

Are Carbon—Halogen Double and Triple Bonds Possible?

Robert Kalescky, Elfi Kraka, and Dieter Cremer*

The carbon—halogen and carbon—chalcogen bonding of 84 molecules was investigated utilizing local vibrational modes calculated at the M06-2X/cc-pVTZ level of theory including anharmonicity corrections in all cases. The relative bond strength order of each CX or CE bond ($X = \text{F, Cl}; E = \text{O, S}$) was derived from the local CX or CE stretching force constant and compared with trends of calculated bond lengths r and bond dissociation energies (BDE) obtained at the G3 level of theory. It is shown that both bond length r and BDE are not reliable bond strength descriptors. The CX double bond is realized for some Cl-substituted carbenium ions, however, not for the cor-

responding F-derivatives. Diatomic CF^+ and CCl^+ possess fully developed double bonds but not, as suggested in the literature, triple bonds. Halonium ions have fractional (electron-deficient) CX bonds, which can be stabilized by σ -donor substituents or by an increased polarizability of the halogen atom as with Cl. Bridged halonium ions are more stable than their acyclic counterparts, which results from more effective two-electron-three-center bonding. © 2014 Wiley Periodicals, Inc.

DOI: 10.1002/qua.24626

Introduction

Halogens such as fluorine or chlorine are known to establish single bonds with C in line with their monovalent character.^[1] In this work, we investigate whether F or Cl can form double or even triple bonds with C in situations where the carbon atom carries a positive charge as in carbenium ions. In such situations, there should be a donation of negative charge from a halogen $p\pi$ lone pair orbital into the empty $2p\pi(\text{C})$ orbital of the carbenium ion thus leading to partial π -bonding (see Fig. 1). In view of the high electronegativity of F ($\chi=3.98$) or even Cl ($\chi=3.16$),^[2] there should be little tendency for F or Cl to form π -bonds via π -back donation. However, both atoms withdraw from C σ -density, which could increase their π -donor capacity. Of course, this argument overlooks the fact that with the positive charge at C its electronegativity increases and, thereby, the transfer of σ -density to the halogen is reduced. Considering all these arguments, it is hard to predict whether a halogen X ($X = \text{F, Cl}$) can establish a fully developed double bond with carbon.

Apart from these electronic structure arguments, there is also the question of how a double bond is defined. In chemistry, this is normally done by using suitable reference bonds. To eliminate core effects, these should be formed from atoms of the same period, that is, it is reasonable to compare the degree of double bonding in a fluorocarbenium or chlorocarbenium ion with that of formaldehyde or thioformaldehyde. Apart from this, there is still the problem of whether the comparison should be done on the basis of bond dissociation energies (BDE), bond lengths, bond electron densities, or other bond properties. For a chemist, the most important quantity is bond strength as it is the decisive quantity determining the stability or reactivity of a molecule. However, a direct definition of bond strength, for example in terms of energy quantities, is an unsolved problem. Therefore, we pursue in this work a completely different approach.

To determine bond strength, we use a dynamic property of the bond. By moving the atoms out of their equilibrium position, a restoring force proportional to the bond strength can be measured. The displacement of the atoms must be such that the electronic structure does not change, which also would change the bond strength. A molecular vibration probes the strength of a bond via small displacements of the nuclei from their equilibrium positions, which are accompanied by small, but finite electronic structure changes.^[3] Nevertheless, the associated force constant correctly reflects the strength of the bond because it corresponds to an infinitesimally small displacement, which does not lead to any electronic structure change of the molecule. Hence, reliable bond strength information can be gained from measured or calculated vibrational spectra provided suitable stretching force constants can be extracted from them.

Over the last 50 years, there is an extended literature documenting numerous attempts to derive bond strength information from vibrational force constants or indirectly from vibrational frequencies, which are less suitable as they depend on the atomic masses^[4–13] (additional references are summarized in Ref. [14]). Most importantly, any attempt to use normal vibrational mode properties for this purpose is flawed by the fact that normal modes are the result of mode–mode coupling. Accordingly, they are delocalized and do not describe the stretching of an individual bond of a molecule. This problem was circumvented by Konkoli and Cremer, who solved the vibrational equation in the mass-decoupled form so that local

R. Kalescky, E. Kraka, and D. Cremer
Computational and Theoretical Chemistry Group (CATCO), Department of
Chemistry, Southern Methodist University, Dallas, Texas, 75275
E-mail: dieter.cremer@gmail.com

Contract grant sponsor: National Science Foundation;
contract grant number: CHE 1152357

© 2014 Wiley Periodicals, Inc.

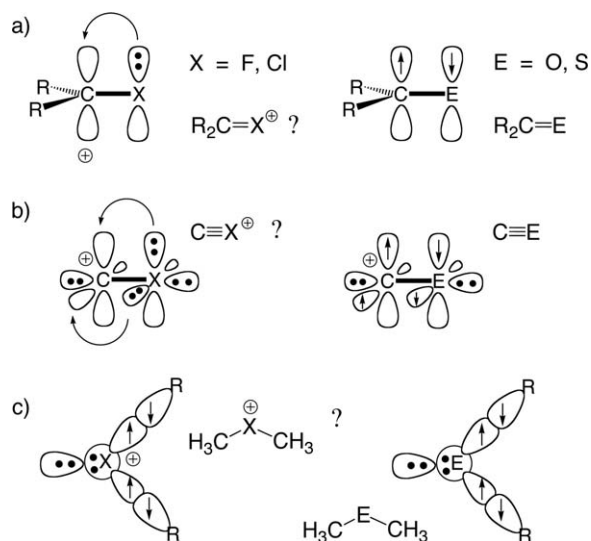


Figure 1. Monovalent halogen X may establish (a) a double or even and (b) a triple bond formally via π -donation from an X lone pair orbital. (c) Divalent X^{\oplus} may be found in halonium ions. Molecules on the left are isoelectronic with the corresponding chalcogen molecules on the right. For the definition of monovalent or divalent X, see text.

rather than normal vibrational modes could be obtained, which are free of any mode–mode coupling.^[15]

Each local vibrational mode is associated with an internal coordinate, the changes of which drive the local mode (leading parameter principle^[15]). The Konkoli–Cremer local modes and their properties are independent of all other internal coordinates used to describe the geometry of a molecule, which is not the case for the normal modes. The local mode frequencies and force constants can be determined from a complete set of measured fundamental frequencies utilizing perturbation theory.^[16] In this way, one can distinguish between calculated harmonic local mode frequencies (force constants) and experimentally based local mode frequencies (force constants), which differ by anharmonicity effects.^[17,18] Each normal vibrational mode can be decomposed into local vibrational mode contributions.^[14,19] Most importantly, local modes can be directly related to the normal vibrational modes via an adiabatic connection scheme.^[20,21] Each local mode is characterized by mode mass, mode force constant, mode frequency, and mode intensity.^[15,16]

