be used to quantitatively assess the strength of the chemical bond in an indirect way. For example, bond dissociation energies depend on both the strength of the bond to be broken and the

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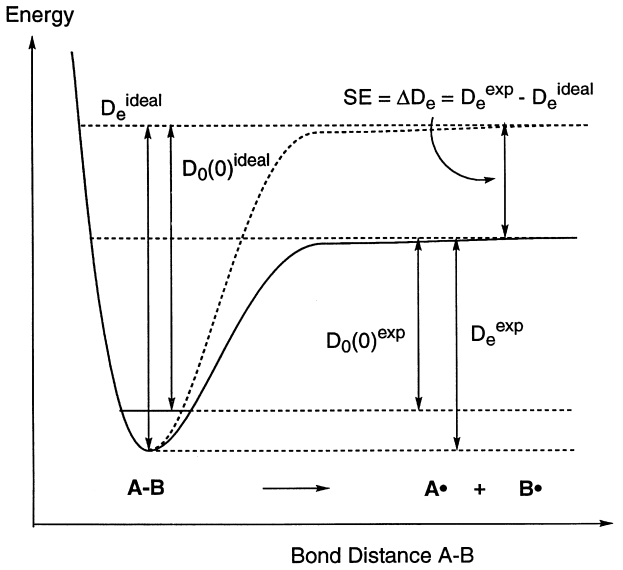


Scheme 1.

stability of the fragments (radicals) obtained after bond cleavage, which in general makes it difficult to assess the strength of a chemical bond. This would only be possible if one would know the stabilization energy (SE) of the fragments of a bond dissociation process so that one could determine ideal dissociation energies D_e^{ideal} corresponding to a dissociation into fragments without any (de)stabilization (see Scheme 1). Ideal dissociation energies (contrary to experimental dissociation energies D_e^{exp}) would be a perfect measure for the equilibrium bond strength[1]. In the case of diatomic molecules, bond energy, and bond dissociation energies are identical, which is the reason why for a long time knowledge about chemical bonds was collected primarily for diatomic molecules [5,6].

In chemistry, it is a generally accepted assumption that measured bond lengths reflect the strength of the corresponding chemical bond. This is certainly true as long as the bond strength is predominantly determined by the accumulation of electron density in the bond region and the screening of the nuclei by this density [7]. However, when electrostatic interactions between the bonded atoms dominate as in the case of polar or ionic bonds, the bond length may no longer be a reliable indicator for the bond strength. Convincing examples are the fluoroamines $NH_{3-n}F_n (n = 0, \ldots, 3)$, for which with increasing fluorination the NF bonds becomes shorter (normally indicating a strengthening of the bond), but the NF bond strength becomes weaker [8]. Also, steric interactions between the substituents attached to a bond may influence its strength in a way that is not necessarily reflected by the bond length. This becomes clear if one considers not just the case of steric repulsion leading to bond weakening and bond lengthening but also that of steric attraction (e.g. in connection with the *cis* effect (see for example Ref. [9])), which may have opposing effects on bond strength and bond length. Therefore, it is advisable to determine other molecular properties, which may complement the description of the chemical bond by bond length and bond dissociation energy.

[1] We note that the term *bond strength* is often used in a misleading way. For example, in the Handbook of Chemistry and Physics, 72. Edition, D.R. Lide, Edt., CRC Press, Boca Raton, 1991, dissociation enthalpies D_0^{exp} are listed under the heading *Bond Strengths in Polyatomic Molecules*, although this quantity reflects both the strength of a bond and the stability of the radical(s) formed. To our opinion, it is not sufficient and still misleading if one distinguishes between an equilibrium bond strength reflected, e.g. by equilibrium bond length and equilibrium stretching force constant and a (non-equilibrium) bond strength reflected, e.g. by bond dissociation energies since the latter quantities cannot be trustful indicators of bond strength.

In this connection, an important contribution has been made by McKean [10,11] who has demonstrated in the case of the CH bonds of many different polyatomic molecules that bond stretching frequencies can provide an excellent measure for the bond strength. The normal mode frequencies of conventional infrared or Raman studies are not suited for this purpose because coupling between the CH stretching motions and other motions or Fermi resonances between CH stretching motions and CH_n bending motions make it difficult to assign an accurate frequency to pure (localized) stretching motion of an individual CH bond.

McKean solved this problem by replacing all but one H atom of a molecule by deuterium (i.e. investigating perdeuterated isotopomers with just one H atom in a CD_2H or CDH group). The frequencies of $CD_{n-1}H$ bending motions are significantly reduced and, as a consequence, Fermi resonances are less strong in the CH stretching region. Couplings of a particular CH stretching mode to other motions of a hydrocarbon are minimized to less than 5 cm^{-1} [10]. McKean called the CH stretching frequencies obtained in this way ''isolated'' (symbol $\nu_{iso}(CH)$) and used them directly as a measure for the properties of the CH bond. He showed that a relationship between isolated CH stretching frequencies and CH bond lengths exists, which can be used to determine unknown r_0 values of CH bond lengths with high accuracy once the corresponding ν_{iso}(CH) value has been measured [10]. A similar correlation with CH bond dissociation energies provided a basis to discuss (de)stabilization effects in molecules and radicals generated by CH bond cleavage [11]. Utilizing these relationships isolated CH stretching frequencies were measured and used in several investigations [12–20].

McKean's investigations have inspired the present work in various ways. First, they clearly demonstrate that, in principle, the vibrational spectra of a molecule contain all the information needed to describe its chemical bonds. Secondly, they show the major problems of using directly measured or calculated normal mode frequencies for this purpose. Finally, they lead to the question whether McKean's approach can be generalized and isolated frequencies can be determined for other than CH bonds. One could think of systematically replacing all but two directly bonded C atoms of a hydrocarbon by ^{13}C isotopes to determine isolated CC stretching frequencies. However, this does not lead to the suppression of mode mixing between CC stretching and other vibrational motions and, therefore, it is obvious that a generalization of McKean's approach is limited to AH or AX bonds with terminal X and a similar relationship between isotope masses as given for the CH group.

Recently, we have developed the theory of the adiabatic internal modes (AIMs) [21–26]. Contrary to the delocalized normal modes of vibrational spectroscopy, AIMs are localized in a particular molecular fragment ϕ_m with two, three or more atoms characterized by an internal coordinate such as the bond length, the bond angle, etc. Therefore, AIMs are pure bond stretching, bond bending, etc. modes that are perfectly suited as reference modes for analyzing the normal vibrational modes of a molecule and to describe the properties of the molecular fragments [21–24]. If one knows the AIMs of a molecule, one should be able to set up McKean relationships between bond lengths and bond stretching frequencies for all its bonds. Hence, the AIMs of a molecule should provide reliable descriptions of the chemical bonds of a molecule.

In this work, we focus on the question whether AIM frequencies are the theoretical equivalents of McKean's isolated stretching frequencies by investigating first 66 CH bonds of 38 different molecules. We also test whether McKean's idea can be extended in those cases where isolated stretching frequencies are difficult to obtain but AIM frequencies are available. Our work is based on standard quantum chemical calculations of the normal modes of a molecule. Because of the approximations made in these calculations (mechanical rather than quantum mechanical description of the vibrational problem, use of a harmonic potential to calculate vibrational frequencies, limitations with regard to basis set and electron correlation effects covered), one obtains harmonic vibrational frequencies, which for stretching modes are about 10% too large. One could improve standard calculations of vibrational modes in various ways, however this would become rather costly and would not guarantee the general applicability of the approach described in this work. Therefore, we will choose another less costly way to apply the concept of the AIMs to measured vibrational spectra and to determine experimental AIM

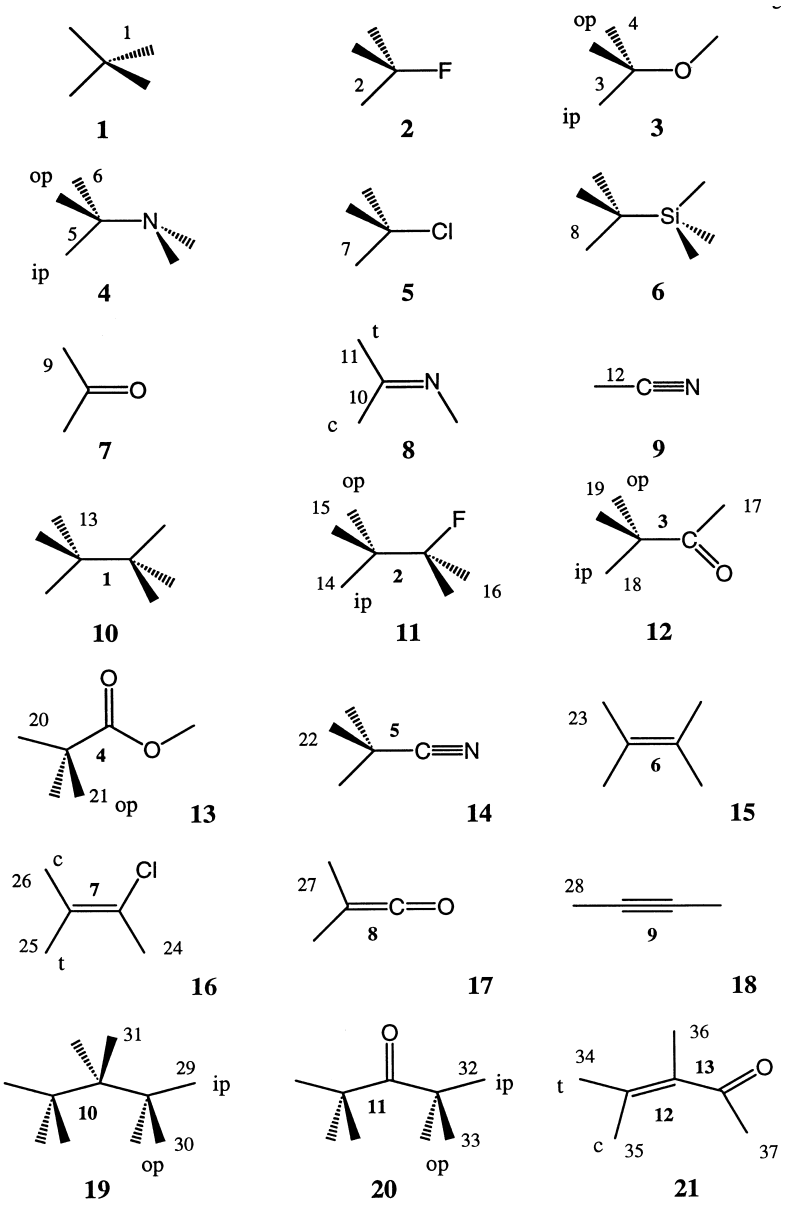


Fig. 1. Molecules **1**–**38** investigated. CH bonds are identified by small numbers in normal print, CC bonds by small numbers in bold print. The following notation is used to distinguish H atoms of a CH_n group: ip: in-plane; op: out-of-plane; ax: axial; eq: equatorial; c: *cis*; t: *trans.*

frequencies that can directly be compared to McKean's isolated stretching frequencies.

To present the results of our investigation, this report is structured in the following way. In Section 2, we will briefly summarize the AIM concept and its theory. The computational methods used in this work are described in Section 3. In Sections 4–6, we will compare isolated CH stretching frequencies with adiabatic CH stretching frequencies obtained either from quantum chemical calculations or experiment, set up McKean relationships with CH bond lengths, and then extend the McKean approach to the CC bond.

