

# Characterization of CF Bonds with Multiple-Bond Character: Bond Lengths, Stretching Force Constants, and Bond Dissociation Energies

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*Isoelectronic C=F<sup>+</sup> and C=O bonds contained in fluoro-substituted carbenium ions, aldehydes, and ketones are investigated with regard to their bond properties by utilizing the vibrational spectra of these molecules. It is demonstrated that bond dissociation energies (BDEs), bond lengths, vibrational stretching frequencies, and bond densities are not reliable descriptors of the bond strength. The latter is related to the intrinsic BDE, which corresponds to nonrelaxed dissociation products retaining the electronic structure and geometry they have in the molecule. It is shown that the harmonic stretching force constants  $k^a$  of the localized internal coordinate vibrations (adiabatic vibrational modes) reflect trends in the intrinsic BDEs. The  $k^a$  values of both CO and CF bonds are related to the bond lengths through a single exponential function. This observation is used to derive a*

*common bond order  $n$  for 46 CO- and CF-containing molecules that reliably describes differences in bonding. CF bonds in fluorinated carbenium ions possess bond orders between 1.3 and 1.7 as a result of significant  $\pi$  back-bonding from F to C, which is sensitive to electronic effects caused by substituents at the carbenium center. Therefore, the strength of the C=F<sup>+</sup> bond can be used as a sensor for (hyper)conjugation and other electronic effects influencing the stability of the carbenium ion. The diatomic C=F<sup>+</sup> ion has a true double bond due to  $\pi$  donation from the F atom. The characterization of CF bonds with the help of adiabatic stretching modes is also applied to fluoronium ions ( $n=0.3-0.6$ ) and transition states involving CF cleavage and HF elimination ( $n=0.7-0.8$ ).*

## 1. Introduction

Despite a century of research work on the nature of the chemical bond, there is still considerable difficulty in assessing its nature in all its variety.<sup>[1-13]</sup> This has predominantly to do with the fact that the properties of the chemical bond are not observable quantities that can be measured.<sup>[14]</sup> Hence, the chemical bond is first of all just a concept, but it is the key concept in chemistry that is responsible for many developments and the progress chemistry has seen in the last 100 years.<sup>[1-13]</sup> The description of the chemical bond has to be based on model quantities, where wave-function calculations play an immanently important role. The primary model quantity used in the descriptions of the chemical bond is its bond order  $n$ ,<sup>[1-3]</sup> which reflects the strength of the chemical bond. There are numerous quantum chemical and empirical recipes for how to determine useful bond orders,<sup>[15-37]</sup> which have been reviewed in the literature.<sup>[9,38]</sup> Most wave-function-based bond order definitions lack a rigorous quantum mechanical derivation and suffer in addition from the fact that they depend on the quantum chemical method used, the basis set, and other technical details of the calculations. Empirical relationships have similar problems, since the available experimental data are limited and accordingly key quantities have to be determined by quantum chemical calculations.

In this work, we approach the problem of defining a suitable bond order that reflects the strength of a bond, its multiplicity, and the number of shared electron pairs by developing an empirical relationship utilizing vibrational spectroscopy. For many molecules, the vibrational frequencies have been measured or

can be determined using the methods of modern quantum chemistry. The frequency and the associated force constant of a vibrational stretching mode are characteristic for a given type of bonding. They should be related in some way to the bond strength, bond length, and bond parameters, such as bond order,  $\pi$ - or multiple-bond indices, bond polarity, the bond density, the Laplace concentration of the electron density, or the energy density in the bond region.

Most of the terms used in connection with the description of the chemical bond are defined within a given model. Herein, we will use the term bond strength in the sense of an energy measure. It is the energy needed to separate two atoms A and B directly connected by a bond without changing their electronic features (degree of hybridization) and their bonds to other atoms, that is, apart from the bond being broken, the electronic structure of the fragments after bond breaking is the same as in the molecule (for a discussion of this definition, see Section 3.1). The definition of bond order used in this work is based on the definition of bond strength described in Section 3.1. By choosing a single bond AB in a

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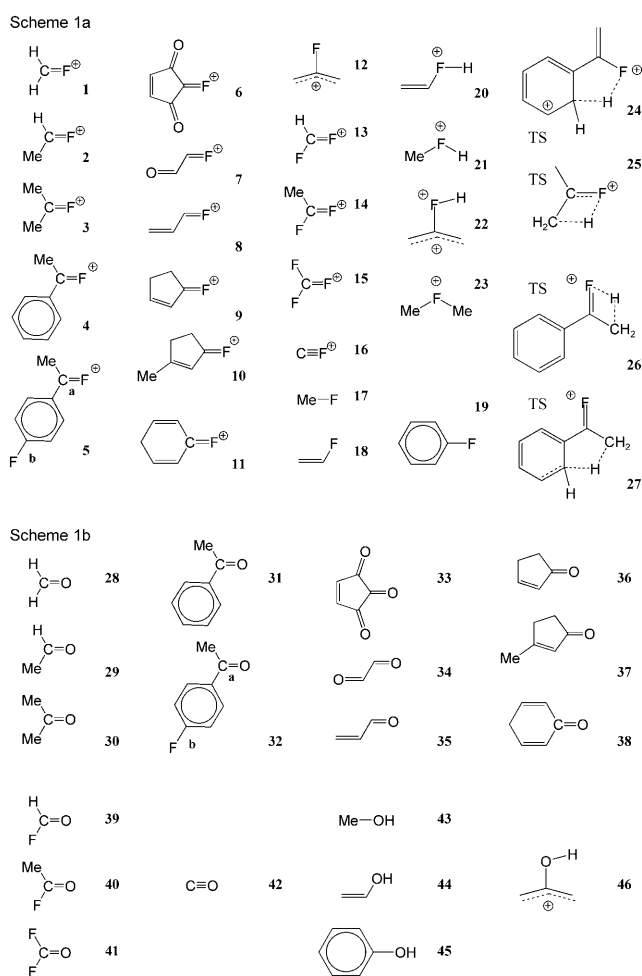
typical molecule as reference bond with bond order 1 ( $n(\text{AB}) = 1$ ), we define the bond order of another bond CD as the ratio of the bond strengths for CD and AB:  $n(\text{CD}) = \text{BS}(\text{CD})/\text{BS}(\text{AB})$ . We will show that the absolute bond strengths BS cannot be directly determined. However, a relative BS that leads to the bond order  $n$  is related to the stretching force constants obtained from the vibrational spectra of a molecule.

The vibrational spectra of a molecule contain detailed information on its geometry and electronic structure. This information is coded because the molecular vibrations are delocalized and seldom or almost never localized in a specific part of a molecule, such as a given bond AB.<sup>[39–44]</sup> Questions like the following: what are the stretching frequency and force constant of a peripheral CC bond in naphthalene as compared to those of the central CC bond? are difficult to answer without the help of theory and a suitable bond model. Herein, we will show that by utilizing the concept of adiabatic internal vibrational modes (AIMOs) originally developed by Cremer and co-workers,<sup>[45,46]</sup> a reliable description of chemical bonds and their bond strength becomes possible. Therefore, we will first discuss the adiabatic mode concept and its applicability and then apply it to a nontrivial chemical problem.

The chemical problem in question concerns the multiple-bond character of the CF bond in fluorinated carbenium ions  $\text{R}_2\text{CF}^+$  and its assessment.<sup>[47,48]</sup> Ions  $\text{R}_2\text{CF}^+$  contain a  $\text{CF}^+$  bond, which is isoelectronic with the carbonyl bond and which by  $\text{p}\pi$  donation from the F atom can obtain double-bond character. This is reflected by an increased gas-phase acidity of the carbenium ions and their enhanced reactivity towards electrophilic attack.<sup>[49,50]</sup> A recent quantum chemical investigation by Kiprof et al.<sup>[51]</sup> assigns bond orders from 1.04 to 1.85 to the  $\text{CF}^+$  bond in  $\text{CF}_3^+$  and  $\text{MeCF}_2^+$  depending on whether Wiberg bond indices<sup>[17,21]</sup> or natural resonance theory bond orders are calculated.<sup>[32]</sup> This is so far unsatisfactory as, depending on the theory used, either CF single or CF double bonds are predicted.