Local modes are perfectly suited to describe the strength of CX bonds in a quantitative rather than just qualitative way. The information gained in this way provides an important insight into the structure, stability, and reactivity of CX containing compounds, which are relevant in many areas of chemistry ranging from synthesis,^[1] spectroscopy,^[22,23] reaction mechanism, and reaction dynamics^[24–27] to astrochemistry.^[28]

Halogenes can stabilize radical intermediates via three-electron (3e) interactions.^[29] The stabilization of carbenium ions by α -halogen substituents is even stronger.^[30] Therefore, the thermochemistry of these molecules and halogen stabilization energies have been thoroughly investigated by Raabe et al.^[31] Spectroscopic evidence for partial CF double bonding in carbenium ions was reported by Morton and

coworkers^[27,32] and quantum chemically confirmed by Kraka and Cremer.^[33] In these ions, the halogen becomes positively charged and (partially) establishes double bond. Therefore, it can be considered (at least formally) to be divalent, which is typical of a halonium ion. However, in this work, we will refrain from using the term halonium ion for X-substituted carbenium ions as we reserve this term for the situation where a positively charged halogen is bonded to two rather than one carbon atom.

It has been speculated that CX^{\oplus} ions possess a triple bond^[34] and we also investigate this possibility. To set CX multiple bonds into the right perspective, we include normal CX single bonds and some halonium bonds into the investigation. In each case, we compare these bonds with the corresponding chalcogen bond CE ($E = \text{O, S}$) in line with the extended Badger rule^[35] and discuss how carbon–halogen bonds differ from the corresponding carbon–chalcogen bonds. The investigation presented in this article is based on the vibrational properties of the 84 molecules shown in Figure 2.

By analyzing the local stretching force constants of CX and CE bonds, a number of chemically relevant questions are answered: (i) How can a suitable bond strength descriptor be derived from the normal vibrational frequencies, which facilitates the discussion of CX or CE bonding? (ii) How does the bond strength vary in comparison to the BDE or bond length r , that is what are the shortcomings of bond strength descriptors based on BDE or r values?—(iii) Does fluorine or chlorine stabilize a carbenium ion better?—(iv) Can one observe a true CF or CCl double or even triple bond?—(v) Can one differentiate between special types of CX bonds or is there a continuous transition from weak to strong CX bonding?—(vi) What is the nature of CX bonding in halonium ions and how can these bonds be strengthened?

The results of this work are presented in the following way. In section Local Vibrational Modes and Relative Bond Strength Orders, the methodology leading to local stretching force constants are summarized and a suitable bond strength descriptor is derived. In section Results and Discussion, the focus is on the identification of CX double and triple bonds, their comparison with the corresponding CE bonds, and the fractional CX bonds of halonium ions. Finally, in the last section the conclusions of this work are summarized.

Local Vibrational Modes and Relative Bond Strength Orders

The search for a procedure to obtain local modes was triggered by the work of Decius and others on compliance constants,^[4] that of McKean on isolated CH stretching modes,^[5–7,36] and that of Henry on the local modes obtained by overtone spectroscopy.^[8] Analyzing McKean's work on isolated CH and NH stretching frequencies, Cremer and coworkers realized that local vibrational modes can be easily obtained by solving the mass-decoupled Euler–Lagrange equations.^[15,16,19,37,38] The local modes, which they obtained in this way, fulfill all criteria for deriving reliable bond strength descriptors. A number of investigations document

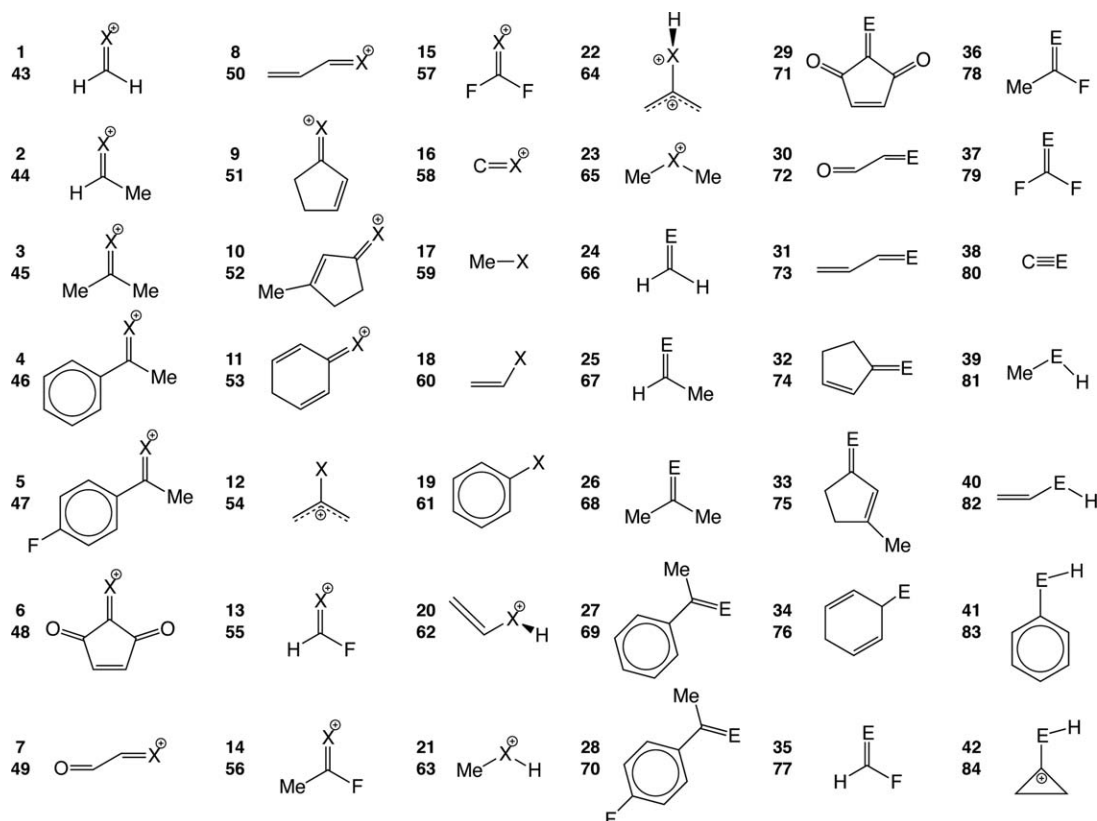


Figure 2. Halogen (X) and chalcogen (E) containing molecules: X = F: 1–23; X = Cl: 43–65; E = O: 24–42; and E = S: 66–84.