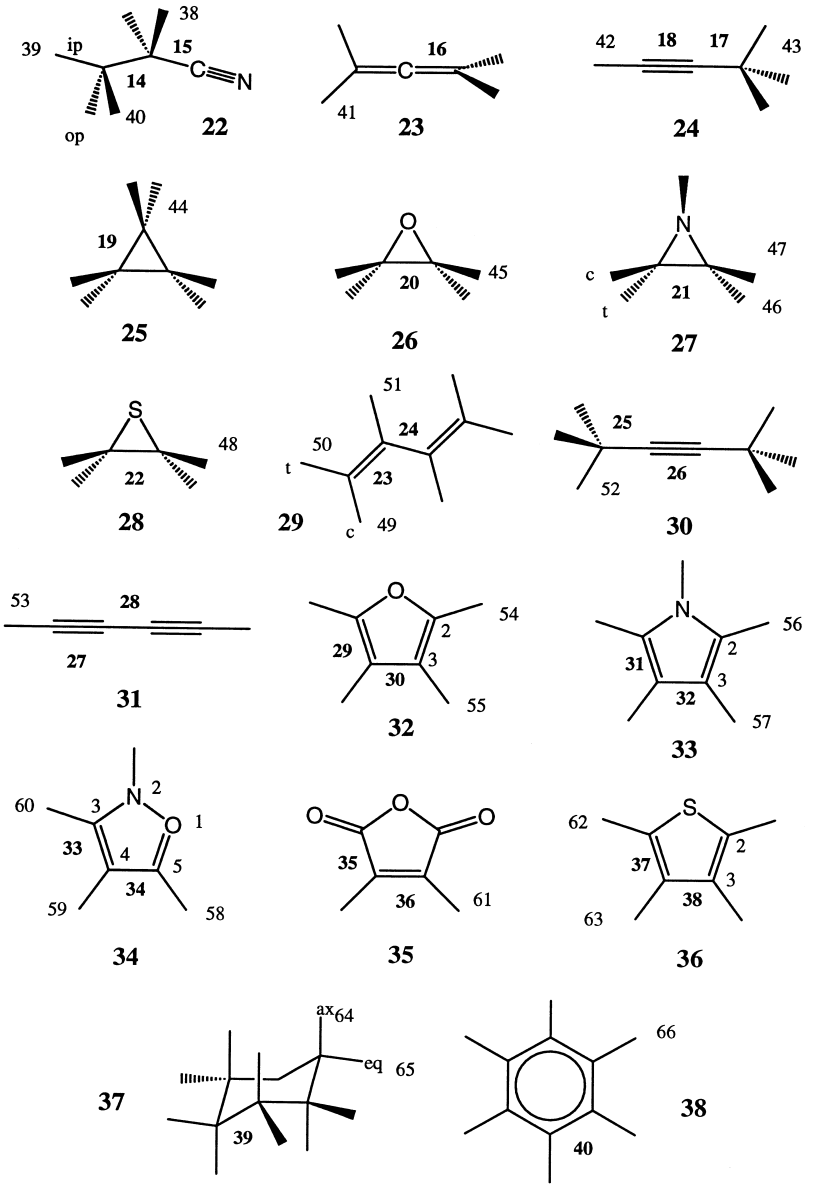


Fig. 1. (*continued*)

2. Theory of adiabatic internal vibrational modes

The basic instrument of vibrational spectroscopy to describe a vibrating molecule in classical terms is the normal mode analysis (NMA) [27–29]. A normal mode $\mathbf{l}_\mu$ expressed in Cartesian coordinate space and associated with a normal coordinate Q_μ ($\mu = 1,\ldots,N_{\text{vib}}$; $N_{\text{vib}} = 3K - L$; K: number of atoms in a molecule; L: number of rotational and translational motions of a molecule) leads to the movement of many or even all atoms of a molecule, i.e. it is a delocalized mode.

$$\mathbf{x} = \mathbf{l}_\mu Q_\mu \tag{1}$$

($\mathbf{x}$: vector of Cartesian displacements with elements x_i, $i = 1,\ldots,3K$). The N_{vib} normal modes $\mathbf{l}_\mu$ of a

Table 1
Comparison of experimentally and theoretically determined properties of CH bonds (B3LYP/6-31G(d,p) calculations)[a]

	Name	Position	r_e	r_0	$\bar{\omega}_\mu$	ω_{BG}	ω_a	ω_{iso}	ν_a^{exp}	ν_a^f	ν_{iso}
1	Methane (**1**)		1.092	1.092	3104	3136	3129	3136	2990	3010	2993
2	Fluromethane (**2**)		1.096		3066	3080	3074	3081	2976	2957	2976
3	Methanol (**3**)	CH_3, ip	1.093		3120	3114	3109	3114	2988	2991	2979
4		CH_3, op	1.101		3009	3015	3004	3015	2897	2890	2921
5	Methylamine (**4**)	CH_3, op	1.104		2964	2972	2959	2971	2818	2846	2880
6		CH_3, op	1.095		3091	3090	3084	3089	2965	2967	2955
7	Chloromethane (**5**)		1.089		3140	3158	3152	3161	3000	3032	3012
8	Methylsilane (**6**)		1.094		3092	3109	3098	3108	2947	2980	2957
9	Formaldehyde (**7**)		1.110		2926	2925	2923	2927	2811	2812	
10	Methyleneimine (**8**)	*cis*	1.099		3026	3040	3038	3044	2937	2923	2936
11		*trans*	1.094		3130	3114	3114	3117	3018	2995	3018
12	Hydrogen cyanide (**9**)		1.069		3475	3408	3404	3475	3241	3274	3312
13	Ethane (**10**)		1.095	1.096	3077	3090	3085	3090	2956	2967	2950
14	Fluroethane (**11**)	CH_2F	1.097		3052	3054	3049	3054	2954	2933	2950
15		CH_3, ip	1.095		3089	3098	3092	3098	2974	2974	2957
16		CH_3, op	1.094		3105	3110	3105	3110	2982	2987	2973
17	Acetaldehyde (**12**)	CHO	1.114		2884	2884	2878	2884	2817	2769	2751
18		CH_3, ip	1.091	1.091	3162	3144	3141	3145	2990	3021	3002
19		CH_3, op	1.097	1.097	3068	3081	3064	3080	2936	2948	2945
20	Acetic acid (**13**)	CH_3, ip	1.089		3186	3167	3164	3169	3031	3044	
21		CH_3, op	1.094		3100	3113	3086	3113	2962	2969	
22	Methylnitrile (**14**)		1.093		3100	3116	3110	3115	2988	2991	2985
23	Ethene (**15**)		1.087	1.085	3193	3190	3188	3195	3052	3067	3053
24	Chloroethene (**16**)	*ipso*	1.084		3229	3223	3222	3230	3079	3100	3082
25		*trans*	1.085		3220	3210	3208	3216	3070	3086	3072
26		*cis*	1.084		3220	3225	3223	3231	3083	3100	3074
27	Ketene (**17**)		1.082		3251	3250	3241	3255	3109	3118	
28	Ethyne (**18**)		1.066	1.060	3487	3439	3437	3492	3283	3307	3336
29	Propane (**19**)	CH_3, ip	1.095	1.096	3072	3090	3085	3090	2956	2968	2950
30		CH_3, op	1.096	1.098	3069	3080	3074	3079	2949	2957	2936
31		CH_2	1.098	1.099	3045	3050	3047	3050	2927	2931	2918
32	Dimethylketone (**20**)	CH_3, ip	1.091		3165	3149	3145	3150	3005	3025	3004
33		CH_3, op	1.096		3074	3086	3052	3085	2944	2936	2946
34	2-propenal (**21**)	*trans*	1.085		3200	3212	3211	3219	3065	3089	
35		*cis*	1.088		3200	3181	3179	3186	3029	3058	
36		*ipso*	1.087		3193	3188	3188	3194	3025	3067	
37		CHO	1.114		2888	2887	2882	2888	2794	2772	
38	Ethylnitrile (**22**)	CH_2	1.096		3073	3076	3071	3075	2874	2954	2952
39		CH_3, ip	1.093		3103	3115	3110	3115	2996	2992	2974
40		CH_3, op	1.093		3117	3120	3115	3120	2992	2997	2974
41	Allene (**23**)		1.087	1.086	3166	3177	3174	3181	3044	3053	3049
42	Propyne (**24**)	CH	1.065	1.060	3492	3443	3442	3492	3286	3311	3334
43		CH_3	1.095	1.095	3072	3085	3079	3084	2974	2962	2958
44	Cyclopropane (**25**)		1.086	1.085	3185	3181	3180	3185	3056	3059	3056
45	Oxirane (**26**)		1.090		3136	3135	3129	3140	3028	3010	
46	Aziridine (**27**)	*trans*	1.087		3158	3164	3161	3169	3046	3041	
47		*cis*	1.088		3158	3148	3144	3152	3032	3025	
48	Thiirane (**28**)		1.086		3184	3182	3178	3187	3048	3058	
49	*trans*-butadiene (**29**)	CH_2, *trans*	1.085		3215	3208	3207	3214	3058	3085	
50		CH_2, *cis*	1.087		3201	3186	3183	3190	3041	3062	
51		CH	1.090		3151	3147	3147	3151	3000	3027	
52	2-butyne (**30**)		1.096	1.096	3063	3076	3070	3075	2952	2953	2950

Table 1 (*continued*)

	Name	Position	r_e	r_0	$\bar{\omega}_\mu$	ω_{BG}	ω_a	ω_{iso}	ν_a^{exp}	ν_a^f	ν_{iso}
53	1,3-butadiyne (**31**)		1.065		3490	3445	3443	3490	3266	3312	
54	Furan (**32**)	C(2)H	1.079		3297	3283	3285	3293	3147	3160	
55		C(3)H	1.080		3265	3260	3261	3269	3130	3137	
56	Pyrrole (**33**)	C(1)H	1.080		3278	3264	3266	3273	3125	3142	
57		C(2)H	1.081		3253	3250	3252	3259	3109	3128	
58	Isoxazole (**34**)	C(5)H	1.080		3288	3271	3273	3282	3127	3148	
59		C(4)H	1.079		3288	3282	3284	3293	3142	3159	
60		C(3)H	1.082		3253	3246	3248	3255	3082	3125	
61	Maleic anhydride (**35**)		1.082		3267	3256	3258	3267	3109	3134	
62	Thiophene (**36**)	C(2)H	1.081		3268	3259	3260	3266	3119	3136	
63		C(3)H	1.084		3221	3217	3218	3223	3089	3096	
64	Cyclohexane (**37**)	ax	1.100		3016	3030	3025	3029	2878	2910	2891
65		eq	1.097		3067	3058	3055	3058	2920	2939	2923
66	Benzene (**38**)		1.086	1.084	3189	3184	3186	3189	3055	3065	3065

[a] Equilibrium bond lengths r_e and spectroscopically determined bond lengths r_0 in Å, calculated averaged harmonic normal mode frequencies $\bar{\omega}_\mu$, harmonic intrinsic frequencies of Boatz and Gordon [52] ω_{BG}, calculated harmonic adiabatic internal coordinate frequencies ω_a, calculated harmonic isolated stretching frequencies ω_{iso}, experimental adiabatic internal coordinate frequencies ν_a^{exp}, scaled harmonic adiabatic internal coordinate frequencies ν_a^f, and experimental isolated stretching frequencies ν_{iso} in cm^{-1}. r_0 and ν_{iso} values from Refs. [10–17]. The following notation is used to distinguish H atoms of a CH_n group: ip: in-plane; op: out-of-plane; ax: axial; eq: equatorial; c: *cis*; t: *trans*.

molecule are obtained by solving Eq. (2)

$$\mathbf{fL} = \mathbf{ML\Lambda} \tag{2}$$

where **f** is the force constant matrix in Cartesian coordinate space, **M** the mass matrix with elements m_i ($i = 1,\ldots,3K$). **L** covers the column vectors $\mathbf{l}_\mu$ with elements $L_{i\mu}$($i = 1,\ldots,3K$) and matrix $\mathbf{\Lambda}$ collects the squares of the normal mode frequencies ω_μ on its diagonal. Eq. (2) can be rewritten for internal coordinate space spanned by the internal coordinates **q**:

$$\mathbf{FD} = \mathbf{G}^{-1}\mathbf{D\Lambda} \tag{3}$$

where **F** is the force constant matrix in this space, matrix **D** contains normal mode vectors $\mathbf{d}_\mu$ in internal coordinate space, and the Wilson **G** matrix is given by $\mathbf{BM}^{-1}\mathbf{B}^\dagger$ where $\mathbf{B} = \partial\mathbf{q}/\partial\mathbf{x}$. A normal mode vector $\mathbf{d}_\mu$ can be transformed to Cartesian coordinate space according to Eq. (4):

$$\mathbf{l}_\mu = \mathbf{Cd}_\mu. \tag{4}$$

One might think that localized internal mode vectors $\mathbf{v}_m$ can be obtained from the normal modes by simply assuming that $(\mathbf{d}_\mu)_m = D_{\mu m} = \delta_{\mu m}$ ($\delta_{\mu m}$: Kronecker delta) since this would lead to $\mathbf{l}_\mu = \mathbf{c}_m$ for $\mu = m$ where each $\mathbf{v}_m = \mathbf{c}_m$ would be associated with a particular internal coordinate q_m. However, even if there is no electronic coupling between displacement vectors $\mathbf{c}_m$ and $\mathbf{c}_n$ (reflected by a diagonal force constant matrix) there will be always mass coupling between these vectors because the **G** matrix of Eq. (3) is non-diagonal, which implies that $D_{\mu m} \neq \delta_{\mu m}$ and $\mathbf{l}_\mu \neq \mathbf{c}_m$. Mass coupling between different internal modes can be avoided by assuming that all masses but the ones which belong to the atoms of a particular molecular fragment ϕ_m are zero. This assumption is equivalent to requiring that the internal parameter q_m of fragment ϕ_m is associated with the generalized momentum $p_m = 0$. With this assumption, the Euler–Lagrange equations of a vibrating molecule take a specific form, which leads directly to the AIMs. [21–24] Alternatively, AIMs can be explained by considering the potential energy of a vibrating molecule. A vibration may be initiated by a change of an internal coordinate associated with molecular fragment ϕ_m from value q_m to q^*_m which will lead to a displacement of the atoms of the molecule. If one relaxes the positions of all atoms but those of fragment ϕ_m so that the molecular energy attains a minimum, the motion caused by the change $q_m \rightarrow q^*_m$ (infinitesimal geometrical perturbation) will be localized in ϕ_m and will represent an AIM. Internal coordinate q_m ''leads'' the AIM (*leading parameter principle*), [21–24] which can