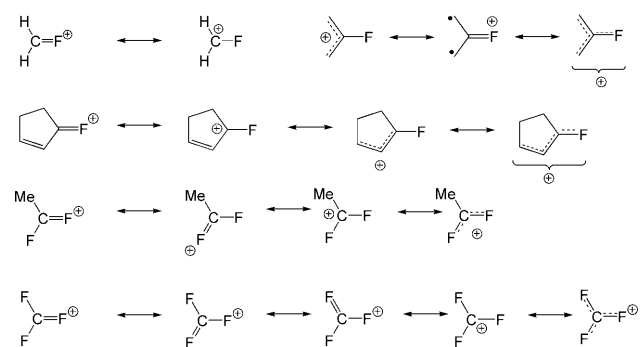
For the purpose of quantifying the double (multiple)-bond character of the  $\text{CF}^+$  bond, we investigated 16 F-substituted carbocations (1–16, Scheme 1) and compared them with some typical CF single bonds in neutral molecules (17–19). We also included fluoronium ions 20–23 that can be considered the result of a protonation or methylation of fluorides, which lead to divalent F with probably weak CF bonds. Molecule 22 is a special example of this class because it represents a protonated F-substituted carbenium ion and therefore carries two positive charges. Also included in Scheme 1 are four transition states (24–27) that have recently been investigated by Morton and co-workers.<sup>[52]</sup> They possess CF bonds at the point of being broken and therefore they are challenging test cases of any bond order definition. The CF bonding in 1–16 is compared with CO bonding in the valence isoelectronic aldehydes and ketones 28–42 (Scheme 1; excluding 12 from the comparison because its isoelectronic CO analogue is a singlet biradical with little interest for this investigation). As reference molecules with single CO bonds, molecules 43–46 are considered.

In Scheme 1, just one of the possible resonance structures is shown in the case of the F-substituted carbocations. However,



**Scheme 1.** The F-substituted hydrocarbons, aldehydes, and ketones examined in this study. TS = transition state.

for the correct assessment of  $\text{C}=\text{F}^+$  bonding, other resonance structures have also to be considered (see Scheme 2).



**Scheme 2.** Resonance structures of the F-substituted carbocations.

The definition of bond strength and bond order requires the definition of a suitable reference. At least two suitable reference molecules with generally accepted bond orders (e.g., in

the case of CC bonding, ethane and ethene with  $n(\text{CC})=1$  and  $n(\text{CC})=2$  are normally chosen) are needed for the determination of bond orders from a given bond property. This is not possible in the case of fluoro-substituted hydrocarbons because the normal C–F interaction is that of a single bond and no other CF bond with well-specified  $n$  is known. In this work, a different approach for determining CF bond orders is developed, which is based on the similarities of isoelectronic bonds. Of course, one has to verify first that it is justified to use isoelectronic bonds for the determination of bond-order relationships. Second, it is not clear which bond property is best suited to function as a source for the derivation of CF bond orders. Finally, there is always a question to what extent a bond-order relationship can be applied. Is it just useful for a given type of bond or can it be applied for any type of bonding between the elements in question?

We will answer these questions by presenting the results of this work in the following way. In Section 2, we will outline the theory of AIMO. The calculated adiabatic frequencies and force constants of 46 different CF and CO bonds are compared in Section 3 utilizing calculated bond dissociation energies (BDEs), bond lengths, and bond densities. The objective of this comparison is to derive a suitable relationship to calculate bond orders for these bonds. In Section 4, the chemical relevance of the latter will be discussed.

## 2. Theory of Adiabatic Internal Vibrational Modes

The basic equations of vibrational spectroscopy can be expressed either in Cartesian coordinate space [Eq. (1)]

$$\mathbf{f} \mathbf{L} = \mathbf{M} \mathbf{L} \mathbf{\Lambda} \quad (1)$$

or in internal coordinate space [Eq. (2)]

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

where the latter equation represents the Wilson GF eigenvalue problem.<sup>[39]</sup> Symbols  $\mathbf{f}$  and  $\mathbf{F}$  denote the force constant matrix expressed in  $3K$  ( $K$ : number of atoms) Cartesian displacement coordinates  $\Delta \mathbf{x}$  and  $N_{\text{vib}}=3K-M$  ( $M$ : number of overall translations and rotations of the molecule) internal displacement coordinates  $\Delta \mathbf{q}$ , respectively [Eqs. (3),(4)]

$$\Delta \mathbf{x} = \mathbf{x} - \mathbf{x}_e \equiv \mathbf{x} = (x_1, y_1, z_1, \dots, x_{3K}, y_{3K}, z_{3K})^\dagger \quad (3)$$

$$\Delta \mathbf{q} = \mathbf{q} - \mathbf{q}_e \equiv \mathbf{q} = (q_1, \dots, q_{N_{\text{vib}}})^\dagger \quad (4)$$

$\mathbf{M}$  is the mass matrix and  $\mathbf{G}$  the Wilson matrix defined by Equations (5) and (6):

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

$$B_{ni} = (\partial q_n(\mathbf{x}) / \partial x_i) \mathbf{x} = \mathbf{x}_e \quad (6)$$

The matrix  $\mathbf{\Lambda}$  contains on its diagonal  $N_{\text{vib}}$  vibrational eigenvalues  $\lambda_\mu$  from which the harmonic vibrational frequencies  $\omega_\mu$

are calculated. Hence, Equations (1) and (2) relate molecular vibrational frequencies to the vibrational normal modes  $\mathbf{l}_\mu$  collected in the eigenvector matrix  $\mathbf{L}$ . In Equation (2), matrix  $\mathbf{D}$  contains the normal mode vectors  $\mathbf{d}_\mu$  ( $\mu=1, \dots, N_{\text{vib}}$ ) expressed in internal coordinates. The relationship between force constant matrices  $\mathbf{f}$  and  $\mathbf{F}$  is given by [Eq. (7)]

$$\mathbf{F} = \mathbf{C}^\dagger \mathbf{f} \mathbf{C} \quad (7)$$

where matrix  $\mathbf{C}$  provides the connection between normal mode vectors  $\mathbf{l}_\mu$  of matrix  $\mathbf{L}$  and normal mode eigenvectors  $\mathbf{d}_\mu$  of matrix  $\mathbf{D}$  according to [Eq. (8)]

$$\mathbf{l}_\mu = \mathbf{C} \mathbf{d}_\mu \quad (8)$$

Matrix  $\mathbf{D}$  gives the transformation from normal coordinates  $\mathbf{Q}$  to internal coordinates  $\mathbf{q}$  according to [Eq. (9)]

$$\mathbf{Q} = \mathbf{D} \mathbf{q} \quad (9)$$

Normal modes  $\mathbf{l}_\mu$  associated with the normal mode frequencies  $\omega_\mu$  are delocalized modes since each normal coordinate is a linear combination of internal coordinate displacements  $q_n$ . Accordingly, one can consider each normal mode as a linear combination of internal coordinate modes  $\mathbf{t}_n$ , each of which is associated with a particular internal coordinate  $q_n$ . The degree of delocalization of a normal mode is determined by the amount of coupling between the internal modes  $\mathbf{t}_n$  constituting the normal mode. In this way, the off-diagonal elements of the force constant matrix represent the coupling force constants. The vectors  $\mathbf{c}_n$  of the transformation matrix  $\mathbf{C}$  can be used as localized internal coordinate modes provided the following conditions are fulfilled [Eq. (10)]

$$(\mathbf{d}_\mu)_n = \delta_{\mu n} \quad (10)$$

with  $\delta_{\mu n}$  being the Kronecker delta. Equation (10) leads to [Eq. (11)]

$$\mathbf{l}_\mu = \mathbf{c}_n \quad (11)$$

where it is assumed that  $\mu=n$ . Equation (11) will hold if 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 requires that both electronic and kinematic coupling between the localized internal modes is zero. Since the  $\mathbf{G}$  matrix of Equation (5) is nondiagonal, kinematic (or mass) coupling can never be zero, but it can be suppressed to some extent if the reduced mass of a diatomic fragment is dominated by the mass of one of the atoms, as in the case of an FH bond. However, if the two masses are comparable neither Equation (10) nor Equation (11) is fulfilled. Often one assumes a diagonal character of the  $\mathbf{G}$  matrix when there is a large mass difference between the atoms participating in the molecular motions, since this assumption is the only basis to discuss measured frequencies in terms of internal mode frequencies.