the usefulness of the local vibrational modes.^{[14],[16–18,21,33],[35,39]}

In the following, the procedure for determining local vibrational modes and their properties is outlined:

The basic equation of vibrational spectroscopy is given by^[40]

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

where \mathbf{F}^q is the force constant matrix in internal coordinates, \mathbf{G} is Wilson's kinetic energy matrix, \mathbf{D} collects the normal mode vectors in internal coordinates, and $\mathbf{\Lambda}$ is a diagonal matrix with $3N - L = N_{\text{vib}}$ vibrational eigenvalues $\lambda_{\mu} = 4\pi^2 c^2 \omega_{\mu}^2$ (ω_{μ} : frequency of normal mode μ ; c : speed of light; N : number of atoms in the molecule; L : number of translational and rotational degrees of freedom). Diagonalization of the force constant matrix yields matrix $\mathbf{K} = \mathbf{D}^{\dagger} \mathbf{F}^q \mathbf{D}$ that contains the force constants k_{μ} associated with frequency ω_{μ} of a given mode μ on its diagonal.

Local mode vectors \mathbf{a}_n can be determined using the diagonal matrix \mathbf{K} and the mode vectors \mathbf{d}_{μ} of the normal modes:^[15,20]

$$\mathbf{a}_n = \frac{\mathbf{K}^{-1} \mathbf{d}_n^{\dagger}}{\mathbf{d}_n \mathbf{K}^{-1} \mathbf{d}_n^{\dagger}} \quad (2)$$

where \mathbf{d}_n is a row vector of matrix \mathbf{D} associated with internal coordinate q_n . The local mode force constant k_n^a is given by Eq. (3):

$$k_n^a = \mathbf{a}_n^{\dagger} \mathbf{K} \mathbf{a}_n \quad (3)$$

and the local mode frequency ω_n^a can be obtained from

$$(\omega_n^a)^2 = \frac{G_{nn} k_n^a}{4\pi^2 c^2} \quad (4)$$

where the G -matrix element G_{nn} corresponds to the local mode mass.^[15] In these equations, the superscript a refers to the adiabatic nature of the local vibrational modes: with a finite displacement of the nuclei involved in a local mode, the positions of the remaining atoms of the molecule are adiabatically relaxed, which leads to a decoupling from other modes in the molecule.

Although local modes associated with two-, three-, four-atom, or multiatom units can be obtained,^[17,18,20,35] we focus in this work exclusively on local bond stretching modes to obtain reliable bond strength descriptors for 46 CX containing molecules (23 different CF and 23 different CCl bonds). To this end, we follow a five-step strategy: (i) We calculate for the F- and Cl-containing molecules the complete sets of N_{vib} normal vibrational modes utilizing the harmonic approximation. (ii) Then, we improve the harmonic vibrational frequencies by calculating anharmonic corrections. (iii) Next, local modes and their properties are derived for both the harmonic and anharmonically corrected modes. (iv) Then, the local mode stretching force constants are used to determine relative bond strength orders (RBSOs),^[35] which makes it possible to analyze

the strength of a bond in relation to a reference molecule. (v) Finally, RBSO values are compared with other bond properties such as bond lengths r or BDE values.

To determine the RBSO value of a bond, suitable reference bonds have to be chosen, which represent a typical single, double, or triple bond according to common chemical understanding. However, in the case of the CX bond, only the prototypical single bond as in $\text{H}_3\text{C}-\text{X}$ is known. In such a situation, the Badger rule^[41] or its extension given by Kraka et al. can be used.^[14,35] According to Badger, stretching force constants k and bond lengths r of diatomic molecules follow one common power relationship, provided only atoms from the same period of the periodic table are involved in bonding. Kraka et al. extended the Badger-rule to polyatomic molecules using local stretching force constants.^[14,42] Their extension of the Badger rule says: "Different bonds between atoms of the same period can be described by one common power relationship relating local mode stretching force constants to bond orders or RBSOs as suitable bond strength descriptors."

Utilizing the extended Badger rule, a power relationship for determining RBSO values from stretching force constants k^a can be derived for CX bonds by referring to CE bonds where E is a chalcogen such as O in the case $\text{X} = \text{F}$ and S in the case $\text{X} = \text{Cl}$. For CO bonds, one can use the methanol CO bond as the typical CO single bond with $\text{RBSO} = 1.00$ and the formaldehyde CO double bond with $n = 2.00$. To set up the power relationship, these two reference bonds are combined with the requirement that for $k^a = 0$ the RBSO value is also zero. Utilizing these references, the CF-bond order of $\text{H}_3\text{C}-\text{F}$ will no longer be 1.00. One can simplify the discussion by shifting $n(\text{H}_3\text{C}-\text{F})$ to 1.00 and discussing all CF bonds relative to that value (in which case we would speak of a bond order rather than a RBSO). However, we keep the CO bond as a suitable reference and compare each CX bond type with the corresponding CE bond type, thus extending the investigation by another 38 CE containing molecules to 84 (see Fig. 2).

According to the Badger rule, different power relationships have to be derived for CCl and CF bonds. It is reasonable to use the thioanalogs of methanol and formaldehyde as references. This procedure excludes that RBSO values for CO and CS (CF and CCl) bonds are directly compared and the misleading conclusion is averted that $\text{H}_2\text{C}=\text{O}$ and $\text{H}_2\text{C}=\text{S}$ have the same $\text{C}=\text{E}$ bond strength. For a direct comparison, the corresponding $k^a(\text{CO})$ and $k^a(\text{CS})$ have to be used. On this basis, it is possible to derive a single power relationship for all 84 molecules investigated in this work. Since only relative trends in bond strengths are discussed in this work, we refrain from deriving such a relationship.

For the calculation of the vibrational frequencies and force constants, we have used density functional theory based on the hybrid exchange-correlation functional M06-2X.^[43] Recent work by Kozuch and Martin^[44] shows that, among 40 different XC functionals tested, M06-2X provides the best account of geometries and binding energies for halogen bonds. Similar observations were also made for other halogen containing molecules.^[45] In this work, only a few XC functionals (M06-2X, B3LYP, BLYP, $\omega\text{B97X-D}$) were tested and it was determined that the M06-2X functional reliably describes vibrational properties.