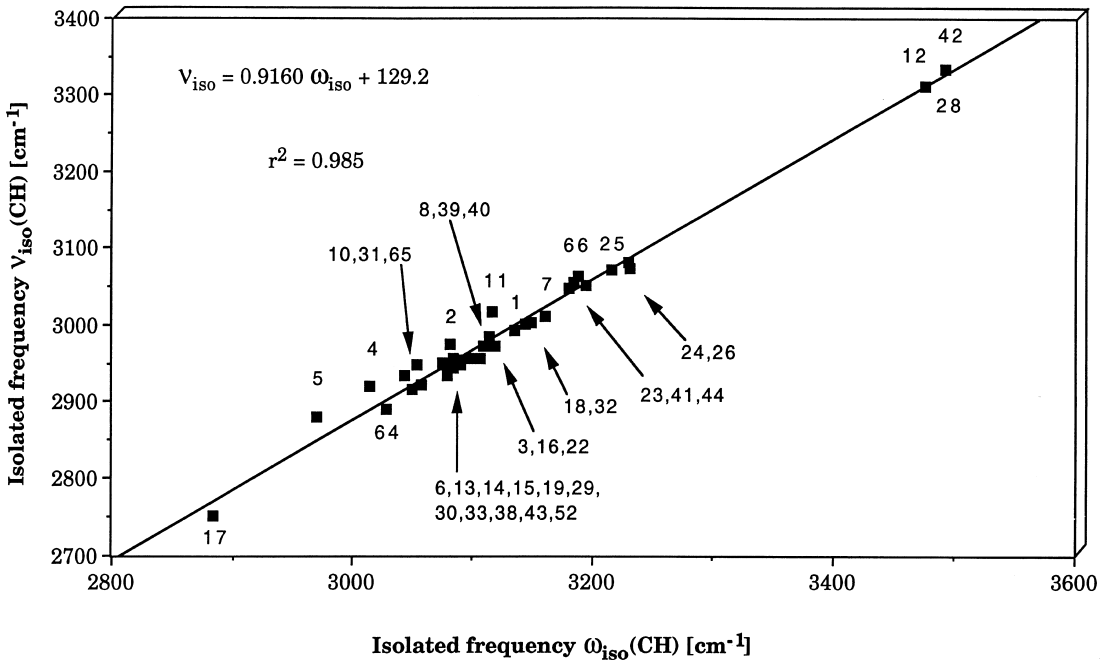


Fig. 2. Comparison of experimental isolated CH stretching frequencies $\nu_{iso}(CH)$ with calculated isolated CH stretching frequencies $\omega_{iso}(CH)$ (B3LYP/6-31G(d,p) calculations). Numbers identify CH bonds listed in Table 1.

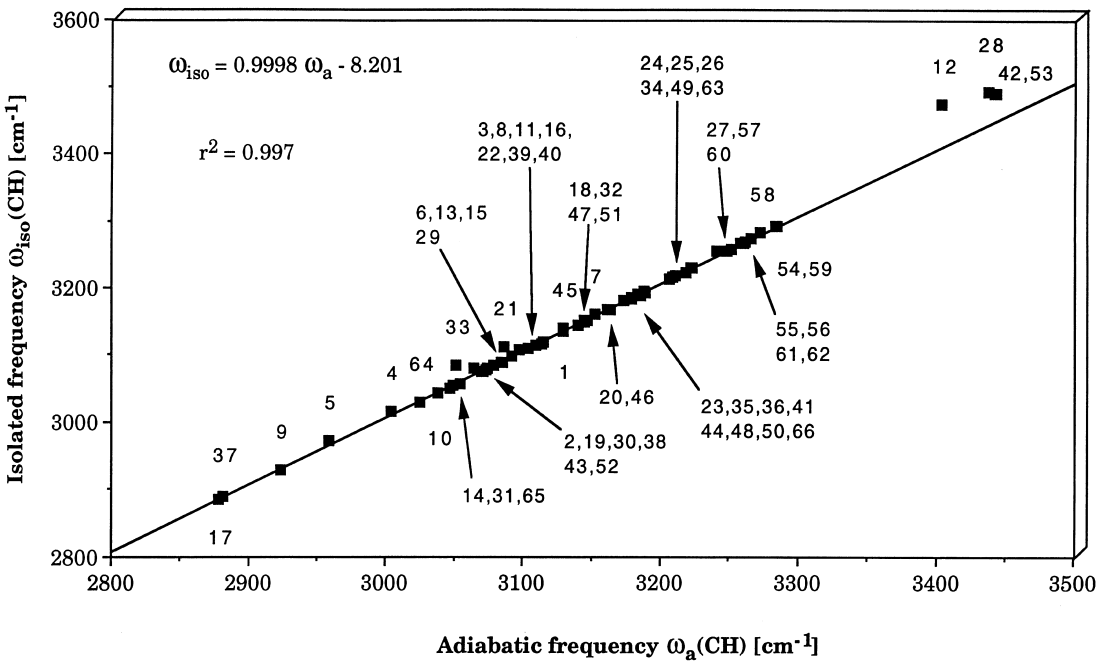


Fig. 3. Comparison of calculated isolated CH stretching frequencies $\omega_{iso}(CH)$ with calculated adiabatic CH stretching frequencies ω_a(CH) (B3LYP/6-31G(d,p) calculations). Numbers identify CH bonds listed in Table 1. Alkyne CH bonds, ≡CH, are not included into the linear regression analysis.

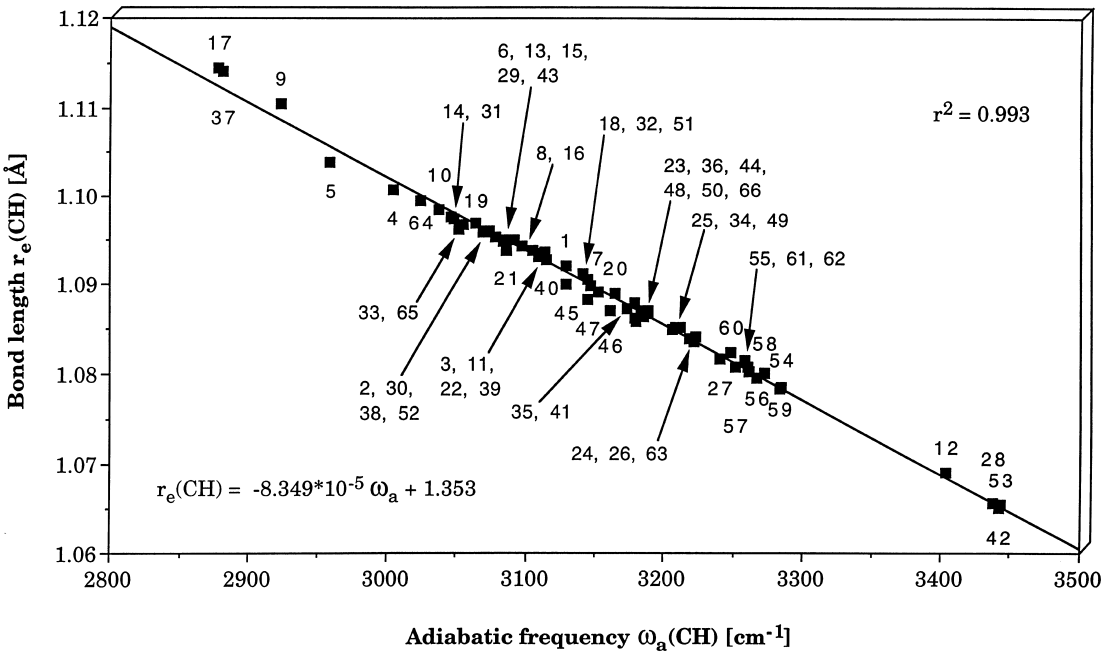


Fig. 4. Bond lengths $r_e(CH)$ given as a function of adiabatic CH stretching frequencies $\omega_a(CH)$ (B3LYP/6-31G(d,p) calculations). Numbers identify CH bonds listed in Table 1.

be calculated by carrying out a minimization of the potential energy Eq. (5a) with the constraint (5b):

$$V(\mathbf{Q}) = \min \tag{5a}$$

$$q_m = \text{const.} = q^*_m. \tag{5b}$$

Condition (5b) can be imposed on minimization (5a) with the help of a Lagrange multiplier λ

$$\frac{\partial}{\partial Q_u}[V(\mathbf{Q}) - \lambda(q_m(\mathbf{Q}) - q^*_m)] = 0. \tag{6}$$

In the harmonic approximation, which is normally used in quantum chemical calculations of vibrational spectra, the potential energy of a molecule at its equilibrium geometry is given by [27–29]:

$$V(\mathbf{Q}) = \frac{1}{2}\sum_{\mu=1}^{N_{\text{vib}}} k_\mu Q_\mu^2 \tag{7}$$

where vector $\mathbf{Q}$ contains the $3K - L$ normal coordinates Q_μ and k_μ is the reduced force constant of normal mode μ as obtained in the normal mode analysis. The internal coordinates can be expressed in terms of normal coordinates [27–29]:

$$q_m(\mathbf{Q}) = \sum_{\mu=1}^{N_{\text{vib}}} D_{m\mu} Q_\mu. \tag{8}$$

The solution for $q_m(\mathbf{Q}) = q^*_m$ Eq. (5b) is denoted $Q_\mu^{(m)}$ and is given by Eq. (9):

$$Q_\mu^{(m)} = \frac{D_{m\mu}}{k_\mu}\lambda. \tag{9}$$

Inserting (9) into (8), constraint (5b) leads to an expression for Lagrange multiplier λ in dependence of q^*_m

$$\lambda = \frac{1}{\sum_{\mu=1}^{N_{\text{vib}}} (D_{m\mu}^2/k_\mu)} q^*_m \tag{10}$$

which in turn can be used to obtain $Q_\mu^{(m)}$ in dependence of q^*_m:

$$Q_\mu^{(m)} = Q_{\mu m}^0 q^*_m \tag{11}$$

Table 2
Determination of CH bond properties with the help of CH bond stretching frequencies

	Ref.	Linear relationship	r^2	Accuracy [Å]
(**1**)	McKean[a]	$r_e(CH) = 1.335 - 0.0000809\nu_{iso}(CH)$	0.980	$\pm$ 0.001_1
(**2**)	This work	$r_e(CH) = 1.353 - 0.0000835\omega_a(CH)$	0.993	$\pm$ 0.000_6
(**3**)	This work	$r_e(CH) = 1.368 - 0.0000923\nu_a^{exp}(CH)$	0.967	$\pm$ 0.001_1
(**4**)	McKean[b,c]	$D_0(T) = 0.08700\nu_{iso}(CH) - 156.1$	0.996	
(**5**)	This work[c]	$D_0(T) = 0.09458\nu_a^{exp}(CH) - 177.7$	1.000	
(**6**)	This work[c]	$D_0(T) = 0.08166\omega_a(CH) - 149.1$	0.994	
(**7**)	This work	$D_e^{ideal} = 0.09497\nu_a^{exp}(CH) - 171.6$	0.999	
(**8**)	This work	$D_e^{ideal} = 0.08768\omega_a(CH) - 161.2$	1.000	

[a] Here r_e values from B3LYP calculations. Calculated values were taken with an accuracy of 10^{-4} Å (see Supporting Information) and after correlation with frequencies results were rounded to reproduce an accuracy of 10^{-3} Å. In Ref. [10], a linear relationship between r_0(CH) and ν_{iso}(CH) is given for a restricted range between 2800 and 3050 cm^{-1}: $r_0(CH) = 1.402 - 0.0001035\nu_{iso}(CH)$, which leads to an accuracy of $\pm$ 0.0005 Å provided certain problem cases are excluded.