The discussion above clearly shows that it is not in general justified to select a special vibrational normal mode of a polyatomic molecule as stretching vibration and to use the associated stretching force constant  $k_\mu$  as a unique property of the bond in question. This can only be done on the basis of the AIMOs.<sup>[45,46]</sup> Suppose the geometry of the molecule is represented by the internal coordinates  $q_m$  and the force constant matrix  $\mathbf{f}$  of the molecule is known. One can obtain localized internal coordinate modes in a two-step approach. First, the molecule is vibrationally excited by distorting all internal coordinates from their equilibrium values. In the second step, the molecular geometry is relaxed for all coordinates  $q_m$  ( $m \neq n$ ) but the target coordinate  $q_n$ , which is supposed to lead the internal coordinate vibration in question, for example, a bond stretching motion. By adiabatic relaxation, a one-dimensional localized motion is projected out of a complex multidimensional motion of the molecule. For obvious reasons, such a motion in one dimension is called an *adiabatic vibration*.<sup>[45]</sup>

The adiabatic vibrational modes are calculated by requiring that the potential energy  $V$  adopts a minimum in all directions  $q_m$  ( $m \neq n$ ) for a fixed displacement  $q_n^*$  in the direction  $q_n$  (leading parameter principle<sup>[45]</sup>) [Eqs. (12),(13)]

$$V(\mathbf{Q}) = \text{minimum} \quad (12)$$

$$q_n = \text{const} = q_n^* \quad (13)$$

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

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

and Equation (15)

$$q_n(\mathbf{Q}) = \frac{1}{2} \sum_{\mu=1}^{N_{\text{vib}}} D_{n,\mu} Q_\mu \quad (15)$$

where  $D_{n,\mu}$  is an element of matrix  $\mathbf{D}$ . Equation (12) with the constraint [Eq. (13)] is solved with the help of a Lagrange multiplier  $\lambda$  [Eq. (16)]

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

The solution of Equation (16) for internal parameter  $q_n$  and the  $\mu$ th normal coordinate is given by [Eq. (17)]

$$Q_\mu^n = \frac{D_{n,\mu}}{k_\mu} q_n^* \quad (17)$$

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

$$Q_\mu^n = (\mathbf{a}_n^{\text{Q}})_\mu q_n^* \quad (18)$$

The AIMO  $\mathbf{a}_n^{\text{Q}}$  can be transformed to AIMO  $\mathbf{a}_n$  expressed in Cartesian coordinates with the help of the  $\mathbf{L}$  matrix [Eq. (19)]

$$\mathbf{a}_n = \mathbf{L} \mathbf{a}_n^{\text{Q}} \quad (19)$$

The force constant, mass, and frequency of an AIMO are defined by Equations (20)–(22)<sup>[45,46]</sup>

$$k_n^{\text{a}} = \mathbf{a}_n^\dagger \mathbf{f} \mathbf{a}_n \quad (20)$$

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

$$\omega_n^{\text{a}} = \frac{(\mathbf{a}_n^\dagger \mathbf{f} \mathbf{a}_n)^2}{\mathbf{G}_{nn}} = \left( \frac{k_n^{\text{a}}}{m_n^{\text{a}}} \right)^{\frac{1}{2}} \quad (22)$$

where vector  $\mathbf{b}_n$  corresponds to the  $n$ th column of the  $\mathbf{B}$  matrix of Equation (6) and where [Eq. (23)]

$$\mathbf{b}_n \mathbf{a}_n^\dagger = 1 \quad (23)$$

since the AIMOs are properly normalized. The AIMO mass is identical to  $G_{nn}^{-1}$  of the  $\mathbf{G}$  matrix and, accordingly, represents a generalization of the reduced mass for internal parameters associated with more than two atoms. Utilizing the definition of AIMOs, each bond of a molecule can be associated uniquely with a bond stretching force constant  $k_n^{\text{a}}$  and frequency  $\omega_n^{\text{a}}$ , which together with bond length  $q_n$  establish a set of bond parameters which may be related to the bond strength. AIMO force constants and frequencies can be calculated with the help of quantum chemical methods or measured vibrational spectra.<sup>[46]</sup>

Another advantage of the AIMO concept is that it can be applied to any set of internal parameters used for the description of the molecular geometry. Hence, one can also determine the AIMOs for a set of symmetry coordinates  $q_s$ , which will become necessary if one wants to describe equivalent bonds of a molecule appropriately. Vibrational spectroscopists prefer to discuss the bonds of a molecule in terms of the force constants  $k_n^{\text{c}}$  of the valence force field of the molecule. As noted above, these force constants are associated with vectors  $\mathbf{c}_n$  of matrix  $\mathbf{C}$ . Following the AIMO approach, one can also define local modes for force constants  $k_n^{\text{c}}$  and, in this way, associate a stretching frequency  $\omega_n^{\text{c}}$  with a  $\mathbf{c}$ -vector mode.<sup>[53]</sup>

For a polyatomic molecule, the bond stretching force constant and bond stretching frequency are nonobservable quantities. This is different in the case of diatomics where the stretching frequency can be directly measured and used to derive a stretching force constant. In this case,  $\omega_n^{\text{a}}$  and  $k_n^{\text{a}}$  are identical with the measured values which, however, is not the case for the stretching force constant of the diatomic molecule calculated by quantum chemical programs.<sup>[54]</sup> This is the consequence of a different definition of the reduced mass  $\mu_n$

being changed because of the normalization of the normal modes  $I_n$ . The latter is necessary to obtain consistent results in the case of polyatomic molecules. The force constant is given by [Eq. (24)]

$$k_n^a = 4\pi^2 c^2 \omega_n^2 \mu_n \quad (24)$$

and thereby depends on the definition of the reduced mass. Hence, the quantum chemical force constant of a diatomic molecule differs from the experimentally derived force constant (mostly larger by a factor close to 2 resulting from a normalization factor  $(a^2 + b^2)^{-1}$  with mode coefficients  $a \approx b \approx 0.5$  for similar atoms). However, when calculating adiabatic bond stretching force constants the reduced mass is defined for the adiabatic vibrational mode of the diatomic fragment, which is already normalized, and therefore the reduced mass does not change irrespective of the other atoms in a polyatomic molecule.

The adiabatic modes have a number of advantages. 1) They are uniquely defined. 2) Electronic and mass effects are separated in the adiabatic modes. Hence, the adiabatic force constant clearly describes the electronic nature of the molecular unit in question. 3) The adiabatic vibrational modes are independent of the coordinate set used for describing the molecule, no matter whether it is nonredundant or redundant. 4) Analysis, comparison, and correlation of the vibrational spectra of different molecules are simplified when using AIMOs. 5) Adiabatic modes can also be derived for measured vibrational spectra.<sup>[46]</sup> 6) Adiabatic modes make it possible to characterize each structural unit in a molecule with the help of vibrational spectroscopy.

In the mid-1970s McKean<sup>[55,56]</sup> introduced what he called isolated CH stretching frequencies. By deuterium substitution of all H atoms of a CH<sub>3</sub> or CH<sub>2</sub> group but one, he could measure CH stretching frequencies that were only a little contaminated by coupling with other modes or Fermi resonances. McKean found that the measured isolated CH stretching frequencies nicely correlated with known  $r_o$  CH bond lengths, and he used this to predict unknown CH bond lengths from measured isolated CH stretching modes with an accuracy of a thousand Ångströms. In a similar way he could determine CH bond strengths, which led to the rather valuable access to many chemical problems ranging from conformational analysis and the investigation of strain to the study of reaction mechanisms always using the CH bond as antenna. Larsson and Cremer<sup>[57]</sup> showed that the isolated CH stretching modes of McKean are a special case of the more general adiabatic stretching modes.

Adiabatic stretching modes can be determined (utilizing measured<sup>[46]</sup> or calculated vibrational spectra<sup>[57]</sup>) even in those cases where McKean's approach reveals disadvantages. 1) The isolated modes suffer in most cases from residual couplings. 2) They are difficult to obtain since they require in most cases tedious syntheses of isotopomers. 3) McKean's idea cannot be extended to any bond of a polyatomic molecule.