All calculations were carried out with a Dunning-type correlation-consistent valence triple zeta basis set (cc-pVTZ).^[46] An ultrafine grid with 99 radial shells and 509 angular points per shell was used to guarantee reliable frequencies. Molecular geometries were optimized at the M06-2X/cc-pVTZ level and verified to correspond to a potential energy surface minimum via vibrational frequency calculations using the harmonic approximation. The same level of theory was used to obtain anharmonic corrections with the second-order vibrational perturbation theory method.^[47] Reliable BDE values were obtained for all CX and CE bonds using the Gaussian-3 (G3) method.^[48] Following the standard representation of G3 results,^[48] all BDE values given in this work include ZPE (zero-point energy) corrections. In those cases, where measured bond dissociation enthalpies at 298 K [BDH(298)] are available,^[49] BDH(298) were calculated for reasons of comparison. The local mode properties were determined using the program ADIA by Konkoli and Cremer^[15,16] as developed for the program package COLOGNE2013.^[50] The G3 calculations were carried out using Gaussian 09.^[51]

Results and Discussion

The 84 molecules studied in this work are shown in Figure 2. For each CX and CE bond, the calculated bond length r , the BDE, the local mode force constant, the local mode frequency, and the RBSO value is listed in Tables 1 and 2. Vibrational properties based on the harmonic and the anharmonic approximation are compared. RBSO values given as a function of the stretching force constant are shown in Figure 3a (CF and CO bonds) and Figure 3b (CCl and CS bonds).

The comparison of harmonic and anharmonically corrected local stretching frequencies ω_{harm}^a and ω_{anharm}^a , respectively, reveals that the trends in dependence of the bond type are similar, if not to say identical in many cases. The same holds for the corresponding stretching force constants k^a . Differences between them are best assessed with the help of the RBSO values n_{harm} and n_{anharm} listed in Tables 1 and 2 (see also Figs. 3a and 3b). In general, anharmonically corrected force constants lead to 2–7% smaller RBSO values than harmonic values in the cases of the CF and CO bonds. The differences are somewhat smaller for the CCl and CS bonds. This decrease is a result of the well-known fact that harmonic force constants exaggerate the bond strength, which is more pronounced for stronger than for weaker bonds.

There are some exceptions from the general trends. The CCl and CS normal stretching modes appear at frequencies below 1200 cm^{-1} where they can couple with bending modes. The coupling pattern is affected by the anharmonicity and this can lead to a slight increase in the local mode stretching frequency and force constant. However, in general, these effects are small and do not influence the trends reflected by the curves in Figures 3a and 3b (harmonic: circles; anharmonic: triangles).

Before discussing RBSO values in more detail, we consider the question whether bond lengths and BDE values can be used as reliable bond strength descriptors. In Figure 3, RBSOs

Table 1. Bond properties for the CF and CO bonds in molecules 1–42 (M06-2X/cc-pVTZ and G3 calculations).^[a]

	Molecule	Sym.	<i>r</i> (Å)	BDE (kcal mol ⁻¹)	Harmonic			Anharmonic		
					<i>k</i> ^a (mdyn/Å)	ω^a (cm ⁻¹)	<i>n</i>	<i>k</i> ^a (mdyn/Å)	ω^a (cm ⁻¹)	<i>n</i>
1	[H ₂ CF] ⁺	C _{2v}	1.226	149.7	11.343	1618	1.713	10.153	1531	1.639
2	[MeHCF] ⁺	C _s	1.248	133.8	9.748	1500	1.543	8.536	1404	1.460
3	[Me ₂ CF] ⁺	C ₂	1.267	132.3	8.509	1401	1.405	8.271	1382	1.430
4	[PhMeCF] ⁺	C _s	1.295	128.7	7.383	1305	1.274	7.294	1297	1.315
5		C _s	1.297	126.6	7.290	1297	1.263	7.019	1273	1.282
6		C _{2v}	1.230	144.2	10.874	1584	1.664	10.215	1535	1.646
7	[O=CHCHF] ⁺	C ₁	1.284	106.8	7.717	1335	1.314	7.516	1317	1.342
8	[H ₂ C=CHCHF] ⁺	C _s	1.264	134.8	8.959	1438	1.456	8.831	1428	1.494
9		C _s	1.275	134.3	8.492	1400	1.403	8.106	1368	1.411
10		C _s	1.280	132.7	8.274	1382	1.378	7.833	1345	1.379
11		C _{2v}	1.291	128.9	7.858	1347	1.330	7.596	1324	1.351
12		C _{2v}	1.312	121.8	7.349	1302	1.270	7.090	1279	1.290
13	[HCF ₂] ⁺	C _s	1.227	142.5	10.785	1578	1.654	10.295	1541	1.654
14	[MeCF ₂] ⁺	C _s	1.245	137.1	9.377	1471	1.502	9.178	1455	1.533
15	[CF ₃] ⁺	D _{3h}	1.229	138.4	10.634	1567	1.638	9.982	1518	1.621
16	[CF] ⁺	C _{∞v}	1.151	179.3	14.756	1845	2.053	13.467	1763	1.979
17	H ₃ CF	C _{3v}	1.377	109.2	5.614	1138	1.055	5.386	1115	1.075
18	[H ₂ C=CHF] ⁺	C _s	1.339	123.3	6.373	1213	1.151	5.892	1166	1.141
19	PhF	C _{2v}	1.342	128.5	6.395	1215	1.154	5.961	1173	1.150
20	[H ₂ C=CH(FH)] ⁺	C _s	1.620	13.3	0.983	476	0.318	0.639	384	0.260
21	[H ₃ CFH] ⁺	C _s	1.588	28.7	1.628	613	0.450	1.383	565	0.434
22		C _s	1.527	29.7	1.963	673	0.511	1.668	620	0.492
23	[H ₃ CFCH ₃] ⁺	C _{2v}	1.506	46.7	2.513	762	0.606	2.281	726	0.606
24	H ₂ C=O	C _{2v}	1.195	177.8	14.204	1875	2.000	13.686	1841	2.000
25	MeHC=O	C _s	1.199	183.0	13.789	1848	1.960	13.226	1809	1.955
26	Me ₂ C=O	C ₂	1.204	186.1	13.338	1817	1.915	12.690	1772	1.902
27	PhMeC=O	C _s	1.208	178.2	12.914	1788	1.873	12.420	1753	1.875
28		C _s	1.208	179.6	12.886	1786	1.870	12.323	1747	1.865
29		C _{2v}	1.189	171.1	14.465	1892	2.025	13.924	1857	2.023
30	O=CHCH=O	C ₁	1.196	171.9	13.954	1859	1.976	13.395	1821	1.972
31	H ₂ C=CHCH=O	C _s	1.202	172.6	13.451	1825	1.926	12.658	1770	1.899
32		C _s	1.203	182.7	13.261	1812	1.908	12.736	1776	1.906
33		C _s	1.204	184.5	13.152	1804	1.897	12.713	1774	1.904
34		C _{2v}	1.213	173.2	12.562	1763	1.838	12.160	1735	1.848
35	HFC=O	C _s	1.173	200.3	15.448	1956	2.119	14.846	1917	2.111
36	MeFC=O	C _s	1.178	203.5	14.874	1919	2.065	14.430	1890	2.072
37	F ₂ C=O	C _{2v}	1.167	214.0	15.873	1982	2.159	15.449	1956	2.168
38	CO	C _{∞v}	1.122	256.7	20.911	2275	2.611	18.559	2143	2.450
39	H ₃ COH	C _s	1.413	89.9	5.194	1134	1.000	4.835	1094	1.000
40	H ₂ C=CH(OH)	C _s	1.361	110.4	6.175	1236	1.127	5.943	1213	1.147
41	PhOH	C _s	1.361	112.7	6.185	1237	1.128	6.095	1228	1.167
42		C _s	1.248	115.7	10.700	1628	1.645	10.273	1595	1.652