[b] Obtained with the same reference compounds as used in this work. In Ref. [10], the equation: $D_0(T) = 0.08616\nu_{iso}$ (CH) − 154.6 is given for the range 2700 and 3100 cm^{-1}.

[c] Here T corresponds to room temperature. For the equations involving $D_0(T)$ the CH molecule is added to the set of reference molecules.

with

$$Q^0_{\mu m} = \frac{D_{m\mu}/k_\mu}{\sum_{\nu=1}^{N_{Vib}} (D^2_{m\nu}/k_\nu)}. \tag{12}$$

According to Eq. (11), internal coordinate q^*_m determines a movement of the atoms of the molecule along the AIM vector $\mathbf{a}_m$:

$$(\mathbf{a}_m)_\mu = Q^0_{m\mu} \tag{13}$$

given by the normal coordinate specific constants $Q^0_{m\mu}$. One can express AIM vectors in the space of Cartesian displacements by using the transformation:

$$(\mathbf{a}_m)_i = \sum_{\mu=1}^{N_{vib}} L_{i\mu}(\mathbf{a}_m)_\mu \qquad i = 1,\ldots,3K. \tag{14}$$

Once AIMs are defined it is straightforward to determine their force constants k_a, the internal mass m_a of fragment ϕ_m and by this also the AIM frequencies ω_a.

$$k_a = \mathbf{a}_m^\dagger \mathbf{f} \mathbf{a}_m \tag{15}$$

$$m_a = \frac{1}{\mathbf{b}_m^\dagger \mathbf{M}^{-1} \mathbf{b}_m} = \frac{1}{G_{mm}} \tag{16}$$

$$\omega_a^2 = \mathbf{a}_m^\dagger \mathbf{f} \mathbf{a}_m G_{mm} = k_a G_{mm} \tag{17}$$

where $\mathbf{b}_m$ is a column vector of the **B** matrix, G_{mm} an element of the **G** matrix, and m_a represents a generalized reduced mass. Since the AIMs are based on a dynamic principle (the leading parameter principle) [21–24] and are obtained directly from a modified form of the Euler–Lagrange equations, they comply with the total symmetry of the molecule and they are independent of the set of internal parameters used to describe a molecule, i.e. AIMs are perfectly suited to represent the local modes of a molecule.

Force constant and frequency of an AIM characterize the electronic properties of the corresponding molecular fragment. In particular, one can describe with the AIM stretching force constant the properties of a bond, with the AIM bending force constant bond–bond interactions in a fragment X–A–Y or with the AIM torsional force constant electronic interactions in a four-atom fragment. One might argue that this is also accomplished by using, for example, the quantum chemically calculated valence bond stretching force constants given by the diagonal elements of the force constant matrix in internal coordinate space. These force constants are associated with the **c**-vectors of the normal mode analysis [21]. Konkoli and coworkers [22] showed that **c**-vectors possess an unphysical form and are not necessarily localized in a particular molecular fragment. This has to do with the fact that they, contrary to the adiabatic modes, are not based on a dynamic principle. Furthermore, **c**-vectors depend on the set of internal coordinates chosen to describe the molecule, which is particularly problematic for cyclic molecules. Hence, **c**-vectors and the

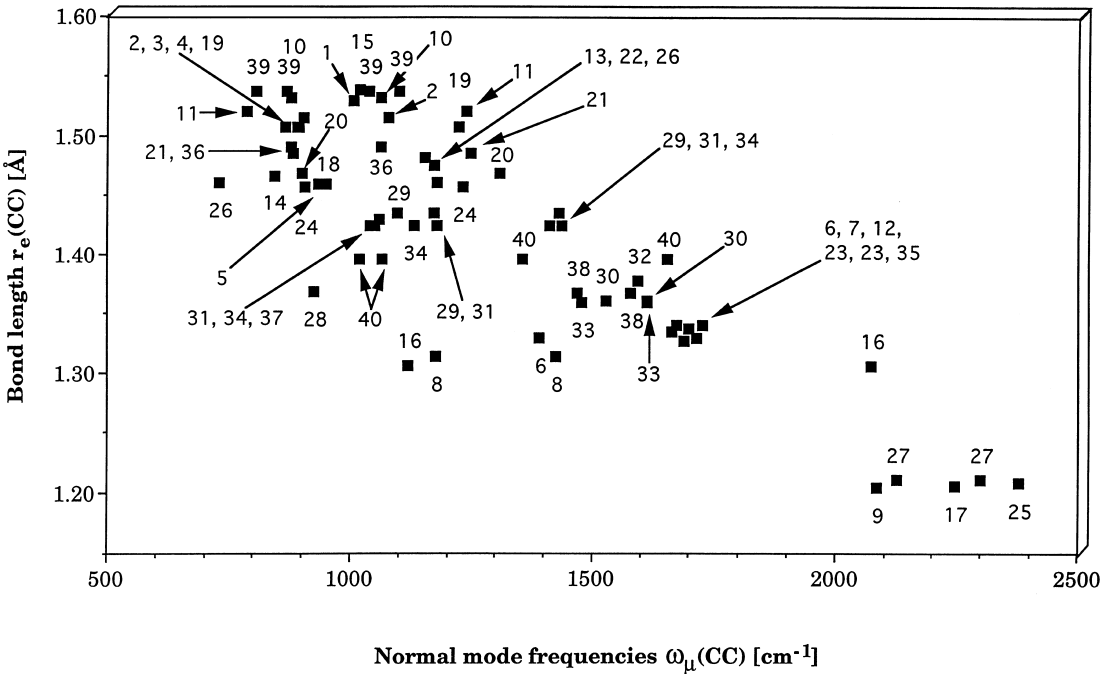


Fig. 5. Bond lengths $r_e(CC)$ given in dependence of normal mode CC stretching frequencies $\omega_\mu(CC)$ (B3LYP/6-31G(d,p) calculations). Numbers identify CC bonds listed in Table 3.

corresponding force constants do not lead to physically or chemically reliable description of internal modes and cannot be recommended for an investigation of molecular properties [22].

It is important to stress that the adiabatic modes can also be defined if a more realistic potential $V(\mathbf{Q})$ is used rather than the harmonic approximation of Eq. (7). However, the calculational cost for such an approach are excessive and, therefore, it is better to revert to an approach which leads to experimental AIM frequencies directly derived from experimental normal mode frequencies. For this purpose, one assumes that the normal mode vectors $\mathbf{d}_\mu$ obtained from Eq. (4) using the harmonic approximation represent a reasonable approximation to the true normal mode vectors $\mathbf{d}'_\mu$ so that $\mathbf{D} \approx \mathbf{D}'$ [29–32]. This assumption makes some sense in view of the fact that experimental frequencies can be predicted from calculated harmonic frequencies by simple scaling procedures [33–37]. The experimental frequencies differ from the harmonic frequencies by increments $\Delta\omega_\mu$. Hence, the eigenvalue matrix $\mathbf{\Lambda}$ of Eq. (3) can be corrected by a matrix $\Delta\mathbf{\Lambda} = \{\Delta\omega_\mu^2\}$, which leads to a new eigenvalue Eq. (18) and a new force constant matrix $\mathbf{F} + \Delta\mathbf{F}$ given by

$$(\mathbf{F} + \Delta\mathbf{F})\mathbf{D} = \mathbf{G}^{-1}\mathbf{D}(\mathbf{\Lambda} + \mathbf{\Delta\Lambda}). \quad (18)$$

The new force constant matrix is used to determine experimentally based AIM force constants k_a^{exp} and AIM vibrational frequencies ν_a^{exp}.

3. Computational methods

Hartree–Fock (HF) calculations using the 6-31G(d,p) basis set [38] were carried out to determine equilibrium geometries and vibrational frequencies of molecules **1**–**38** shown in Fig. 1. Utilizing Eqs. 12–17 adiabatic force constants and vibrational frequencies where determined with the program ADIA, which is a part of COLOGNE96 [39]. AIMs were checked by verifying localization with a dynamic visualization program being a part of COLOGNE96.

In the second step of the investigation, calculations were repeated with density functional theory (DFT) using Becke's three parameter functional B3LYP

Table 3
Comparison of CC bond properties calculated at the B3LYP/6-31G(d,p) level of theory[a]

	Molecule	CC bond	r_e	$\tilde{\omega}_\mu$	ω_{BG}	ω_a	ν_a^{exp}
1	Ethane (**10**)		1.530	1006	1025	1083	1068
2	Fluroethane (**11**)		1.516	990	1041	1099	1069
3	Acetaldehyde (**12**)		1.507	889	1007	1074	1086
4	Acetic acid (**13**)		1.507	866	1023	1098	1083
5	Methylnitrile (**14**)		1.460	934	1170	1202	1178
6	Ethene (**15**)		1.330	1552	1647	1674	1594
7	Chloroethene (**16**)		1.327	1688	1641	1666	1596
8	Ketene (**17**)		1.314	1300	1627	1666	1597
9	Ethyne (**18**)		1.205	2086	2239	2234	2115
10	Propane (**19**)		1.532	970	1011	1072	1059
11	Dimethylketone (**20**)		1.520	1011	971	1044	1032
12	2-propenal (**21**)	Double	1.337	1698	1599	1631	1569
13		Single	1.475	1174	1066	1138	1116
14	Ethylnitrile (**22**)	H_2C–CN	1.466	844	1134	1169	1151
15		H_3C–CH_2	1.539	1018	993	1053	1037
16	Allene (**23**)		1.306	1596	1704	1729	1645
17	Propyne (**24**)	Triple	1.207	2247	2215	2216	2119
18		Single	1.459	949	1186	1219	1190
19	Cyclopropane (**25**)		1.508	1058	1052	1082	1049
20	Oxirane (**26**)		1.469	1105	1198	1230	1194
21	Aziridine (**27**)		1.485	1064	1138	1162	1078
22	Thiirane (**28**)		1.481	1155	1124	1136	1098
23	*trans*-butadiene (**29**)	Double	1.340	1700	1588	1622	1550
24		Single	1.457	1070	1145	1207	1176
25	2-butyne (**30**)	Triple	1.209	2378	2196	2202	2091
26		Single	1.461	954	1185	1218	1193
27	1,3-butadiyne (**31**)	Triple	1.212	2213	2157	2172	2061
28		Single	1.369	925	1414	1474	1395
29	Furane (**32**)	C3–C4	1.435	1233	1222	1255	1218
30		C2–C3	1.361	1571	1480	1507	1461
31	Pyrrole (**33**)	C3–C4	1.425	1220	1250	1282	1288
32		C2–C3	1.378	1595	1416	1444	1404
33	Isoxazole (**34**)	C3–C4	1.360	1546	1526	1506	1476
34		C4–C5	1.424	1199	1245	1281	1277
35	Maleic anhydride (**35**)	C3–C4	1.335	1665	1611	1636	1570
36		C2–C3	1.491	970	1047	1099	1079
37	Thiophene (**36**)	C3–C4	1.430	1059	1232	1269	1231
38		C2–C3	1.367	1523	1449	1472	1414
39	Cyclohexane (**37**)		1.537	953	983	1053	1038
40	Benzene (**38**)		1.396	1274	1322	1366	1326

[a] Bond lengths in Å, frequencies in cm^{-1}. For an explanation of symbols, see Text and Table 1.

[40,41] and the 6-31G(d,p) basis where these calculations were carried out with GAUSSIAN94 [42]. B3LYP covers a relatively large amount of correlation corrections and is known to lead to reliable geometries and vibrational frequencies, often of the quality of MP2 or even CCSD(T) results. Accordingly, B3LYP/6-31G(d,p) results were used to solve Eq. (18) and to determine experimental AIM frequencies. For this purpose, the appropriate sets of experimental frequencies were taken from the literature [43–45].