Herein, we calculate the adiabatic CX (X=F, O) stretching modes of the 46 structures shown in Scheme 1. For this purpose we use B3LYP density functional theory (DFT)<sup>[58–60]</sup> in

combination with the augmented VDZ basis set 6-31G(d,p).<sup>[61]</sup> The natural bond order (NBO) analysis is applied to determine atomic charges.<sup>[32]</sup> In addition, the electron density  $\rho_c = \rho(\mathbf{r}_c)$  at the bond critical point  $\mathbf{r}_c$  is computed to obtain a measure for the bond density.<sup>[9]</sup> G3 (Gaussian-3) model chemistry<sup>[62]</sup> is used to determine reliable CF and CO BDE values that can be compared with calculated bond lengths, bond stretching frequencies, bond stretching force constants, and bond densities. All calculations are carried out with the program packages COLOGNE08<sup>[63]</sup> and Gaussian03.<sup>[64]</sup>

### 3. Results and Discussion

In Table 1, the CX (X=F, O) bond lengths  $R(\text{CX})$ , adiabatic CX stretching frequencies  $\omega^a(\text{CX})$ , adiabatic stretching force constants  $k^a(\text{CX})$ , bond densities  $\rho_c(\text{CX})$  calculated at the critical point of the CX bond  $\mathbf{r}_c$ , and BDE(CX) values are listed for the 46 molecules and transition states shown in Scheme 1.

The adiabatic CF frequencies obtained for F-substituted molecules 1–19 are shown in Figure 1 as an exponential function of the CF bond length. Contrary to the harmonic vibrational modes with dominant CF stretching character, which strongly scatter in dependence on  $R$  (for a related example, see Ref. [57], Figure 5), the adiabatic CF stretching frequencies nicely fit to the exponential relationship. Figure 1 also shows that a similar exponential dependence is obtained for the adiabatic stretching frequencies of the isoelectronic CO systems 28–42 and the reference molecules 43–46. The CO frequencies decrease more strongly with increasing  $R(\text{CO})$ , where one has to consider that the  $R$  values stretch from 1.138 to 1.419 Å whereas the corresponding CF bond lengths stretch just from 1.169 to 1.383 Å. Apart from the fact that the adiabatic CX frequencies relate to another bond property, that is, the bond length  $R(\text{CX})$ , and therefore can be considered as a bond rather than a molecular quantity, there is no conclusive information on the similarity of CO and CF bonds. The CF bonds of 1–16 seem to be weaker and those of the reference molecules 17–19 stronger than the corresponding CO bonds (Figure 1).

The question is whether the adiabatic stretching frequency can be used as a parameter to describe reliably the features of a chemical bond. It is scaled by the reduced mass  $\mu$  of the two-atom unit CX according to [Eq. (25)]

$$\omega_n^{a,2} = k_n^a / (4\pi^2 c^2 \mu) \quad (25)$$

and because of the different masses of F and O, there is no possibility of getting identical or similar exponential relationships of the type  $\omega = f(R)$  (Figure 1) for the isoelectronic bond fragments.

The question about the bond parameter that best reflects the strength of a bond has to be considered from a more elementary perspective. In Figure 1, the bond length  $R(\text{CX})$  has been chosen as a unique descriptor of the chemical bond. In general, a smaller  $R$  value is interpreted as indicating a stronger bond and vice versa. There are numerous investigations that utilize the bond length as a descriptor of the bond strength.<sup>[9–13,15–38]</sup> However, there are also scattered reports



**Table 1.** Calculated properties of CX (X = F, O) bonds for molecules 1–46.<sup>[a]</sup>

	Molecule	$R(\text{CX})$ [Å]	$\omega^{\text{a}}(\text{CX})$ [cm <sup>-1</sup> ]	$k^{\text{c}}(\text{CX})$ [mdyne Å <sup>-1</sup> ]	$k^{\text{d}}(\text{CX})$ [mdyne Å <sup>-1</sup> ]	$\rho_{\text{c}}(\text{CX})$ [e Å <sup>-3</sup> ]	BDE(CX) [kcal mol <sup>-1</sup> ]	Bond order, $n$
CF bonds	1	1.240	1572	10.89	10.71	2.265	150.3	1.70
	2	1.260	1472	9.61	9.29	2.161	134.4	1.55
	3	1.282	1365	8.66	8.08	2.057	132.9	1.41
	4	1.310	1273	7.77	7.03	1.915	129.3	1.28
	5a	1.313	1268	8.6	6.96	1.905	127.2	1.28
	5b	1.314	1295	7.78	7.27	1.896	na	1.31
	6	1.249	1514	10.09	9.93	2.197	144.8	1.62
	7	1.252	1501	10.09	9.77	2.193	104.6	1.60
	8	1.278	1410	9.03	8.61	2.067	135.4	1.47
	9	1.288	1376	8.56	8.21	2.017	134.9	1.43
	10	1.293	1359	8.36	8.01	1.990	133.3	1.40
	11	1.304	1325	7.97	7.60	1.948	129.5	1.35
	12	1.319	1284	7.63	7.14	1.913	122.4	1.30
	13	1.241	1534	10.55	10.19	2.339	143.0	1.65
	14	1.259	1446	9.53	9.06	2.242	137.7	1.52
	15	1.243	1519	10.38	10.00	2.547	139.0	1.63
	16	1.169	1782	13.76	13.76	2.666	199.7	2.02
	17	1.383	1116	5.95	5.39	1.614	109.8	1.07
	18	1.347	1195	6.57	6.19	1.722	123.9	1.18
	19	1.351	1195	6.47	6.19	1.711	129.1	1.18
	20	1.663	445	1.37	0.86	0.728	13.9	0.31
	21	1.617	580	1.98	1.46	0.785	29.3	0.45
	22	1.574	582	2.08	1.47	0.860	30.3	0.45
	23	1.533	703	2.81	2.14	0.999	47.3	0.58
	24	1.526	832	3.65	3.00	1.088	na	0.72
	25	1.510	848	3.23	3.12	1.204	na	0.74
	26	1.571	654	2.74	1.85	1.031	na	0.52
27	1.311	1301	8.03	7.33	1.909	na	1.32	
CO bonds	28	1.207	1836	13.97	13.62	2.770	178.4	2.00
	29	1.211	1810	13.71	13.23	2.754	183.6	1.96
	30	1.216	1778	13.37	12.77	2.733	186.7	1.92
	31	1.222	1736	12.79	12.18	2.702	178.8	1.86
	32	1.222	1734	12.75	12.15	2.703	180.2	1.85
	33	1.204	1832	13.93	13.55	2.782	171.7	2.00
	34	1.213	1785	13.49	12.87	2.739	172.5	1.93
	35	1.215	1773	13.28	12.70	2.731	173.2	1.91
	36	1.216	1770	13.21	12.65	2.733	183.3	1.91
	37	1.217	1765	13.13	12.58	2.728	185.1	1.90
	38	1.228	1711	12.44	11.83	2.677	173.8	1.82
	39	1.186	1919	15.43	14.88	2.945	200.9	2.12
	40	1.191	1886	14.98	14.36	2.923	204.1	2.07
	41	1.180	1940	15.71	15.23	3.012	214.6	2.15
	42	1.138	2209	19.71	19.71	3.180	257.3	2.56
	43	1.419	1095	5.58	4.84	1.755	90.5	1.00
	44	1.369	1217	6.57	5.98	1.906	107.6	1.15
	45	1.368	1220	6.48	6.01	1.921	113.3	1.16
	46	1.332	1320	7.75	7.04	2.128	116.3	1.29

[a]  $R(\text{CX})$  denotes the CX bond length,  $\omega^{\text{a}}(\text{CX})$  the adiabatic CX stretching frequency,  $k^{\text{c}}(\text{CX})$  the CX stretching force constant based on c vectors,  $k^{\text{d}}(\text{CX})$  the adiabatic CX stretching force constant,  $\rho_{\text{c}}(\text{CX})$  the CX bond density at the bond critical point, BDE(CX) the CX bond dissociation energy, and  $n$  the CX bond order. B3LYP/6-31G-(d,p) and G3 calculations.

distribution that resembles closely that of its cation. The cation of A has a smaller covalent radius than A itself, which means that the AX bond is much smaller than in the case of  $\text{AH}_p\text{X}_q$ . At the same time, the AX bond strength should increase (increased ionic character) provided there are no other electronic effects that hinder the increase. Such an effect could be, for example, lone-pair repulsion in the case that both A and X possess electron lone pairs. At a shorter distance, lone-pair repulsion increases and can outweigh any bond strengthening with the result that for the shorter bond length  $R$  a weaker bond is obtained. Such a situation can be found in various fluoro-substituted hetero compounds, for example, the fluoroamines<sup>[65,66]</sup> or in the series HOF and FOF.<sup>[69]</sup>