[a] CF or CO bond length *r*, bond dissociation energy BDE(CF) or BDE(CO), local stretching force constant *k*^a, local stretching frequency ω^a , and relative bond strength order (RBSO) *n*. The BDE values include ZPE corrections. To facilitate the readability of the data, molecular formulas, which can be easily presented, are given in the second column.

are given as a function of harmonic and anharmonically corrected local mode force constants. Anharmonic corrections lower the harmonic frequencies and bring them in better agreement with measured frequencies. This also holds for the local mode force constants and frequencies. However, the difference between the anharmonically corrected (circles) and harmonic (triangles) data is minimal, that is, both sets of data display the same trends.

In Figures 4 and 5, the local mode force constants *k*^a, calculated using the harmonic approximation, are compared with bond lengths *r* for all CF, CO, CCl, and CS bonds. Although there are closely related power relationships between *k*^a and *r* (indicated by a solid line for CF bonds and by a dashed line

for CO bonds), these are more qualitative than quantitative, that is the scattering of data points is significant, especially for the CF bonds. Apart from carbon monoxide, only two types of CO bonds (single and double) are compared in this work, which prevents a strong scattering of the CO data points (*R*^[2] = 0.996). However, four different CF bond types are considered: CF⁺, F-substituted carbenium ions with partial double bond character, normal CF single bonds, and CF bonds in halonium structures.

For each of the four types of bonds, F and, even more so, the C atoms bonded to F exhibit different covalent radii, which leads to a preference for different bond length ranges. The covalent radius depends on the charge at F (from positive to

Table 2. Bond properties for the CCl and CS bonds in molecules **43–84** (M06-2X/cc-pVTZ and G3 calculations).^[a]

	Sym.	Mol.	<i>r</i> (Å)	BDE (kcal mol ⁻¹)	Harmonic			Anharmonic		
					<i>k</i> ^a (mdyn/Å)	ω^a (cm ⁻¹)	<i>n</i>	<i>k</i> ^a (mdyn/Å)	ω^a (cm ⁻¹)	<i>n</i>
43	C _{2v}	[H ₂ CCl] ⁺	1.588	132.5	6.754	1133	1.886	6.827	1139	1.994
44	C _s	[MeHCCl] ⁺	1.618	108.7	5.717	1042	1.652	5.598	1031	1.695
45	C ₂	[Me ₂ CCl] ⁺	1.645	102.0	4.853	960	1.450	4.588	934	1.441
46	C _s	[PhMeCCl] ⁺	1.684	96.4	4.146	888	1.279	4.501	925	1.419
47	C _s		1.688	94.4	4.104	883	1.268	4.117	884	1.319
48	C _{2v}		1.587	128.3	6.552	1116	1.841	6.116	1078	1.822
49	C ₁	[O=CHCHCl] ⁺	1.599	84.3	6.302	1094	1.785	6.092	1076	1.817
50	C _s	[H ₂ C=CHCHCl] ⁺	1.637	109.0	5.243	998	1.542	5.268	1000	1.613
51	C _s		1.657	106.1	4.854	960	1.450	4.732	948	1.478
52	C _s		1.664	104.0	4.722	947	1.418	4.918	967	1.525
53	C _{2v}		1.678	99.2	4.491	924	1.363	4.403	915	1.393
54	C _{2v}		1.707	93.3	4.225	896	1.298	5.289	1002	1.618
55	C _s	[HFCCl] ⁺	1.604	117.3	6.095	1076	1.738	7.071	1159	2.052
56	C _s	[MeFCCl] ⁺	1.628	106.8	5.327	1006	1.561	5.283	1002	1.617
57	C _{2v}	[F ₂ CCl] ⁺	1.614	115.4	5.790	1049	1.669	5.773	1047	1.738
58	C _{∞v}	[CCl] ⁺	1.534	152.1	7.768	1215	2.109	7.269	1175	2.099
59	C _{3v}	H ₃ CCl	1.783	81.9	3.218	782	1.045	2.987	753	1.015
60	C _s	[H ₂ C=CHCl] ⁺	1.733	93.6	3.630	830	1.150	3.829	853	1.243
61	C _{2v}	PhCl	1.739	99.0	3.626	830	1.149	3.585	825	1.178
62	C _s	[H ₂ C=CH(CIH)] ⁺	1.831	28.3	1.703	569	0.629	1.591	550	0.606
63	C _s	[H ₃ CCIH] ⁺	1.857	46.6	1.836	591	0.668	1.824	589	0.678
64	C _s		1.819	58.1	2.312	663	0.803	2.153	640	0.777
65	C _{2v}	[H ₃ CCICH ₃] ⁺	1.821	64.7	2.278	658	0.794	2.207	648	0.792
66	C _{2v}	H ₂ C=S	1.601	130.4	7.268	1189	2.000	6.853	1155	2.000
67	C _s	MeHC=S	1.609	133.2	6.892	1158	1.917	6.740	1145	1.973
68	C ₂	Me ₂ C=S	1.619	134.8	6.570	1131	1.845	5.784	1061	1.741
69	C _s	PhMeC=S	1.629	128.2	6.167	1095	1.755	5.700	1060	1.721
70	C _s		1.629	129.0	6.075	1087	1.734	5.654	1049	1.709
71	C _{2v}		1.594	128.8	7.293	1191	2.005	6.698	1141	1.963
72	C ₁	O=CHCH=S	1.604	126.1	7.042	1170	1.950	6.716	1143	1.967
73	C _s	H ₂ C=CHCH=S	1.617	125.1	6.657	1138	1.865	6.550	1129	1.927
74	C _s		1.624	133.9	6.341	1111	1.794	6.046	1084	1.805
75	C _s		1.627	135.8	6.242	1102	1.772	5.937	1075	1.779
76	C _{2v}		1.637	126.7	6.014	1082	1.720	5.886	1070	1.766
77	C _s	HFC=S	1.590	140.2	7.257	1188	1.998	6.981	1165	2.030
78	C _s	MeFC=S	1.602	142.6	6.807	1151	1.898	6.160	1095	1.833
79	C _{2v}	F ₂ C=S	1.592	152.4	6.998	1167	1.941	6.747	1146	1.975
80	C _{∞v}	CS	1.528	170.9	9.410	1353	2.457	8.492	1285	2.383
81	C _s	H ₃ CSH	1.816	72.2	3.045	770	1.000	2.934	755	1.000
82	C _s	H ₂ C=CH(SH)	1.763	88.4	3.436	818	1.101	2.521	700	0.883
83	C _s	PhSH	1.770	89.8	3.413	815	1.095	3.211	790	1.076
84	C _s		1.614	90.7	5.957	1077	1.707	5.605	1044	1.697