Calculations used standard convergence criteria for SCF and geometry optimization (convergence threshold for the changes in the density matrix:10^{-8}; convergence thresholds for rms changes in the force and the displacement vectors: 3×10^{-4} and 1.2×10^{-3}). For the DFT calculations, the standard pruned

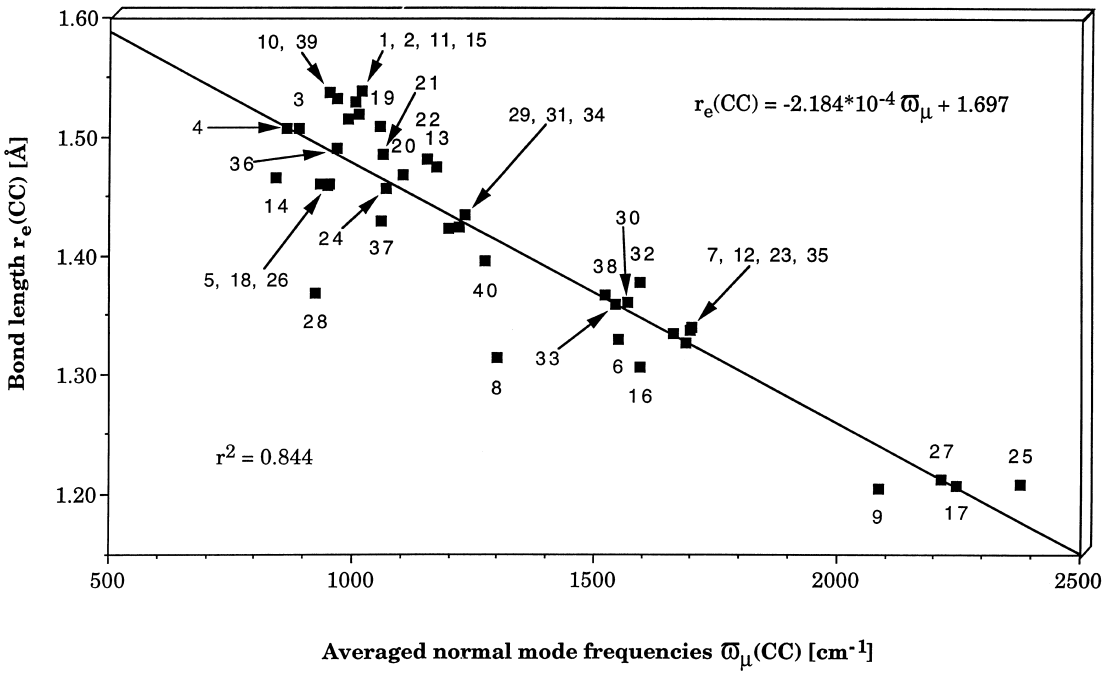


Fig. 6. Bond lengths $r_e(CC)$ given in dependence of averaged normal mode CC stretching frequencies $\bar{\omega}_\mu$(CC) (B3LYP/6-31G(d,p) calculations). Numbers identify CC bonds listed in Table 3.

(75,302) fine grid was used, which is a reasonable compromise between calculational time and accuracy. We also performed test calculations with a tighter convergence criterion for the geometry optimization (convergence thresholds for rms changes in the forces and the displacement vectors: 1×10^{-5} and 4×10^{-5}) and found that calculated geometries and frequencies differed by maximally 10^{-4} Å (bond lengths), 0.01° (bond angles), and 2 cm^{-1} (see examples in the Supporting Information) from the corresponding parameters calculated with the less stringent convergence criteria. We considered the latter criterion sufficient for the present work and used it throughout all calculations.

Isolated stretching frequencies ω_{iso} (CH) were calculated by determining CH stretching frequencies for these isotopomers, in which all H atoms but the target H are replaced by D atoms. These frequencies

Table 4
Comparison of B3LYP and HF results obtained with the 6-31G(d, p) basis

Frequency	Bond property	Number of points	B3LYP r^2	HF r^2
ω_a(CH)	r_e(CH)	66	0.993	0.992
ν_a^{exp}(*CH*)	r_e(CH)	66	0.967	0.976
ω_a(CC)	r_e(CC)	40	0.991	0.995
ν_a^{exp}(CC)	r_e(CC)	40	0.990	0.993
$\bar{\omega}_\mu$(CC)	r_e(CC)	40	0.844	0.898
ω_a(CH)	D_0(*T*, CH)	24	0.994[a]	0.981[a]
ν_a^{exp}(CH)	D_0(*T*, CH)	24	1.000[a]	1.000[a]
ω_a(CH)	ν_{iso}(CH)	40	0.976	0.972
ν_a^{exp}(CH)	ν_{iso}(CH)	40	0.953	0.966

[a] The linear regression is based on data points 1, 9, 23, 28, 66 and the CH molecule. For an explanation of symbols, see Text and Table 1.

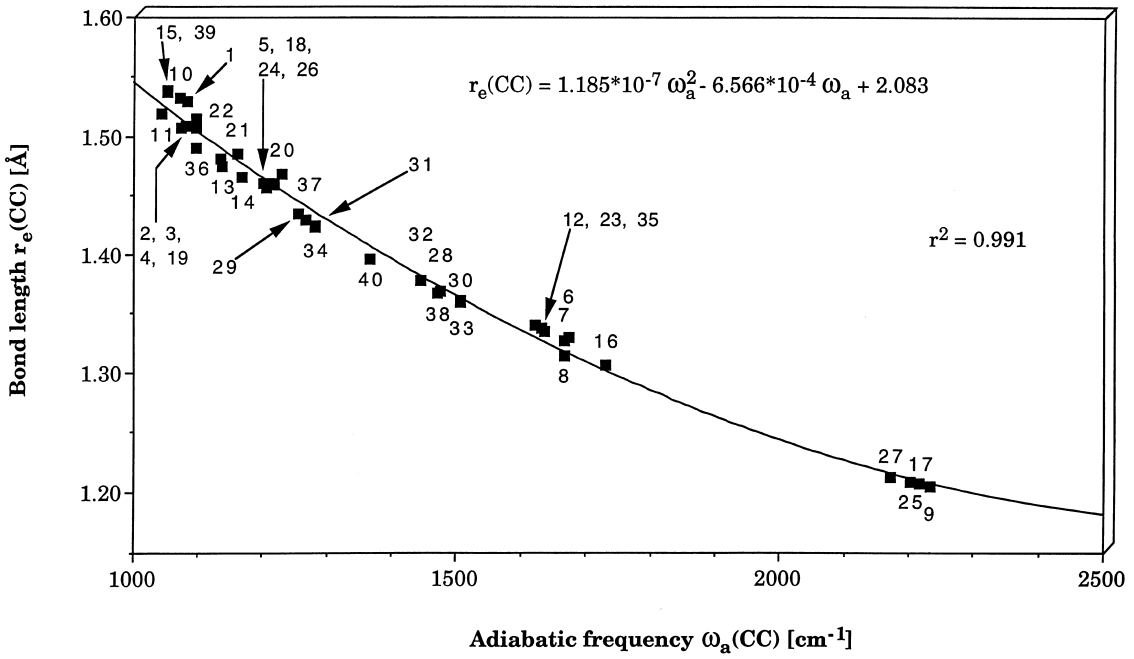


Fig. 7. Bond lengths $r_e(CC)$ given in dependence of adiabatic CC stretching frequencies $\omega_a(CC)$ (B3LYP/6-31G(d,p) calculations). Numbers identify CC bonds listed in Table 3.

Table 5
Comparison of the properties of standard CH and standard CC bonds (B3LYP/6-31G(d, p) calculations)[a]

Bonds	Molecule	r_e	ω_a	ν_a^{exp}
CH bonds				
C–H	CH	1.113	2792	2734
$C(sp^3)$– H	$H_3C–CH_3$	1.095	3085	2956
$C(sp^2)$– H	$H_2C=CH_2$	1.087	3188	3052
$C(sp^2)$– H	c-C_3H_6	1.086	3180	3056
$C(sp^2)$– H	c-C_6H_6	1.086	3186	3055
C(sp)– H	HC≡CH	1.066	3437	3283
CC bonds				
$C(sp^3)$– $C(sp^3)$	$H_3C–CH_3$	1.530	1083	1068
$C(sp^2)$– $C(sp^2)$	$H_2C=CH–CH=CH_2$	1.457	1207	1176
C(sp)– C(sp)	HC≡C–C ≡ CH	1.369	1474	1395
$C(sp^2)$=$C(sp^2)$	$H_2C=CH_2$	1.330	1674	1594
C(sp)≡C(sp)	HC≡CH	1.205	2234	2115
$C(sp^2)\cdots C(sp^2)$	c-C_6H_6	1.396	1366	1326
$C(sp^n)$– $C(sp^n)$	c-C_3H_6	1.508	1082	1049

[a] Bond lengths in Å, frequencies in cm^{-1}. For cyclopropane, sp^2 hybridization is assumed for the CH bonds, while hybridization is not specified for the CC bonds.

can be used to check on the accuracy of experimentally determined isolated CH stretching frequencies. We will distinguish between experimental and calculated frequencies using symbols ν and ω (harmonic) where approximations to experimental frequencies obtained after scaling or the procedure given by Eq. (18) will be denoted as ν^f, ν^{exp}, etc. For example, there will be three sets of isolated CH stretching frequencies to be discussed, namely experimentally determined values ν_{iso}, calculated harmonic values ω_{iso}, and scaled calculated values ν_{iso}^f. Subscripts μ, aν, and a will denote normal (ω_μ), averaged normal ($\omega_{\mu,av} = \overline{\omega}_\mu$), and adiabatic frequencies (ω_a).

4. Comparison of isolated and AIM frequencies

In Table 1, calculated and experimental CH bond properties are compared: B3LYP/6-31G(d,p) CH bond lengths r_e, experimentally determined CH bond lengths r_0 taken from McKean's work [10], AIM frequencies ω_a calculated at B3LYP/6-31G(d,p) and experimentally corrected AIM frequencies ν_a^{exp}.

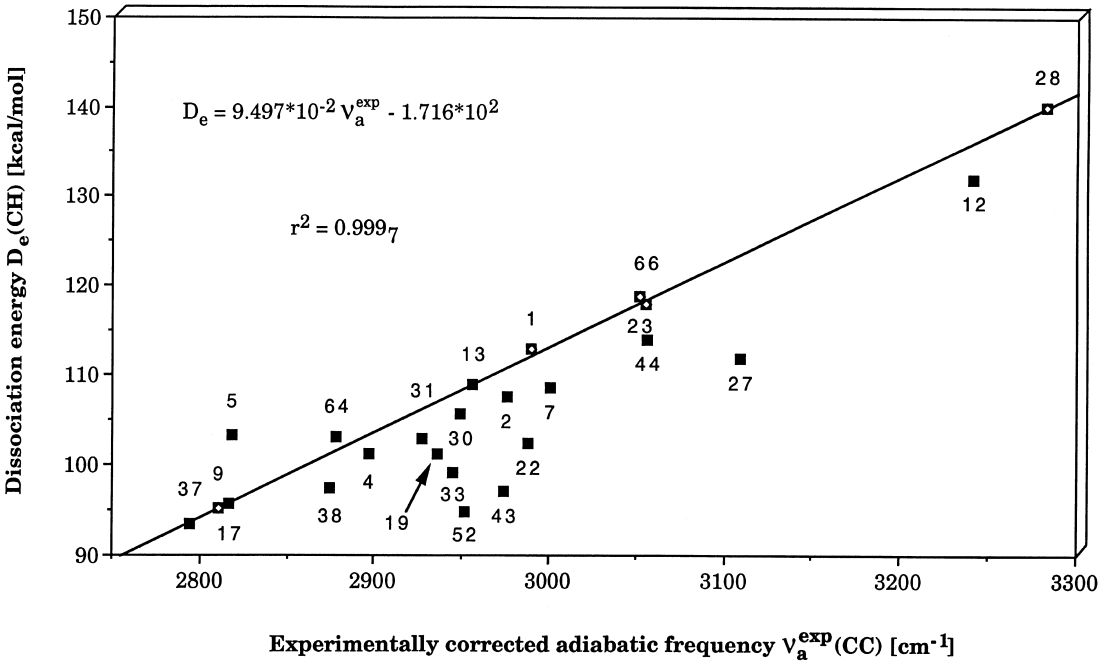


Fig. 8. Dissociation energies D_e(CH) given in dependence of the experimentally based adiabatic CH stretching frequencies ν_a^{exp}(CH) (B3LYP/6-31G(d,p) calculations). Numbers identify CH bonds listed in Table 6. The five reference points 1, 9, 23, 28, and 66 determine the linear relationship between $D_e(CH)^{ideal}$ and ν_a^{exp}(CH).