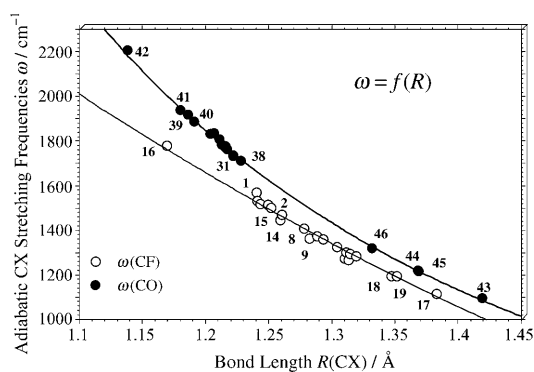
Bond length  $R$  also turns out to be an unreliable parameter when trying to relate it to bond strength in the case of relativistic effects. The relativistic mass-velocity effect leads to a shortening of the bond length. Again, this can increase lone-pair repulsion as found, for example, with mercury halides  $\text{HgX}$  or mercury chalcogenides  $\text{HgE}$ .<sup>[67]</sup> Another example is  $\text{AuCl}$ , although in this case a different explanation has been given for the bond weakening upon relativistic bond shortening.<sup>[68]</sup> Hence, a shorter bond does not always indicate a stronger bond for heavy-atom compounds with distinct relativistic effects. Even more complicated is the situation in excited states where bond length  $R$  often does not reflect the strength of the bond.<sup>[68]</sup> We con-

clude that  $R$  is not a reliable descriptor of the bond strength and therefore should not be used to derive a bond order  $n$ .

clude that  $R$  is not a reliable descriptor of the bond strength and therefore should not be used to derive a bond order  $n$ . Bader's work on virial partitioning of the molecular electron density distribution<sup>[9]</sup> suggests that a much better descriptor of bond strength should be directly derived from the bond density. However, the bond density is a quantity that lacks a rigorously defined bond region. The virial partitioning approach leads to a definition of atoms in molecules separated

that shed some doubt on the reliability of a relationship between bond strength and bond length.<sup>[65–68]</sup> Without going into much detail, one can easily derive a situation where  $R$  is no longer a reliable descriptor of bond strength.

Suppose a central atom A in  $\text{AH}_p\text{X}_q$  is successively bonded to more strongly electronegative substituents X by stepwise replacement of H by X. The partial positive charge of A will increase so that for a given  $p$  and  $q$  central atom A has a charge

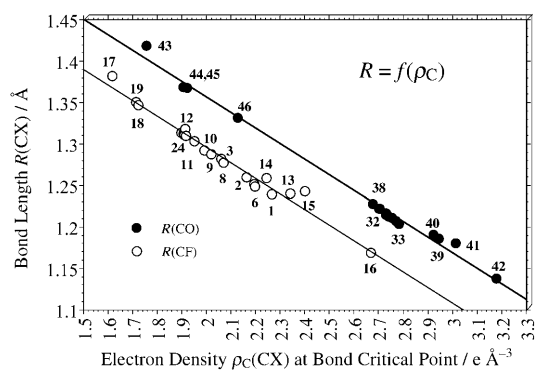


**Figure 1.** Adiabatic CX stretching frequencies  $\omega^a$  as power functions of the CX bond length  $R$  for molecules 1–19 and 28–46. For numbering, see Scheme 1. B3LYP/6-31G(d,p) calculations.

by zero-flux surfaces of the electron density.<sup>[9]</sup> The point of largest electron density in a zero-flux surface is the bond critical point, which in three-dimensional space corresponds to a saddle point of first order in  $\rho(r)$ . Along the maximum electron density path connecting the nuclei of the bonded atoms it is a minimum, whereas in the two directions spanning the zero-flux surface it is a maximum.<sup>[9]</sup>

There have been attempts to base empirical relationships for the bond order on the electron density at the bond critical point  $r_c$  ("bond density  $\rho_c$ ").<sup>[12,27]</sup> These were useful when constrained to a smaller group of closely related bonds (for example, just CC bonds) with chemically well-accepted references (the CC bonds in ethane and ethene leading to  $n=1$  and  $n=2$ ). However, a generally defined bond order is difficult to determine in this way. A single bond-density value, even if determined at a characteristic and unique location of the bond region, cannot be a measure for the bond strength, which depends on the total density distribution in the region close to the bond path as well as farther away from the bond path in the nonbonding region. The tail densities in the latter region can have a significant effect on adjusting bond strength to the effects of bond eclipsing, lone-pair repulsion, conjugation, or hyperconjugation. Therefore, it is not surprising that the linear relationships between  $R$  and bond density  $\rho(r_c)$  for CO and CF bonds shown in Figure 2 suffer from some scattering of points. The problem of using the bond density  $\rho(r_c)$  becomes apparent when comparing mono-, di-, and trifluoro-substituted carbonium ions.

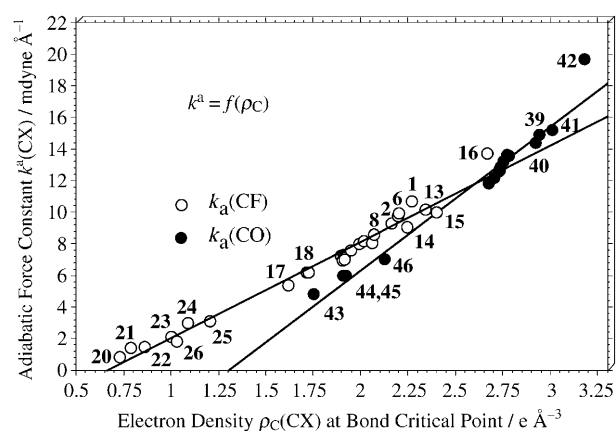
Four out of five bond parameters listed in Table 1 ( $R$ ,  $\omega^a$ ,  $k^a$ , BDE) suggest that the  $\text{CF}^+$  bond should decrease in strength in the series 1, 13, 15. However the calculated bond densities increase in this sequence (Table 1), thus suggesting an increase rather than a decrease of bond strength. Considering that the positive charge is localized in the  $\pi$  system, it is easy to see that from 1 to 13 and 15, the positive charge per  $\text{CF}^+$  bond decreases from 1 to 1/3 and therefore the  $\pi$  density per CF has to increase. At the same time,  $\pi$  back-donation from F to C decreases from 0.31 to 0.21 (NBO charges), thus lowering the double-bond character of the  $\text{CF}^+$  bond and thereby its strength. A similar observation can be made for the series 28,



**Figure 2.** CX bond lengths  $R$  as linear functions of the CX bond density  $\rho_c$  for molecules 1–19 and 28–46. For numbering, see Scheme 1. B3LYP/6-31G(d,p) calculations.

39, 41 (Table 1, Figure 2). Hence, the bond density is an inappropriate property to indicate bond strength and to compare the isoelectronic  $\text{C}=\text{O}$  and  $\text{C}=\text{F}^+$  bonds, as is reflected by the scattering of data points in Figure 2.