[a] CCl or CS bond length *r*, bond dissociation energy BDE(CF) or BDE(CO), local stretching force constant *k*^a, local stretching frequency ω^a , and relative bond strength order (RBSO) *n*. The BDE values include ZPE corrections. To facilitate the readability of the data, molecular formulas, which can be easily presented, are given in the third column.

significantly negative) and C, which does not necessarily have to do with the bond strength, although there should be some qualitative relationship. Because of the complex situation resulting for the different CF bond types, the CF data tends to a stronger scattering ($R^{[2]} = 0.986$).

The scattering of data points is stronger for CCl ($R^{[2]} = 0.967$) and CS ($R^{[2]} = 0.986$, Fig. 5), which has to do with the larger polarizabilities of Cl and S (as compared to F and O) and the resulting larger variation of the covalent radii of these third row atoms. Badger solved this problem by introducing empirical compressibility parameters that account for the influence of core shells on the covalent radius. However, such parameters cannot account for changes in the valence shell. Therefore, it is difficult to determine effective bond lengths

that can be used as reliable bond strength descriptors. Some of our recent results indicate that this may be even impossible for principal reasons.^[42] In any case, there exist *k*^a–*r* relationships for the four bond types investigated, which are in line with the extended Badger rule.^[14,35] The hard-sphere assumption of the Badger rule is less applicable for elements from the third period and care has to be taken when assuming that a shorter bond is necessarily a stronger bond.

In Table 3, calculated BDH(298) values obtained with the G3 method are compared with measured values. Apart from larger deviations found for CF⁺ and CCl⁺ (see below), the average deviation is 1.1 kcal/mol. Hence, the calculated BDE values can be considered as being reliable. Their potential as bond strength descriptors is analyzed in Figures 6 and 7. There is some kind

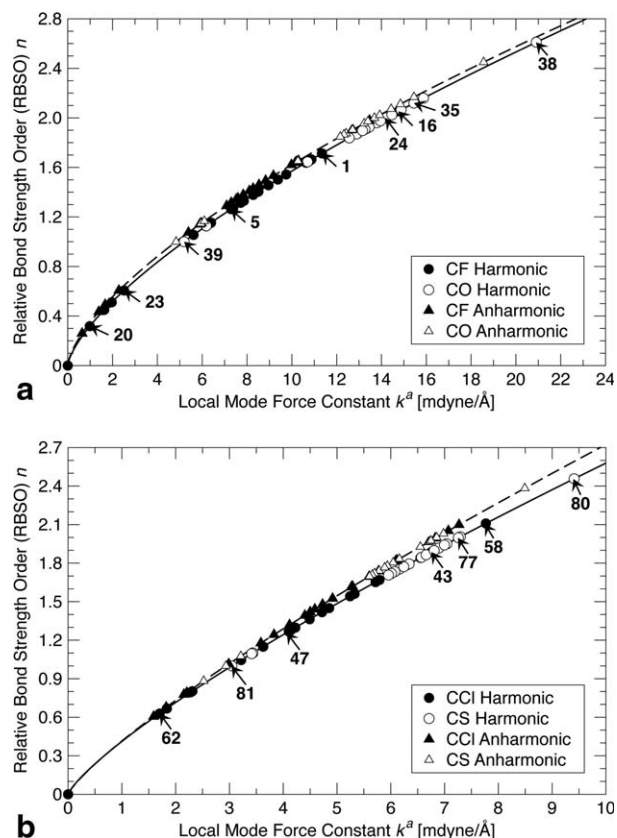


Figure 3. RBSOs n are given as a function of the local mode force constants k^a derived from harmonic (circles and solid curve) or anharmonically corrected normal mode frequencies (triangles and dashed curve). (a) Molecules with CO and CF bonds: $n_{\text{harm}} = 0.3276 (k_{\text{harm}}^a)^{0.6774}$ and $n_{\text{anharm}} = 0.3563 (k_{\text{anharm}}^a)^{0.6549}$. (b) Molecules with CS and CCl bonds: $n_{\text{harm}} = 0.4693 (k_{\text{harm}}^a)^{0.6734}$ and $n_{\text{anharm}} = 0.4724 (k_{\text{anharm}}^a)^{0.6968}$. For numbering of molecules, see Figure 2. (M06-2X/cc-pVTZ calculations).

of a linear relationship between RBSO and BDE values in both cases, verifying that both quantities are bond strength descriptors. However, the scattering of the BDE values is strong for CF and CO bonds ($R^{[2]} = 0.946$) and even stronger for CCl and CS bonds ($R^{[2]} = 0.865$; Figs. 6 and 7). This has to do with the fact

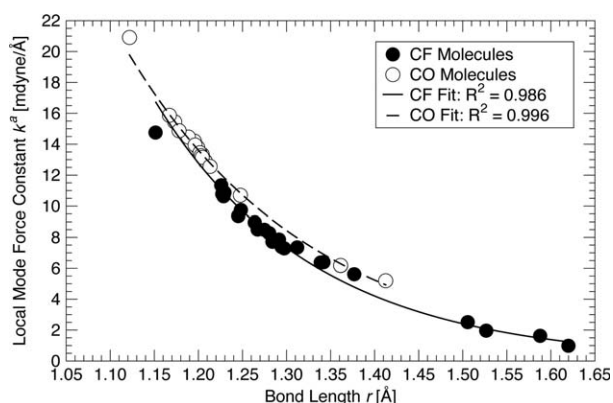


Figure 4. Harmonic local stretching force constants k^a are compared with bond lengths r for molecules with CO (circles) or CF (dots) bonds (M06-2X/cc-pVTZ calculations). Correlations are given for CF (solid line) and CO bonds (dashed): $k^a = 1008.3^{-5.5588r}$ and $k^a = 4214.9^{-4.7795r}$, respectively, both verifying the extended Badger rule.