Calculated energies and geometries of molecules **1**–**38** are given in the Supporting Information.

In total, 66 different CH bonds (Fig. 1) were investigated in this work where the whole range from relatively strong CH bonds as in alkynes (≡C–H: bond length 1.060 Å; AIM frequency 3283 cm^{-1}) to relatively weak CH bonds as in aldehydes (O=C–H: bond length 1.110 Å; AIM frequency 2811 cm^{-1}, Table 1) was covered. The molecules investigated comprise alkanes, alkenes, alkynes, alcohols, amines, halogenated hydrocarbons, aldehydes, ketones, acids, cyanides, etc. so that CH bonds in different hybridization states of C and under the impact of different substituents could be investigated. Only those molecules were studied, for which a full set of reliable experimental frequencies is available [43–45] and for which isolated CH stretching frequencies could be measured [10–18].

Calculated CH bond lengths represent equilibrium values r_e, which are not directly comparable with experimentally determined r_0 values. Nevertheless, a correlation of the calculated r_e values with the available r_0 data (Table 1) reveals that both HF and B3LYP theory reproduce trends in CH bond lengths well. B3LYP/6-31G(d,p) CH bond lengths agree within 0.002 Å with the corresponding r_0 values while HF/6-31G(d,p) bond lengths are about 0.010 Å smaller. The only exceptions are the CH bonds in alkynes (#28, #42), which are calculated 0.006 Å too long at the B3LYP/6-31G(d,p) level of theory while the HF/6-31G(d,p) values are 0.003–0.004 Å too short. CCSD(T)/TZ+2P calculations [46] lead to CH bond lengths in these cases close to the experimental r_0 values, which clearly indicates that B3LYP underestimates the strength of the CH bond in alkynes. Apart from these cases, the comparison of calculated and experimental geometries suggests that the B3LYP/6-31G(d,p) geometries are more reliable than the corresponding HF geometries and, therefore, the following discussion will focus on the B3LYP/6-31G(d,p) results.

Calculated and measured isolated CH stretching frequencies are compared in Fig. 2. The two sets of frequencies differ on the average by 134 cm^{-1}, which

simply reflects the fact that calculated frequencies are based on the harmonic approximation. By proper scaling with an average scaling factor of 0.957 this difference can be reduced to 12 cm^{-1}. Clearly, there is a reasonable correlation between experimental and calculated CH stretching frequencies ($r^2 = 0.985$), however the remaining difference after scaling indicates errors in either calculated or experimental frequencies. Although all molecules investigated are standard closed shell molecules, which can reasonably be described by B3LYP, the residual error of 12 cm^{-1} is probably due to deficiencies in the basis and higher order correlation effects not covered by B3LYP. Isolated CH stretching frequencies are considered to be accurate to $\pm$ 5 cm^{-1} as estimated by McKean. [10] More recent studies of Quack [47,48] and Duncan [49,50] suggest that it will be possible to determine isolated CH stretching frequencies with an accuracy of $\pm$ 1 cm^{-1} or better using techniques such as isotope selective overtone spectroscopy.

A correlation of ω_a(CH) and ω_{iso}(CH) (Fig. 3) values reveals a linear relationship between these quantities ($r^2 = 0.976$) suggesting that they are closely related. Actually, the relationship can be improved ($r^2 = 0.997$, Fig. 3) by deleting the three data points corresponding to ≡C–H bonds, which is in line with the fact that in the case of alkynes isolated CH stretching modes still contain considerable residual coupling with the C≡C stretching modes (errors in the theoretical description of the ≡C–H bonds cancel since two calculated quantities are compared). We have also compared experimentally corrected frequencies ν_a^{exp} obtained utilizing Eq. (18) with isolated frequencies ν_{iso}. As is reflected by the data of Table 1, ν_a^{exp}(CH) values and ν_{iso}(CH) values differ on the average by just 16 cm^{-1} where there are just five cases (bonds #5, #12, #17, #28, and #42, Table 1) with differences larger than 30 cm^{-1}. Excluding the latter the mean deviation is just 7 cm^{-1}, which is excellent in view of the approximations and limitations of the quantum chemical calculations and the error probably contained in experimental isolated CH stretching frequencies (5 cm^{-1}). We conclude that the AIM CH stretching frequencies are indeed the theoretical equivalents of the isolated CH stretching frequencies of McKean and that the AIMs, in particular if they are based on experimental data, can play the same role as McKean's isolated stretching frequencies for describing chemical bonds.

In passing we note that even if the length of a CH bond such as #17, #28, and #42 is reasonably described by theory, the assumption $\mathbf{D} = \mathbf{D}'$ of Eq. (18) may not be correct thus leading to inaccurate ν_a^{exp}(CH) values and larger deviations with regard to ν_{iso}(CH) frequencies. Based on the observation that calculated and experimentally determined isolated CH stretching frequencies scale well, we have investigated whether better ν_a^{exp}(CH) can be obtained by using a scaling procedure. Scaling covers errors due to the harmonic approximation but also those caused by deficiencies of method and basis set. It is more efficient when done separately for different types of bonds [33,35] and, therefore, scaling of calculated CH stretching frequencies should lead to reasonable estimates of the true ν_a^{exp}(CH) values. With the help of the available ν_{iso}(CH) values, we calculate scaling factors $0.954 \leq f = \nu_{iso}/\omega_a \leq 0.973$ suggesting an average f_{av} value of 0.961, which is close to what was found when comparing experimental and calculated isolated CH stretching frequencies [33–37]. Using f_{av}, the ν_a^f values of Table 1 were obtained, which differ from ν_{iso}(CH) frequencies on the average by 16 cm^{-1} identical with the deviation found for ν_a^{exp} values. Noteworthy, however, is that the critical CH bonds #5, #12, #17, #28, and #42 are in better agreement with experiment, which simply reflects the fact that scaling covers also some of the method errors while use of Eq. (18) leads to an enhancement of method errors. We conclude that scaling of AIM frequencies represents an alternative for getting frequencies that are directly comparable with isolated stretching frequencies. The local AIMs can be much easier classified than normal modes and, therefore, group-specific scaling should be more efficient for the former than that for the normal modes. Accordingly, it will be interesting to see whether scaling can be improved by a cyclic process leading from calculated ω_μ to ω_a, scaled ν_a^f and back to scaled frequencies $f\omega_\mu = \nu_\mu^f$, which should be in better agreement with measured normal mode frequencies than directly scaled ω_μ values (of course, this cyclic process implies the scaling of the elements of the force constant matrix [51]).

Since AIM and isolated frequencies for CH

stretching modes are closely related, it is obvious that the McKean relationship between CH bond lengths and ν_{iso}(CH) should also hold for AIM frequencies. In Fig. 4, AIM frequencies ω_a are correlated with theoretical CH bond lengths r_e both calculated at the B3LYP/6-31G(d,p) level of theory. There is a high correlation between these two quantities (r^2 = 0.993, Fig. 4) even higher as the one found by McKean. [10,11] The correlation coefficient is somewhat smaller when ν_a^{exp}(CH) values are correlated with r_e (r^2 = 0.967), but use of ν_a^f reinstalls a high correlation coefficient (r^2 = 0.993). Hence, we can confirm McKean's conclusion that CH bond lengths can be predicted with an accuracy of 0.001 Å or better once an isolated or AIM CH stretching frequency is known. This is obvious from a comparison of linear regression data as obtained in McKean's and in our work (see Table 2).

Before we consider the question whether the McKean relationship can be extended to other bonds, we investigate whether other definitions of local mode frequencies may also be used to set up McKean relationships. For example, often one takes the average of symmetric and antisymmetric CH stretching frequencies ω_μ and uses these averaged normal mode values $\overline{\omega}_\mu$ as substitutes for local mode frequencies. Values of $\overline{\omega}_\mu$(CH) (Table 1) differ from AIM frequencies on the average by 10 cm^{-1} and seem to provide also a good basis for the correlation between CH bond lengths and local mode frequencies (r^2 = 0.981). However, we will see in the following that averaging of normal mode frequencies does not lead to useful quantities in general. Boatz and Gordon [52] derived from normal mode frequencies intrinsic frequencies, which can be viewed as internal mode frequencies based on the averaging of the normal mode frequencies [21–24]. The intrinsic CH stretching frequencies ω_{BG} given in Table 1 differ from AIM frequencies on the average just by 4 cm^{-1}. They correlate nicely with r_e(CH) distances (r^2 = 0.994), which confirms that they are useful to describe CH bonds. In contrast, a caveat is necessary since intrinsic frequencies are frequencies without a vibrational mode, which simply results from the fact that they are a mathematical construction and have not been derived from a dynamic principle as in the case of the AIMs [21]. Their deficiencies have been described and it has been concluded that in general they are not suitable to represent the local internal modes of a molecule [22].

5. Extension of the McKean relationship to CC bond

Experimentally, the determination of isolated CC stretching frequencies is hampered by immense difficulties in the case of molecules with symmetry equivalent CC bonds. Use of ^{13}C or even ^{14}C isotopes cannot suppress the coupling between the possible CC stretching modes (or between CC and other internal modes) and, therefore, makes the extension of the McKean relationship to CC bonds very difficult, if not impossible. Of course, one could think of using measured normal mode frequencies in some way to get approximate isolated CC stretching frequencies.

In Fig. 5, calculated normal mode frequencies of CC stretching modes ω_μ(CC) are compared with r_e(CC) bond lengths as obtained at the B3LYP/6-31G(d,p) level of theory (see Table 3). There is little correlation between the two quantities, which has to do with the fact that in those cases where CC stretching modes are coupled with symmetry equivalent CC stretching modes (or with other internal modes) two or even more ω_μ(CC) values have to be given for the same r_e(CC). The situation is somewhat improved when CC stretching frequencies involving the same CC bond are averaged (Fig. 6), however the correlation coefficient in this case is still rather small (r^2 = 0.844, Fig. 6). This clearly shows that in general averaging of normal mode frequencies cannot be considered to lead to useful substitutes for local mode frequencies, which help to describe the chemical bond.

AIM frequencies obtained at the B3LYP/6-31G(d,p) level of theory (for results with HF/6-31G(d,p), see Table 4) correlate well with r_e(CC) bond lengths (Fig. 7) since the AIMs are localized and determined by the properties of each particular CC bond. Contrary to the linear relationship for CH bonds, the ω_a(CC) − r_e(CC) relationship is quadratic, which is reasonable in view of the fact that previous bond length–stretching frequency relationships also involved higher powers of r_e, in particular if the bond in question can vary strongly (see for example Refs. [53,54]). In the present case, CC bond lengths

Table 6
Comparison of experimental and ideal dissociation energies[a]

	Molecule	CH bond	$D_0^{exp}(T)$	D_e^{exp}	D_e^{ideal}	ΔD_e
1	Methane (**1**)		104.9	112.9	112.3	0.5
2	Fluoromethane (**2**)		100	107.5	111.0	−3.4
3	Methanol (**3**)	CH_3, ip			112.1	
4		CH_3, op	94	101.2	103.6	−2.3
5	Methylamine (**4**)	CH_3, ip	96.1	103.3	96.0	7.3
6		CH_3, op			110.0	
7	Chloromethane (**5**)		100.9	108.6	113.4	−4.7
8	Methylsilane (**6**)				108.3	
9	Formaldehyde (**7**)		88.0	95.1	95.4	−0.2
10	Methyleneimine (**8**)	*cis*			107.3	
11		*trans*			115.1	
12	Hydrogen cyanide (**9**)		126.1	132.0	136.2	−4.3
13	Ethane (**10**)		101.1	109.0	109.2	−0.1
14	Fluoroethane (**11**)	CH_2F			109.0	
15		CH_3, ip			110.8	
16		CH_3, op			111.6	
17	Acetaldehyde (**12**)	CHO	89.4	95.6	95.9	−0.3
18		CH_3, ip			112.3	
19		CH_3, op	94.3	101.2	107.2	−6.0
20	Acetic acid (**13**)	CH_3, ip			116.3	
21		CH_3, op			109.7	
22	Methylnitrile (**14**)		94.8	102.3	112.1	−9.8
23	Ethene (**15**)		111.2	118.8	118.2	0.5
24	Chloroethene (**16**)	*ipso*			120.8	
25		*trans*			119.9	
26		*cis*			121.2	
27	Ketene (**17**)		105.3	111.9	123.7	−11.7
28	Ethyne (**18**)		132.8	140.1	140.2	−0.1
29	Propane (**19**)	CH_3, ip			109.1	
30		CH_3, op	97.9	105.6	108.5	−2.9
31		CH_2	95.1	102.9	106.4	−3.4
32	Dimethylketone (**20**)	CH_3, ip			113.8	
33		CH_3, op	92	99.1	108.0	−9.0
34	2-propenal (**21**)	trans			119.5	
35		cis			116.1	
36		ipso			115.7	
37		CHO	87.1	93.4	93.7	−0.3
38	Ethylnitrile (**22**)	CH_2	89.9	97.3	101.4	−4.1
39		CH_3, ip			112.9	
40		CH_3, op			112.5	
41	Allene (**23**)				117.5	
42	Propyne (**24**)	CH			140.5	
43		CH_3	89.4	97.0	110.9	−13.9
44	Cyclopropane (**25**)		106.3	113.9	118.7	−4.7
45	Oxirane (**26**)				116.0	
46	Aziridine (**27**)	*trans*			117.7	
47		*cis*			116.3	
48	Thiirane (**28**)				117.9	
49	*trans*-butadiene (**29**)	CH_2, *trans*			118.9	
50		CH_2, *cis*			117.2	
51		CH			113.3	
52	2-butyne (**30**)		87.2	94.7	108.7	−14.0