An even stronger scattering of data points is observed when correlating adiabatic stretching force constants with the bond density  $\rho(r_c)$  (Figure 3). As in the case of Figure 2, the CF and CO bonds behave differently and their isoelectronic nature does not become apparent. Depending on the type of bonding, the bond density  $\rho(r_c)$  and the density in the nonbonded region may behave differently upon changes in  $k^a$ . For the purpose of accessing these changes, one could take besides  $\rho(r_c)$  also the bond Laplacian  $\nabla^2\rho(r_c)$  to derive a relationship between bond order/bond strength and bond density. Cremer and Gauss<sup>[70]</sup> took a more direct approach to the problem by using the density in the zero-flux surface  $Z$  between the bonded atoms as bond density  $\rho(Z)$ . In this way they derived a property relating to the strength of a bond in the case of simple hydrocarbons.<sup>[70]</sup> A generalization of this approach failed, because with the help of  $\rho(Z)$  only the covalent part of the chemical bond is assessed. In addition, one has to consider

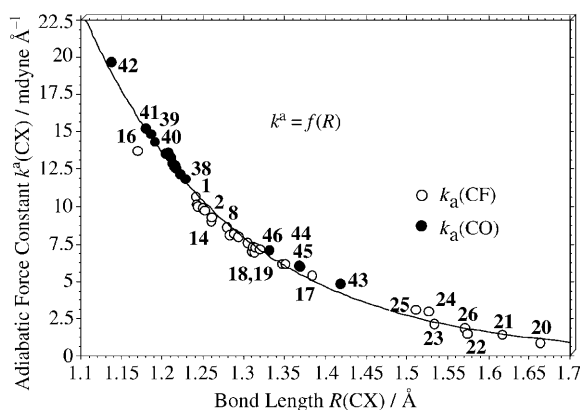


**Figure 3.** Adiabatic CX stretching force constants  $k^a$  as linear functions of the CX bond density  $\rho_c$  for molecules 1–19 and 28–46. For numbering, see Scheme 1. B3LYP/6-31G(d,p) calculations.

the ionic character of the bond, which can be assessed from the position of the zero-flux surface  $Z$  (and the bond critical point  $r_c$ ) relative to the bond midpoint, that is, how much  $Z$  is shifted to one or the other bonding partner. Alternatively, the virial charges of the bonding partners can be directly used to describe the ionic character of the bond. However, no general procedure has been worked out for this purpose, and therefore one cannot make any prediction with regard to the usefulness of an improved definition of the bond density. We conclude that the bond density  $\rho(r_c)$  is not appropriate to define a measure for bond order and bond strength.

The adiabatic CX stretching force constant  $k^a$  is a more reliable parameter for describing bond order and bond strength. It is sensitive to the overall electron density accumulation in the bond region rather than just to that at the bond critical point. Therefore, it should be sensitive to erroneous predictions of bond strength by either the bond density or the bond length  $R$ .

In Figure 4, the adiabatic CX stretching force constants  $k^a$  are related to the bond lengths  $R$ . Despite the fact that  $R$  is not a reliable descriptor of bond strength, two important ob-



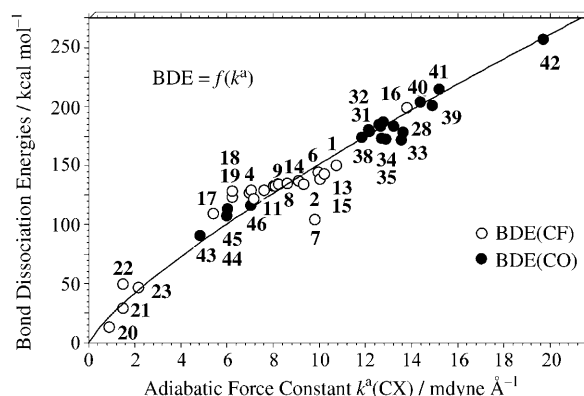
**Figure 4.** Adiabatic CX stretching force constants  $k^a$  as an exponential function of the CX bond length for molecules 1–46. For numbering, see Scheme 1. B3LYP/6-31G(d,p) calculations.

servations can be made when inspecting Figure 4. 1) For CO and CF bonds of a very different nature, just one exponential relationship  $k^a = f(R)$  is obtained, which shows for the first time that there is a close connection between the isoelectronic CX bonds. 2) There is some scattering of data points, which we attribute to the problem of using bond length  $R$  as a descriptor of bond strength. We conclude that the adiabatic force constant reflects in a consistent way the changes in bond strength, which makes it possible to compare the two types of isoelectronic CX bonds. Before utilizing  $k^a$  as a suitable descriptor of bond strength, we will first discuss the CX bond strength on the basis of calculated BDE values.

### 3.1. Bond Strength and Bond Dissociation Energies

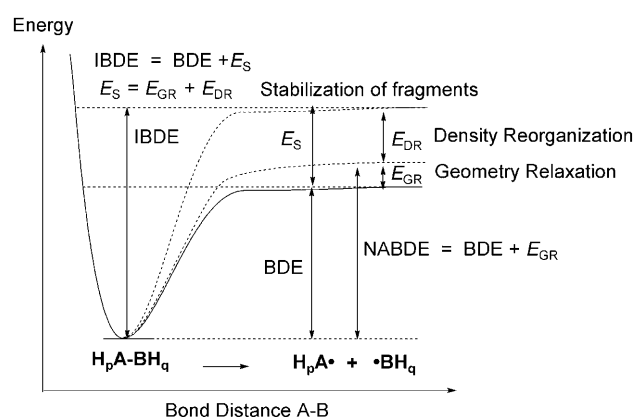
Commonly, the BDE is taken as a measure for the bond strength. The G3 BDE values of the molecules investigated (ex-

cluded are only the TSs 24–27) are also listed in Table 1. They increase with increasing adiabatic stretching force constant according to a single power relationship (Figure 5); however,



**Figure 5.** Calculated BDEs of CF and CO bonds (G3 values) as a power function of the adiabatic CX stretching force constants  $k^a$  for molecules 1–46. For numbering, see Scheme 1.

there is too much scattering of data points to claim that the two quantities describe bond strength in the same way. BDE values depend on two energy properties, namely, the bond strength and the stability of the dissociation fragments. This is illustrated in Figure 6.



**Figure 6.** Explanation of real, intrinsic, and nonadiabatic bond dissociation energies (BDE, IBDE, and NABDE, respectively). The IBDE is given as the sum  $BDE + E_s$  where the latter term is the stabilization energy of the fragments. The quantity  $E_s$  in turn splits up in the energy lowering caused by density reorganization,  $E_{DR}$ , and the energy lowering caused by geometry relaxation,  $E_{GR}$ . Hence, the NABDE is given as the sum  $BDE + E_{GR}$ .

Upon dissociation of a molecule  $R_2CX$  into  $R_2C$  and  $X$ , the fragments will undergo electronic reorganization followed by a change in the overall geometry (provided a polyatomic fragment is formed). The reorganization process may comprise charge redistribution and rehybridization effects,  $\pi$  delocalization (if one or both dissociation fragments are conjugated systems), hyperconjugation, three-electron delocalization, anomeric delocalization, etc. There is no simple way to determine the



(de)stabilization of the dissociation products by a suitable calculation (let alone an independent experiment), because the reorganization energy is referenced with regard to an artificial state that the dissociation fragments would have if the same electronic features existing in the equilibrium form of the molecule were retained. The corresponding BDE has been called the intrinsic BDE (IBDE, Figure 6)<sup>[53,57]</sup> and can be considered as a true measure of the bond strength. There are no methods available to directly determine IBDE values and hence bond strengths. Instead, one can introduce another BDE quantity and relate it to the adiabatic stretching force constants.

### 3.2. Adiabatic Force Constants and Bond Order

In view of the previous section, we focus on the adiabatic stretching force constants as suitable parameters to determine the bond strength and to derive a bond order. Stretching force constants correspond to the second derivatives of the energy at the equilibrium with regard to the dissociation coordinate, that is, they describe the curvature of the potential energy surface (PES) at the energy minimum in the direction of the bond stretching parameter. Adiabatic stretching force constants are based on the relaxation of all other geometrical parameters upon bond stretching and therefore they relate to the BDE. The latter reflects the bond strength but also the (in)stability of the dissociation products. The question is to what extent (de)stabilization of the products is felt by the adiabatic force constants. For the purpose of answering this question we use the stretching force constants  $k^c$  that are also associated with localized internal coordinate modes. However, they are derived from the  $c$  vectors of Equation (8) under the assumption that a distortion of the internal coordinate  $q_n$  leaves all other internal coordinates  $q_m$  unchanged. Hence, these localized internal  $c$  modes relate to a hypothetical BDE that would not involve any geometry relaxation of the fragments and that might be called nonadiabatic BDE (NABDE).

In Table 1, the stretching force constants  $k^c$  of the nonadiabatic stretching modes are listed. On average, the  $k^c$  values are 0.58 mdyne Å<sup>-1</sup> larger than the  $k^a$  force constants ( $k^c \approx k^a + 0.58$ ), thus reflecting the fact that bond stretching requires more energy for a rigid geometry. There are, however, no other differences, which suggests that the curvature of the PES at the equilibrium point does depend first of all on the CX bond strength and much less on the (in)stability of the dissociation products. Therefore, we take the adiabatic stretching force constants  $k^a(\text{CX})$  ( $X = \text{O}, \text{F}$ ) as a suitable descriptor of the bond strength that relates to the IBDE.