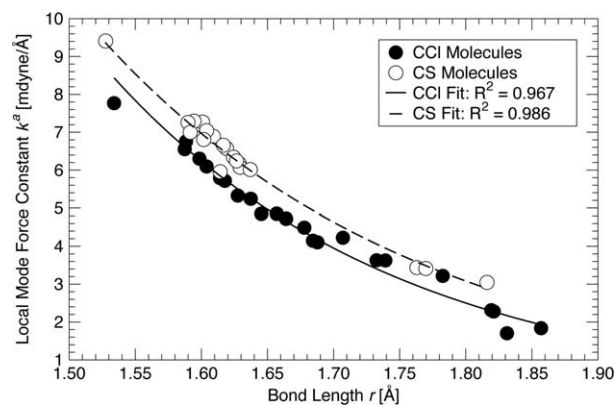


Figure 5. Harmonic local stretching force constants k^a are compared with bond lengths r for molecules with CS (circles) or CCl (dots) bonds (M06-2X/cc-pVTZ calculations). Correlations are given for CCl (solid line) and CS bonds (dashed): $k^a = 9334.1^{-4.5692r}$ and $k^a = 4736.1^{-4.0762r}$, respectively, both verifying the extended Badger rule.

that BDE values depend on both the strength of the bond to be broken and the stabilization of the fragments to be formed by geometry and electron density relaxation. In recent work, we have shown that the relaxation effects vary significantly from case to case^[3,35] and accordingly the BDE values, similarly to the bond lengths, can be at best qualitative bond strength descriptors in those cases where the relaxation mechanisms caused by bond dissociation are closely related.

In the following, we use exclusively local stretching force constants as quantitative bond strength descriptors where the corresponding RBSO values are based on anharmonically corrected local force constants as these are more reliable than the harmonic ones.

Search for the CX double bond

The RBSO values for the CF bond in fluoromethane (17) and the CO bond in its chalcogen analog methanol (39) are both single bonds; however, the former is stronger because of its larger polarity. This is confirmed by the local mode force constants of 5.386–4.835 mydn/Å, the increase in the bond

Table 3. Comparison of experimental and calculated bond dissociation enthalpies (BDHs) at 298 K.^[a]

#	Molecule	BDH(298) exp. (kcal mol ⁻¹)	BDH(298) G3 (kcal mol ⁻¹)	ΔBDH (kcal mol ⁻¹)
16	CF ⁺	172	179.9	-7.9
17	CH ₃ F	110	109.7	0.3
43	H ₂ CCl ⁺	131.2	133.0	-1.8
58	CCl ⁺	148.8	152.7	-3.9
59	CH ₃ Cl	83.7	84.9	-1.2
24	CH ₂ O	180.6	178.4	2.2
38	CO	257.3	257.3	0.0
39	CH ₃ OH	92	90.5	1.5
66	CH ₂ S	131.2	131.0	0.2
80	CS	170.5	171.5	-1.0
81	CH ₃ SH	74.7	72.8	1.9

[a] Experimental values have been taken from Luo's compilation of BDHs^[49] whereas the theoretical values are based on G3-calculations.^[48]

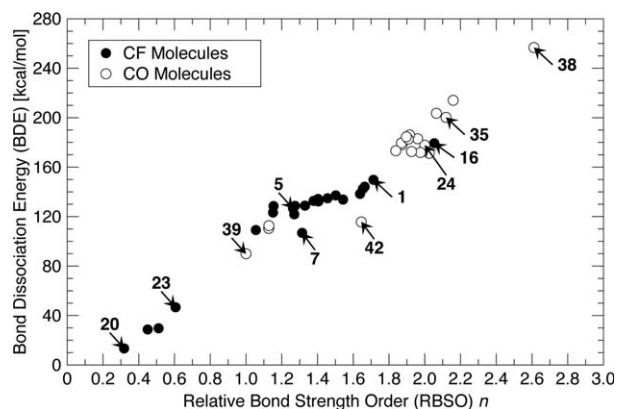


Figure 6. Bond dissociation energies are compared with RBSO values n for the molecules with CF (filled circles) or CO bonds (open circles). The bond dissociation energies are calculated using the G3 method and the RBSOs are based on local stretching force constants calculated at the M06-2X/cc-pVTZ level of theory including anharmonicity corrections.

lengths from 1.377 to 1.413 Å, and the decrease in the BDE values from 109.2 to 89.9 kcal/mol, respectively (see Table 1). The corresponding RBSO values are 1.075 and 1.000 where the latter is the reference value used in this study.

None of the RBSO values of the F-substituted carbenium ions is close to the double bond value of formaldehyde ($n = 2.000$). The RBSO value of the CF bond in the fluorocarbenium ion **1** is 1.639 (Table 1). Considering the RBSO values of the reference bonds, π -bonding in **1** is formally established to just somewhat over 50% rather than 100% as in formaldehyde. However, this does not consider the change in the bond polarity relative to that in **17**, which may be also responsible for the moderate increase in the double bond character. In cation **1**, the higher electronegativity of the strongly positively charged carbon leads to a reduced charge transfer to F, which is lowered by the π -back donation from F to C^+ . We conclude that the CF bond of fluoro-substituted carbenium ions has partial double bond character, but is not a fully developed double bond.

The comparison of chloromethane (**59**) and thiomethanol (**81**) reveals that local mode force constants (2.987 vs. 2.934 mdyne/Å), bond lengths (1.783–1.816 Å), and the BDE values (81.9 vs. 72.2 kcal/mol) are in line with RBSO values of 1.015 and 1.000 (Table 2). The C–Cl bond is somewhat stronger than the C–S bond, but the difference between the two bonds is smaller than that between C–F and C–O, which has to do with the reduced polarity of the C–Cl bond in line with the decreasing difference in C,X versus C,E electronegativities ($\chi(C) = 2.55$, $\chi(O) = 3.44$, $\chi(F) = 3.98$, $\chi(S) = 2.58$, $\chi(Cl) = 3.16$).^[2]

The RBSO for the CCl bond of the chlorocarbenium ion (**43**) is 1.994 ($k^a = 6.827$ mdyn/Å; $r = 1.588$ Å; BDE = 132.5 kcal/mol; Table 2) and corresponds to a fully developed double bond. Of course, this only means that the double bonds of the reference molecule thioformaldehyde (**66**) ($n = 2.000$; $k^a = 6.853$ mdyn/Å; $r = 1.601$ Å; BDE = 130.4 kcal/mol; Table 2) and **43** are similar. However, this does not imply that **43** has a double bond similar to that of formaldehyde (**24**).

Comparing C=O and C=S, the double bond strength of the latter is lower due to a reduced $p\pi$ overlap ($2p\pi-2p\pi$ for CO

vs. $2p\pi-3p\pi$ for CS). This is reflected by a 50% reduction of the local stretching force constants and a 33% reduction in the BDE values. For the halogen-substituted carbenium ions **1** and **43**, these reductions are just 27 and 12%, respectively, which explains why C=S and C=Cl⁺ bonds are relatively alike. These trends preferentially have to do with the positive charge of the carbenium ions and the increased polarizability of Cl compared to F. A similar increase of the polarizability of S (compared to O) does not lead to additional stabilization as the C in C=S carries a much smaller positive partial charge.