Table 6 (*continued*)

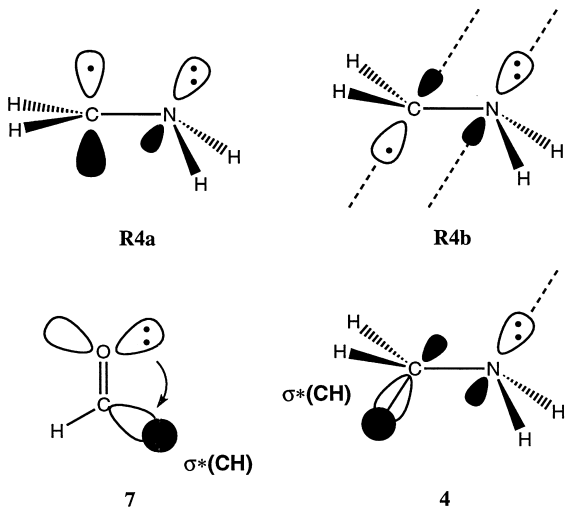
	Molecule	CH bond	$D_0^{exp}(T)$	D_e^{exp}	D_e^{ideal}	ΔD_e
53	1,3-butadiyne (**31**)				138.6	
54	Furan (**32**)	C(2)H			127.3	
55		C(3)H			125.7	
56	Pyrrole (**33**)	C(1)H			125.2	
57		C(2)H			123.7	
58	Isoxazole (**34**)	C(5)H			125.4	
59		C(4)H			126.8	
60		C(3)H			121.1	
61	Maleic anhydride (**35**)				123.7	
62	Thiophene (**36**)	C(2)H			124.6	
63		C(3)H			121.7	
64	Cyclohexane (**37**)	ax	95.5	103.1	101.8	1.3
65		eq			105.8	
66	Benzene (**38**)		111.2	118.0	118.6	−0.6

[a] All values in kcal/mol. Experimental dissociation enthalpies $D_0^{exp}(T)$ for $T = 298$ or 300 K from Ref. [57] (**1**, **4**, **7**, **9**, **10**, **12**, **14**, **15**, **17**, **18**, **37**, **38**), Ref. [58] (**2**, **3**, **5**, **19**, **22**, **24**, **25**, **30**), and Ref. [59] (**20**). The corresponding D_e^{exp} were calculated using B3LYP/6-31G (d, p) zero-point energies and thermal corrections according to Eq. (20). Values of D_e^{ideal} from Eq. (7) of Table 2. $\Delta D_e = D_e^{exp} - D_e^{ideal}$ is the stabilization/destabilization enthalpy of the radical excluding rehybridization effects.

range from 1.20 to 1.54 Å, which represents a considerably larger area than covered by the CH bonds investigated in Section 4. However, even for the CH bond correlations somewhat better correlation coefficients are found when a quadratic fit is used and when particularly long (e.g. the CH bond in methine: 1.133 Å) or particularly short CH bonds are included in the data set.

CC stretching frequencies ν^{exp}(CC) based on Eq. (18) are also given in Table 3. They show that typical CC stretching frequencies are in the region from 1000 to 2100 cm^{-1} depending on the degree of hybridization at the C atoms and delocalization of π-electrons in the molecule considered. In Table 5, a classification of CC bonds based on calculated ν_a^{exp}(CC) values is given. Values for single, double and triple bond are ca. 1070, 1600 and 2100 cm^{-1}, respectively, suggesting an increase of about 500 cm^{-1} for an increase in bond order by one. The stretching frequencies of CC single bonds increase to 1086 (**12**,3), 1176 (**29**,24) and 1395 cm^{-1} (**31**,28) if one sp^2, two sp^2 or even two sp hybridized C atoms participate in bonding. The aromatic CC bond possesses an AIM frequency of 1326 cm^{-1}. The degree of π-delocalization in the five-membered rings **32** to **36** can nicely be assessed by comparing the ν_a^{exp} values of formal single and formal double bonds where the average of these frequencies seems to be always close to the benzene AIM frequency of 1326 cm^{-1}. Hence, there is the possibility of assessing π-delocalization and the degree of aromaticity by an analysis of AIM frequencies.

A characterization of CC bonds as presented in Table 5 is rather difficult if just normal mode frequencies from experiment would be known. Of course, one could argue that because of the relationship between ω_a(CC) or ν_a^{exp}(CC) and r_e(CC), the same classification would be obtained if bond lengths would be used. Although this is true in most cases, one has to consider the fact that bond lengths not always reflect environmental effects influencing the bond strength. For example, the CC bonds of cyclopropane are known to be weakened by ring strain [55,56]. In contrast, the CC bond length measured (calculated) for **25** is just 1.51 (1.50) Å [55,56] suggesting that the bonds are stronger than normal CC single bonds of 1.54 Å, which of course would contradict all energetic investigations of **25**. The ν_a^{exp}(CC) of **25** (Table 5) is just 1049 cm^{-1} and by this suggests that the CC bonds of **25** are weaker than normal CC single bonds. Clearly AIM frequencies are a more reliable measure for bond strength than measured or calculated bond lengths.



Scheme 2.

6. Use of AIM frequencies for the description of CH bond strengths

McKean [10,11] showed that isolated CH stretching frequencies provide a reliable measure for the CH bond strength. Therefore, this should also be true in the case of AIM frequencies and we expect that ω_a values correlate with CH dissociation energies. There are two effects, which make this correlation problematic. First, experimental dissociation energies D_0 at T (K) ($T = 298$ or 300 K) [57–59][2] measured for the reaction

$$\text{R–H} \rightarrow \text{R}\cdot + \cdot\text{H}$$

can be expressed according to the following equation:

$$\Delta\Delta H_f^0(T) = \Delta H_f^0(T, \text{R}\cdot) + \Delta H_f^0(T, \text{H}\cdot) - \Delta H_f^0(T, \text{R–H}) = D_0(T). \quad (19)$$

Obviously, dissociation energy $D_0(T)$, which according to (19) is actually an enthalpy rather than an energy, covers besides the energy difference between dissociating molecules and fragments also the zero-point energy difference $\Delta\text{ZPE} = \text{ZPE}(\text{R}\cdot) - \text{ZPE}(\text{R–H})$ and the difference in thermal corrections $\Delta\text{THERM}(T) = \text{THERM}(T, \text{R}\cdot) + \text{THERM}(T, \text{H}\cdot) - \text{THERM}(T, \text{R–H})$ where $\text{THERM}(T, \text{H}\cdot)$ contains just the translational contributions to the thermal correction while for the other THERM values both translational, rotational and vibrational contributions are covered. Neither ΔZPE nor $\Delta\text{THERM}(T)$ are constant and may not necessarily vary linearly with ω_a. Therefore, we have derived equilibrium dissociation energies, D_e, from experimental $D_0(T)$ values utilizing calculated ΔZPE and $\Delta\text{THERM}(T)$ values in connection with Eq. (20). Since these dissociation energies are based on experimental dissociation energies $D_0(T)$ we denote them D_e^{exp} to distinguish them from directly calculated dissociation energies D_e^{cal}.

$$D_e^{exp} = E(\text{R}\cdot) + E(\text{H}\cdot) - E(\text{R–H}) = D_0 - \Delta\text{ZPE} - \Delta\text{THERM}(T) - \text{RT}. \quad (20)$$

The dissociation energies thus obtained should give a direct measure of the CH bond strength provided there are no new (de)stabilization effects in radical R $\cdot$, which are not encountered in molecule R–H. Actually none of the molecules considered leads to a radical which does not stabilize itself by rehybridization at the carbon center and subsequent changes in the geometry at the radical center (bond length, bond angle, and even conformational changes). We refrain from considering these stabilization effects in detail and instead concentrate just on additional effects caused by delocalization of the single electron via three-electron interactions or π-conjugation. There are just a few molecules of those shown in Fig. 1, which upon CH bond breakage lead to radicals R $\cdot$ without these extra-(de)stabilization effects, namely methane (**1**), formaldehyde (**7**), ethene (**15**), ethine (**18**), benzene (**38**). Accordingly, these molecules were chosen to determine ideal dissociation energies D_e^{ideal} (see Scheme 1) for the correlation with the corresponding ν_a^{exp}(CH) values (see Fig. 8). A linear relationship is obtained ($r^2 = 0.999$), which confirms that the increase in AIM frequencies is proportional to the strength of the CH bond and which can be used to predict D_e^{ideal} values for CH bonds (Table 6) and by this their bond strength utilizing adiabatic CH stretching frequencies.

For 25, CH bonds, measured dissociation energies are known and, therefore experimentally based D_e^{exp} values and predicted D_e^{ideal} values can be compared.

[2] The value of 92 kcal/mol for the $(CH_3)_2C{=}O$ bond was taken from Ref. [59].

The difference $SE = \Delta D_e = D_e^{exp} - D_e^{ideal}$ (see Scheme 1) also given in Table 6 quantifies (de)stabilization effects in R·.

Four classes of molecules with different (de)stabilization effects in radicals R· can be distinguished:

A. Radicals with 3-electron stabilization effects: entries #2: −3.4, #4: −2.3, #7: −4.7, #30: −2.9, #31: −3.4, #44: −4.7 kcal/mol (Table 6).
B. Radicals with π-conjugation: entries #19: −6.0, #22: −9.8, #27: −11.7, #33: −9.0, #38: −4.1, #43: −13.9, #52: −14.0 kcal/mol (Table 6).
C. Destabilized radicals: entry #5: 7.3 kcal/mol (Table 6).
D. Radicals with a stabilization/destabilization, which is vanishingly small (radicals derived from the reference molecules) or which in view of the errors in experimental $D_0(T)$ values cannot be considered to be significant: entries #13, #17, #37, #64 (Table 6).

Of course, each of group D radicals is stabilized by rehybridization at the radical center, e.g. the methyl radical by about 6 kcal/mol as can easily be verified by appropriate calculations. This standard stabilization, which is not considered in this work, is similar for group D systems and, therefore, it is possible to derive ideal dissociation energies D_e^{ideal} in the way described above.

The radicals of group A benefit from the rehybridization-effect and, in addition, from stabilizing three-electron interactions involving the single electron and the lone pair at F (**2**, CH bond 2), O (**3**, CH bond 4), and Cl (**5**, CH bond 7) or from hyperconjugative interactions as in **19** (CH bonds 30 and 31) and **25** (CH bond 44).

Radicals of group B molecules are stabilized by delocalization of the single electron into a neighboring π-system. Examples are: **12** (CH bond 19; conjugative interaction with the CO double bond), **14** (CH bond 22; conjugative interaction with the CN triple bond), **17** (CH bond 27; conjugative interaction with the ketene π-system), **20** (CH bond 33; conjugative interaction with the CO double bond), **22** (CH bond 38; conjugative interaction with the CN triple bond), **24** (CH bond 43; conjugative interaction with the CC triple bond), and **30** (CH bond 52; conjugative interaction with the CC triple bond). Extra-stabilization by π-electron delocalization is two to three times as large (−6 to −14 kcal/mol) as extra-stabilization by three-electron or hyperconjugative interactions (−3 to −5 kcal/mol).