In this sense, anharmonic corrections to the harmonic force constants used do not necessarily improve the procedure developed to obtain a reliable descriptor for the bond strength. Any higher energy derivative (cubic or quartic) with regard to bond stretching introduces more nonlocal features into the  $k^a$  value, which in this way adjusts more to the real dissociation process and the (de)stabilization of the dissociation products as reflected by the BDE values.

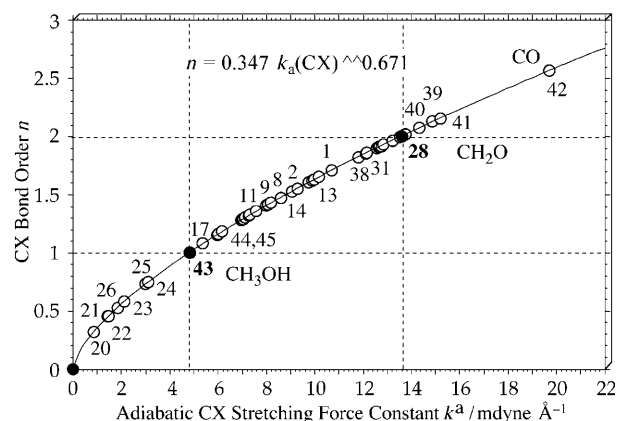
Utilizing the calculated adiabatic stretching force constants  $k^a$ , we have applied the following procedure to derive for CO and CF bonds a bond order  $n$ :

- In view of the fact that we obtained for both CO and CF bonds a single exponential relationship  $k^a = f(R)$  (Figure 4), we seek a common relationship between bond order  $n$  and  $k^a$ .
- Since the calculated BDE values change with  $k^a$ , by and large according to power function (Figure 5), we use a similar function to express the bond order  $n$  as a function of  $k^a$ .
- Two reference values have to be fixed to specify the prefactor and exponent of the power function. For the CF bonds this would lead to some arbitrariness because, besides the CF bond for **17** with  $n = 1$ , there is no other CF bond for which a reasonable value of  $n$  can be specified. For the CO bonds, suitable reference bonds are given by **43** and **28** with  $n = 1$  and  $n = 2$ .
- Because of (a), the same reference bonds are also used for the CF bonds. Consequently, the CF single bond in **17** ( $k^a = 5.39$  mdyne Å<sup>-1</sup>) is by a factor of 1.1 stronger than the CO single bond in **43** (4.84 mdyne Å<sup>-1</sup>), which may be compared with a factor of 1.21 derived from the BDEs of Table 1, although the BDE values do not reflect relative bond strength in a reliable way (Section 3.1).

By following the procedure a) to d) the relationship [Eq. (26)]

$$n(\text{CX}) = 0.347 k^a(\text{CX})^{0.671} \quad (26)$$

shown in Figure 7 is obtained, which exactly fulfills the condition that for  $k^a = 0$  the bond order  $n$  must also be 0. By using Equation (26) and the adiabatic force constant of carbon monoxide (**42**;  $k^a = 19.71$  mdyne Å<sup>-1</sup>, Table 1), a bond order of 2.56 is calculated, which may be compared with a BDE ratio of 2.84 for **42** and **43**. A BDE ratio of 2.56 would result if the BDE of **43** were 10 kcal mol<sup>-1</sup> larger (100.5 kcal mol<sup>-1</sup>) than the calcu-



**Figure 7.** Derivation of the bond order  $n$  as a function of the adiabatic stretching force constant  $k^a$ . The black dots  $n = 1$  (methanol, **43**) and  $n = 2$  (formaldehyde, **28**) give the reference points. The resulting function  $n = f(k^a)$  fulfills the condition  $n = 0$  for  $k^a = 0$ . Bond orders for molecules 1–46 are given. For numbering, see Scheme 1.

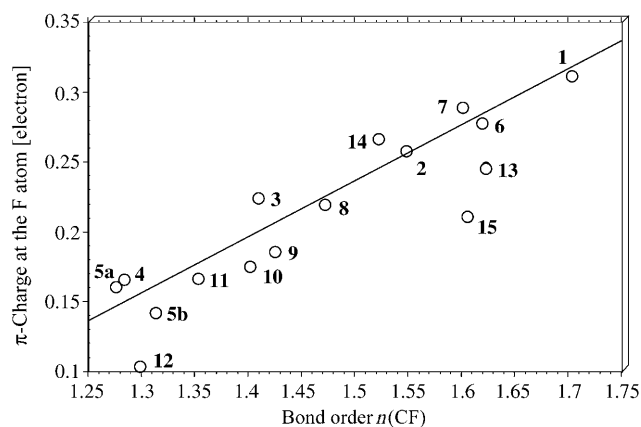
lated value of 90.5 (Table 1). Considering that the methyl radical relaxes from a pyramidal ( $sp^3$  hybridized) form to a planar  $\pi$  radical and that the OH radical has a  $^2\Pi$  state rather than a  $^2A'$  state ( $sp^2$  hybridization at O), a reorganization energy of  $10 \text{ kcal mol}^{-1}$  upon CO dissociation of methanol is reasonable and explains the fact that  $n$  of carbon monoxide is smaller than might be expected on the basis of the BDEs or simple molecular orbital (MO) theory (occupation of one  $\sigma$ - and two  $\pi$ -bonding MOs yields  $n=3$ ). In the following, we will discuss some trends reflected by the bond order  $n$  obtained from Equation (26) (see Table 1 and Figure 7).

### 3.2.1. $CF^+$ Molecule (16)

The carbon monoxide analogue **16** has been observed in interstellar space,<sup>[71]</sup> furthermore, it plays a role in the fragmentation process of F-substituted hydrocarbons in the mass spectrometer<sup>[72]</sup> and in the production of semiconductors.<sup>[73]</sup> Pyykkö et al. considered **16** as a molecule with a triple bond in a comparison of 324 potential triple-bonded systems.<sup>[74]</sup> However, the bond order of **16** is calculated in this work to be 2.0, which describes the bond as somewhat weaker than suggested by the BDE values of **16** and **43** (ratio: 2.21). Again, this suggests a reorganization energy of  $10 \text{ kcal mol}^{-1}$  in the case of **43**. Considering the fact that the adiabatic stretching force constant of **16** is comparable in magnitude to that of **28** ( $13.8$  vs.  $13.6 \text{ mdyne } \text{Å}^{-1}$ , Table 1), a bond order close to 2 is reasonable. Although  $CF^+$  is isoelectronic with  $N_2$  it does not possess a triple bond, which is a result of the increased electronegativity of F and a limited  $\pi$ -donor ability that does not allow it to share both of its  $\pi$ -electron pairs with C (the NBO charge at C is  $+1.164$  electrons).

### 3.2.2. Multiple-Bond Character in Fluoro-Substituted Carbenium Ions

The highest CF double-bond character is found for the formaldehyde analogue **1** ( $n=1.70$ , Table 1). This suggests that a fully established double bond similar to that in **28** cannot be formed, again because of the limited  $\pi$ -donor ability of F. If the  $C=F^+$  bond is part of a conjugated or hyperconjugated system that can interact with the carbenium center,  $\pi$  donation from the F to the C atom is reduced. The bond order of the  $C=F^+$  bond is a sensitive antenna for the degree of conjugation in the substituted carbenium ion and the amount of  $\pi$  charge at the carbenium carbon atom. We confirmed this by calculating the loss of  $\pi$  charge at the F atom (NBO charges) and correlating this value with the calculated bond order  $n$  (see Figure 8). For molecules that do not provide any conjugative effect (e.g., **1**), F is a strong  $\pi$  donor (0.31 electrons) whereas the inclusion of the carbenium center into a fully conjugated system as, for example, in the case of the allyl cation of **12**, reduces  $\pi$  donation to 0.11 electrons (Figure 8). The diagram in Figure 8 confirms that the bond order in F-substituted carbenium ions reflects the degree of double-bond ( $\pi$ -bond) character.



**Figure 8.** Bond orders  $n(C=F^+)$  are related to the NBO  $\pi$  charges at F for molecules **1**–**15**. For numbering, see Scheme 1. B3LYP/6-31G(d,p) calculations.