There is only one molecule that forms a radical belonging to group C (Fig. 8, Table 6), namely **4**. The methylamine radical is significantly stabilized by rehybridization at the radical center, which becomes obvious by the changes in CH bond lengths (from 1.095 to 1.085 Å), the CN bond length (from 1.464 to 1.400 Å), and the HCN/HCH angles (from to 109.3/107.5 to 115.9/117.6). However, the stabilization due to rehybridization is partially offset by a destabilizing three-electron interactions, which depend on the overlap between the lone pair orbital at N (orbital energy ϵ) and the single electron orbital at C (orbital energy $\epsilon_1 - \epsilon_2$). It has been shown that three-electron effects can be either stabilizing (small overlap and a relatively large orbital energy difference $\Delta\epsilon = \epsilon_1 - \epsilon_2$) or destabilizing (large overlap and a relatively small orbital energy difference $\Delta\epsilon$). [60] For the hydroxmethyl, chloromethyl or fluromethyl radical, $\Delta\epsilon$ is relatively large while for the aminomethyl radical it is relatively small. Also, the overlap between the interacting orbitals is larger in form **R4a** than in form **R4b** (Scheme 2) so that both factors lead to a destabilizing three-electron interaction. Calculations show that radical **R4** can stabilize itself by 12 kcal/mol because of rehybridization (i.e. changing from **R4a** to **R4b**), but looses at the same time 7 kcal/mol because of destabilizing three-electron effects so that the net-stabilization is just 5 kcal/mol.

If one considers the D_e^{ideal} values, the classification of CH bonds given in Table 5 can be complemented. The range of CH energies is about 45 kcal/mol (from 95 to 140 kcal/mol, Table 6), where the CH bonds in aldehydes (at the C=O double bond) are the weakest and those in alkynes the strongest. Anomeric lone pair delocalization into a vicinal CH bond combined with the inductive effect of an electronegative X in a CX bond leads to significant bond weakening as in aldehydes **7** (Scheme 2) and **12**, in imine **8** (*cis* position) or in amine **4** (anti position) where the destabilizing effect can be 10–15 kcal/mol. The CH bonds of CH_3 groups possess D_e^{ideal} value of about 110 kcal/mol while those of a CH_2 group with sp^2 hybridized C are close to 119 kcal/mol. It is interesting to note that the CH bonds in ethene, cyclopropane, and benzene have the same bond strength, which confirms

that cyclopropane is related to alkenes. The ring strain of the three-membered ring is partially compensated by the extra-stability of the CH bonds (as compared to the CH bonds of the methylene group in propane) [55].

Substitution by an electronegative atom withdraws negative charge from the CH bonds (inductive effect) and by this leads to some CH bond weakening. These effects can be quantified with the help of the data in Table 6, however effects are relatively small and difficult to discuss in view of the uncertainties of experimental dissociation energies [57–59]. In contrast, experimental vibrational frequencies are much more accurate than measured dissociation energies, which means that ideal dissociation energies based on experimental adiabatic frequencies provide a reliable measure for trends in bond strengths. We conclude that the adiabatic CH stretching frequencies can be used to discuss CH bond strengths with high reliability. In addition, the deviation of the ideal dissociation energy from the corresponding experimental dissociation energy provides information on extra-stabilization/destabilization of the associated radical not contained in the parent system.

7. Conclusions

The vibrational spectrum of a molecule contains valuable information on its electronic structure and bonding situation. However, to decode this information in a way that it can be used in chemistry, the vibrational normal modes of a molecule must be transformed into localized internal coordinate modes that are associated with a particular internal coordinate such as the bond length. The adiabatic modes described recently [21–24] are based on such a transformation derived from a dynamic principle. Adiabatic modes turn out to be particularly useful since they provide detailed insight into bond properties. They are the theoretical counterparts of McKean's isolated stretching modes, however compared to the latter they posses several important advantages.

1. The adiabatic modes are strictly localized thus representing modes associated with just one internal coordinate. The isolated stretching modes in contrast are contaminated by residual couplings with other modes as in the case of alkynes.
2. Contrary to the isolated stretching modes, determination of the adiabatic modes leads to both a stretching frequency and a force constant since the adiabatic mode concept implies the unique definition of a mass [21–24].
3. Adiabatic modes can be determined for any bond in any molecule and, therefore, they provide the basis for an elegant extension of the isolated stretching modes, which so far could only be determined for CH bonds.

It is another advantage of the adiabatic modes that they can be determined for experimental spectra. As shown in this paper, experimentally based adiabatic stretching modes can replace the isolated CH stretching modes of McKean in correlations with bond lengths and bond dissociation energies. Contrary to bond length and bond dissociation energy, they represent a useful and reliable tool to characterize the strength of the chemical bond via the ideal dissociation energies derived from adiabatic frequencies as shown in this work. While we applied the adiabatic mode concept just to CH and CC bonds in this work, it should be straightforward to set up general relationships between bond properties and adiabatic stretching force constants for any bond of interest. Work is in progress to demonstrate this.

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References

[1] L. Pauling, The Nature of the Chemical Bond, 3rd edition, Cornell University Press, Ithaca, New York, 1960.
[2] R. McWeeny, Coulsons Chemische Bindung, Hirzel, Stuttgart, 1984.
[3] R.T. Sanderson, Chemical Bonds and Bond Energy, Academic Press, New York, 1976.
[4] Z.B. Maksic (Ed.), Theoretical Models of Chemical Bonding, Part 2: The Concept of the Chemical Bond Springer, Heidelberg, 1990.
[5] G. Herzberg, Molecular Spectra and Molecular Structure, I.

Spectra of Diatomic Molecules, van Nostrand, New York, 1950.
[6] R.S. Mulliken, W.C. Ermler, Diatomic Molecules, Results of ab initio Calculations, Academic, New York, 1977.
[7] E. Kraka, D. Cremer, in: Z.B. Maksic (Ed.), Theoretical Models of Chemical Bonding, Part 2: The Concept of the Chemical Bond, Springer, Heidelberg, 1990, pp. 453.
[8] H.G. Mack, D. Christen, H. Oberhammer, J. Mol. Struct. 190 (1988) 215.
[9] D. Cremer, Chem. Phys. Lett. 81 (1981) 481.
[10] D.C. McKean, Chem. Soc. Rev. 7 (1978) 399.
[11] D.C. McKean, Int. J. Chem. Kinet. 21 (1989) 445.
[12] D.C. McKean, J.L. Duncan, L. Batt, Spectrochim. Acta 29A (1973) 1037.
[13] D.C. McKean, Spectrochim. Acta 31A (1975) 1167.
[14] D.C. McKean, I. Torto, J. Mol. Struct. 81 (1982) 51.
[15] J.L. Duncan, J.L. Harvie, D.C. McKean, S. Cradock, J. Mol. Struct. 145 (1986) 225.
[16] W.F. Murphy, F. Zerbetto, J.L. Duncan, D.C. McKean, J. Phys. Chem. 97 (1993) 581.
[17] J. Caillod, O. Saur, J.-C. Lavalley, Spectrochim. Acta 36A (1980) 185.
[18] R.G. Snyder, A.L. Aljibury, H.L. Strauss, H.L. Casal, K.M. Gough, W.J. Murphy, J. Chem. Phys. 81 (1984) 5352.
[19] A.L. Aljibury, R.G. Snyder, H.L. Strauss, K. Raghavachari, J. Chem. Phys. 84 (1986) 6872.
[20] K. Raghavachari, J. Chem. Phys. 81 (1984) 2717.
[21] Z. Konkoli, D. Cremer, Int. J. Quant. Chem. 67 (1998) 1.
[22] Z. Konkoli, J.A. Larsson, D. Cremer, Int. J. Quant. Chem. 67 (1998) 11.
[23] Z. Konkoli, D. Cremer, Int. J. Quant. Chem. 67 (1998) 29.
[24] Z. Konkoli, J.A. Larsson, D. Cremer, Int. J. Quant. Chem. 67 (1998) 41.
[25] D. Cremer, J.A. Larsson, E. Kraka, in: C. Párkányi (Ed.), Theoretical and Computational Chemistry, Vol. 5, Theoretical Organic Chemistry, Elsevier, Amsterdam, 1998, pp. 259.
[26] Z. Konkoli, E. Kraka, D. Cremer, J. Phys. Chem. A. 101 (1997) 1742.
[27] E.B. Wilson Jr., J.C. Decius, P.C. Cross, Molecular Vibrations, McGraw-Hill, New York, 1955.
[28] L.A. Woodward, Introduction to the Theory of Molecular Vibrations and Vibrational Spectroscopy, Oxford University Press, London, 1972.
[29] P. Gans, Vibrating Molecules, Chapman and Hall Ltd., 1971, p. 50.
[30] S. Dasgupta, W.A. Goddard III, J. Chem. Phys. 90 (1989) 7207.
[31] J.A. Wendel, W.A. Goddard III, J. Chem. Phys. 97 (1992) 5048.
[32] A. Vijay, D.N. Sathyanarayana, J. Mol. Struct. 328 (1994) 269.
[33] P. Pulay, W. Meyer, Mol. Phys. 27 (1974) 473.
[34] J.A. Pople, H.B. Schlegel, R. Krishnan, D.J. Defrees, J.S. Binkley, M.J. Frisch, R.A. Whiteside, R.F. Hout, W.J. Hehre, Int. J. Quantum Chem. Quantum Chem. Symp. 15 (1981) 269.
[35] G. Fogarasi, P. Pulay, in: J.R. Durig (Ed.), Vibrational Spectra and Structure, Elsevier, Amsterdam, 1985, pp. 125.
[36] A.P. Scott, L. Radom, J. Phys. Chem. A 100 (1996) 16502.
[37] J. Baker, A.A. Jarzecki, P. Pulay, J. Phys. Chem. A 102 (1998) 1412.
[38] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1980) 4244.
[39] E. Kraka, J. Gräfenstein, J. Gauss, F. Reichel, L. Olsson, Z. Konkoli, Z. He, D. Cremer, Cologne 96, Göteborg University, Göteborg, 1996.
[40] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[41] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[42] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M. W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Revision C.3, Gaussian, Inc., Pittsburgh PA, 1995.
[43] T. Shimanouchi, Tables of Molecular Vibrational Frequencies, Consolidated Vol. I, Nat. Stand. Ref. Data Ser. 39, 1972.
[44] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.
[45] M.J.S. Dewar, G.P. Ford, J. Am. Chem. Soc. 99 (1977) 1685.
[46] J. Gauss, D. Cremer, Adv. Quantum Chem. 27 (1990) 101.
[47] M. Hippler, M. Quack, Ber. Busenges. Phys. Chem. 101 (1997) 356.
[48] H. Hollenstein, D. Luckhaus, M. Quack, J. Mol. Struct. 294 (1993) 65.
[49] M.M. Law, J.L. Duncan, Mol. Phys. 93 (1998) 821.
[50] M.M. Law, J.L. Duncan, Mol. Phys. 93 (1998) 809.
[51] J.A. Larsson, D. Cremer, to be published.
[52] J.A. Boatz, M.S. Gordon, J. Phys. Chem. 93 (1989) 1819.
[53] Y.P. Varshni, J. Chem. Phys. 28 (1958) 1078.
[54] Y.P. Varshni, J. Chem. Phys. 28 (1958) 1081.
[55] D. Cremer, E. Kraka, in: J.F. Liebman, A. Greenberg (Eds.), Molecular Structure and Energetics, Structure and Reactivity, 7, VCH Publishers, Deerfield Beach, USA, 1988, pp. 65.
[56] D. Cremer, E. Kraka, K.J. Szabo, in: Z. Rappoport (Ed.), The Chemistry of Functional Groups, The Chemistry of the Cyclopropyl Group, Vol. 2, Wiley, New York, 1995, pp. 43.
[57] J. Berkowitz, G.B. Ellison, D. Gutman, J. Phys. Chem. 98 (1994) 2744.
[58] D.F. McMillen, D.M. Golden, Ann. Rev. Phys. Chem. 33 (1982) 493.
[59] J.L. Holmes, F.P. Lossing, J.K. Terlouw, J. Am. Chem. Soc. 108 (1986) 1086.
[60] F. Bernardi, N.D. Epiotis, W. Cherry, H.B. Schlegel, M.-H. Whangbo, S. Wolfe, J. Am. Chem. Soc. 98 (1976) 469.