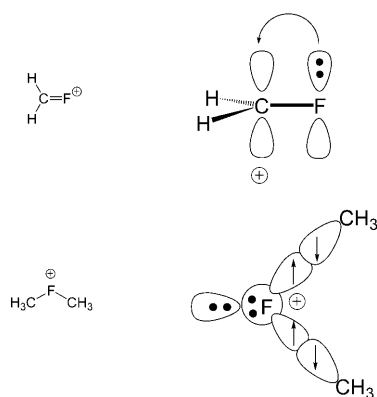
$\pi$  Conjugation as in **8** reduces  $n$  by 0.23 from 1.70 to 1.47, whereas methyl hyperconjugation lowers  $n$  by 0.15 to 1.55 as in **2**. A second methyl group reduces  $n$  by another 0.14 units (**3**:  $n=1.41$ ). A strong conjugative effect is provided by the phenyl group in **4**:  $n$  is reduced by  $\Delta n=0.27$  from 1.55 in **2** down to 1.28. The two  $\pi$ -conjugative systems in **11** also have a strong effect. The bond order is calculated to be 1.35, in line with a  $\Delta n$  of 0.35 relative to  $n(1)$ . The strongest effect ( $\Delta n=0.40$ ) is found for the allyl system **12** ( $n=1.30$ ), as already mentioned above.

In molecule **9**, both hyperconjugation and  $\pi$  conjugation lead to an increase of the  $\pi$  charge at the carbenium C atom and consequently  $n$  is lowered from 1.70 to 1.43. A remote methyl group in **10** leads to further reduction of  $n$  by 0.03. Although these  $\Delta n$  changes are small they are relevant because the adiabatic frequency changes by  $17 \text{ cm}^{-1}$  and the  $k^2$  value by  $0.2 \text{ mdyne } \text{Å}^{-1}$ , which are significant and make it possible to identify these small effects.

One can increase the double-bond character of the  $CF^+$  bond by withdrawing  $\pi$  charge from the carbenium center. This is realized in molecules **6** and **7**, which possess  $n$  values significantly larger (1.62, 1.60; Table 1) than those of their counterparts **9** and **8** (1.43, 1.47). These trends are not reflected by the calculated BDEs because the radical cation generated by dissociation of **7** is strongly stabilized, thus leading to a BDE value of just  $104.6 \text{ kcal mol}^{-1}$ ,  $30 \text{ kcal mol}^{-1}$  below that of **8** (Table 1, Figure 5). Obviously, the bond orders based on the adiabatic stretching force constants are reliable parameters to design CF bonds of desirable strength by suitable substitution at the carbenium center.

### 3.2.3. CF Bonds in Fluoronium Ions

Fluoronium ions possess a different mode of CF bonding, as is pointed out in Scheme 3. For **20**–**23** bond orders between 0.3 and 0.6 (BDE values between  $14$  and  $47 \text{ kcal mol}^{-1}$ , Table 1) are calculated. This is a direct reflection of the fact that F has lost one  $\sigma$  electron (see Scheme 3), the F nucleus is no longer sufficiently shielded, and nuclear repulsion leads to a lengthening



Scheme 3. CF bonding in fluoronium ions.

of the CF bonds. Methyl groups can donate  $\sigma$  density whereas a vinyl group can only donate  $\pi$  density, which helps little to strengthen the CF bonds. Accordingly, **20** has the weakest and **23** the strongest CF bond among the fluoronium ions investigated. Molecule **22** is interesting since repulsion between two positive charges should weaken the CF bond, whereas the chance of establishing CF double-bond character as in **12** should strengthen the CF bond. It seems that these opposing effects compensate each other largely as suggested by a calculated  $n=0.45$  similar to that of **21**.

### 3.2.4. CF Bonds in Transition States

A  $\text{CF}^+$  bond at the point of being broken in a TS of an FH elimination reaction (**24–26**) should be very weak. The calculated CF stretching force constants (Table 1) are between 1.8 and 3  $\text{mdyne \AA}^{-1}$  and the corresponding  $n$  values between 0.5 and 0.7, that is, the CF bonds of TSs **24–26** are stronger than those of the fluoronium ions **20–23**. This result shows that fluoronium ion bonding is not realized in the TSs because the F–H distances are still very large, whereas the CF bonds are only lengthened by 0.2  $\text{\AA}$  from 1.31 to 1.51–1.57  $\text{\AA}$  (Table 1). The reactions investigated are strongly exothermic and accordingly the respective TS is positioned early along the reaction path. Also, the calculated bond orders suggest that CF bond breaking precedes FH bond formation. However, further investigations have to confirm this.<sup>[75]</sup> TS **27** does not include a breaking of the CF bond. Therefore, the CF bond order is comparable to that in **4**.

## 4. Comparison of the Isoelectronic Bonds

The fact that CO and CF bonds of different types can be described by one bond parameter  $k^a$  shows that these bonds are closely related (Figure 4). One could conclude that there should be an even closer relationship between the CO and the CF bond if these are isoelectronic, as in the case of the  $\text{C=O}$  and the  $\text{C=F}^+$  bonds. However, this is not confirmed by the data in Table 1. The  $\text{C=O}$  bond is 30–50  $\text{kcal mol}^{-1}$  stronger than the  $\text{C=F}^+$  bond, has a much shorter bond length, and is much stiffer, that is, variations in BDE,  $R$ ,  $\omega^a$ ,  $k^a$ , and the bond

density are much smaller than in the case of the  $\text{C=F}^+$  bond. Since both C and O contribute one  $\pi$  electron for the formation of the CO  $\pi$  bond, charge transfer from C to O is much less sensitive to substituent effects than  $\pi$  transfer from F to C in the  $\text{C=F}^+$  bond.

In line with these observations is also the fact that trends in the  $\text{C=F}^+$  bond properties do not correlate with those observed for the bond properties of the  $\text{C=O}$  bond. For closely related bonds as in the series **28–30** and **1–3** some similarities can be found; however, these change strongly when considering **36–38** and **9–11**. In short, the  $\text{C=F}^+$  bond as an antenna for substituent effects behaves differently and much more sensitively than the  $\text{C=O}$  bond.

## 5. Conclusions

This work has shown that BDE, bond length, stretching frequency, or bond density are not reliable parameters to describe the strength of a bond. A reliable descriptor of the bond strength is the stretching force constant provided it is determined for adiabatic internal coordinate modes that are localized in the bond fragment and do not couple with other vibrational modes. We have also shown that the adiabatic stretching force constant can be used to derive a bond order. The fact that CO and CF adiabatic stretching force constants can be presented by one exponential function depending on the bond length  $R(\text{CX})$  made it possible to take as suitable reference bonds the CO bond in methanol and formaldehyde ( $n=1$  and  $n=2$ ), thus refraining from arbitrarily fixing bond-order values for two CF bonds.

Utilizing the adiabatic force constants and the bond orders derived from the latter, we can distinguish between CF bonds in fluorinated carbenium ions that involve  $\text{sp}$ -hybridized fluorine donating  $\pi$  density to C and CF bonds in fluoronium ions that involve divalent  $\text{sp}^2$ -hybridized F cations. A true  $\text{CF}^+$  double bond is realized in the case of the diatomic  $\text{C=F}^+$  (**16**). In all other cases, the double-bond character is between 1.3 and 1.7, in line with most of the relatively large BDEs.

Although the adiabatic force constant relates to the BDE rather than the IBDE of a bond, in the harmonic approximation it is strongly localized and therefore does not reflect (de)stabilization of the bond dissociation products. This fact makes the adiabatic force constants a suitable descriptor of bond strength and bond order.

It will be interesting to extend the current work to other carbon–halogen bonds and to investigate whether these can also be compared with the corresponding carbon–chalcogen bonds. Work is in progress to extend the application of the adiabatic mode concept in this way and to exploit vibrational spectroscopy as a major tool for describing bond strength and the electronic structure of molecules.

The adiabatic mode concept can be applied for any atom combination within a molecule and therefore it is possible to describe nonclassical bonds, H bonding, agostic bonds, or any nonbonded intramolecular interaction. In the case of intermolecular interactions, one has to define a supermolecule or intermolecular complex and determine the adiabatic modes for this

system. In this way, host–guest interactions in endohedral compounds or any other intermolecular interaction can be described with the appropriate adiabatic force constants. The derivation of a bond order from the AIMO force constants as achieved in this work requires suitable reference systems, for which standard bond orders are set and the corresponding interaction energies are calculated.

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