We conclude that for the chloro-substituted carbenium ion **43**, a double bond similar to that in thioformaldehyde is fully realized, but that the bond strength is just 73% of that of **1**. Hence, we can confirm that C=Cl⁺ double bonds exist and are in line with the orbital description of Figure 1. The question arises whether a triple bond of the type C≡Cl⁺ is possible.

Search for a CX triple bond

It has been speculated that the diatomic cation CF^+ (**16**) could be the only molecule with a C≡F triple bond (see Fig. 1). Pyykkö et al. compared 324 molecules with potential triple bonds and suggested that CF^+ contains a triple bond.^[34] The arguments used resemble those used in the case of the diatomic CO (**38**), which is expected to have a triple bond due to doubly occupied three bonding molecular orbitals. However, the RBSO value of **38** is 2.611 (harm) or 2.450 (anharm; Table 1), which is a consequence of the fact that both bonding and antibonding σ -MOs are doubly occupied and the latter always lead to a larger destabilization than the former are stabilizing. It is interesting to note that the ratios of the experimental BDE values of **38**, **24**, and **39** (see Table 3) suggest a bond order close to 2.8 or 2.9, which is flawed by the different relaxation effects of the fragments. Thus, the stretching mode describes the CO bond in **38** as being two and a half rather than three times stronger than the CO single bond in methanol.

The ion CF^+ (**16**) is isoelectronic with **80** and should have a similar bond as the latter. However, this implies that F is

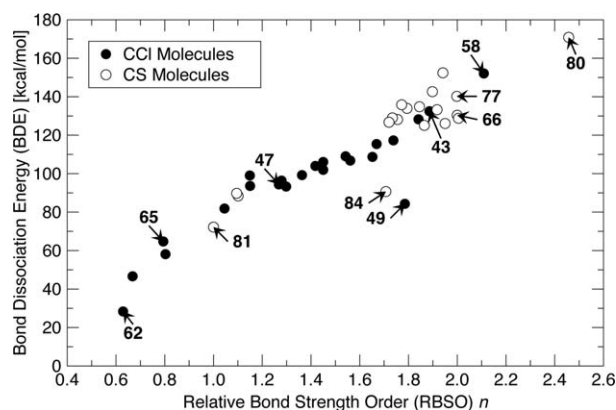


Figure 7. Bond dissociation energies are compared with RBSO values n for the molecules with CCl (filled circles) or CS bonds (open circles). The bond dissociation energies are calculated using the G3 method and the RBSOs are based on local stretching force constants calculated at the M06-2X/cc-pVTZ level of theory including anharmonicity corrections.

strongly involved in two π -back donation interactions, which is not likely. The stretching force constant is 13.467 rather than 18.559 mdyn/Å and the BDE value 179.3 rather than 256.7 kcal/mol (Table 2), which suggests a significant bond strength lowering. We obtain an RBSO value of $n = 1.979$, which suggests that **16** possesses a double rather than a triple bond. A triple bond cannot be established due to the fact that the ability of F to donate two π electron pairs to the carbon is limited by its high electronegativity.

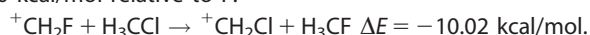
The RBSO values for CCl^+ (**58**) and CS (**38**) are 2.099 and 2.383, respectively (Table 2). The CCl bond is 0.2 RBSO units stronger in comparison to the CS bond than CF^+ in comparison to CO. However, the CS bond is weaker than the CO bond in **38**, which is a result of the decreased bond polarity and the reduction in overlap between the π -orbitals of C and S as compared to C and O. The RBSOs underscore that CX^+ molecules can have a double bond at most and that CE molecules do not have triple bonds.

The data obtained in this work is in excellent agreement with measured values. Wu et al.^[23] studied the photolytic decomposition of CH_3F in neon at 3 K and observe various species including cation **16**. They measured vibrational frequencies of 1759.9 and 1762.9 cm^{-1} for CF^+ , which are close to the anharmonically corrected value of 1763 cm^{-1} obtained in this work.

Reactions involving HF, CF^+ , and HCl in diffuse and dense interstellar molecular clouds were studied by Neufeld and Wolfire.^[28] The ion CF^+ is observed in the Orion Bar region of the Orion Nebula whereas, CCl^+ is not found. The interstellar abundance of CCl^+ was expected to be low noting that while the reaction of C^+ and HCl is rapid, there is little overlap between regions containing these molecules.^[28]

Stabilization of carbenium ions by halogens

The halocarbenium ions studied in this work exhibit double bond character with chloro-substituted ions being more stabilizing than the fluoro-substituted ions. This can be shown by considering the following reactions: $^+\text{CH}_3 + \text{H}_3\text{CX} \rightarrow ^+\text{CH}_2\text{X} + \text{CH}_4$, which is exothermic for X = F by 21.95 kcal/mol and for X = Cl by 31.97 kcal/mol (G3 calculations including ZPE corrections). This shows that Cl stabilizes carbenium ions by 10 kcal/mol relative to F:



This is in line with the higher RBSO values obtained for chloro-substituted carbenium ions (Tables 1 and 2) and results from the fact that Cl has a higher polarizability and lower electronegativity, which both make Cl a better π -donor than F.

Any electronic effect, which increases the π -density in the empty $2p\pi(\text{C})$ -orbital of the carbenium ion should reduce the CX double bond character. To study this effect, we have investigated both hyperconjugative and conjugative interactions with the CX^+ group (**1–5**). Methyl groups lower the RBSO value of **1** from 1.639 to first 1.460 and then 1.430 for X = F. For X = Cl, the reduction is from 1.994 to 1.695 and 1.441, that is, the CCl group is more sensitive to hyperconjugation. However, the π -character of the CCl bond remains larger than that

of the CF bond. Conjugative and hyperconjugative effects in **4** and **5** (**46** and **47**) lead to an even stronger reduction of the π -character (see Table 2). In this way, the RBSO values for **8–11** (**50–53**) are stepwise reduced by double bond conjugation, double bond conjugation plus methylene group hyperconjugation, double bond conjugation plus methyl group hyperconjugation, and conjugation with two double bonds.

If conjugation takes place in combination with an electron withdrawing group such as the carbonyl group (**6**, **7**, **48**, **49**), a moderate lowering of the RBSO value or even a slight increase is observed (from 1.639 in the case of **1** to 1.646 in the case of **6**), which is due to the increase of the positive character of the C atom. For CCl, this effect cannot be expected as an increase of the positive charge at C leads to a contraction of the $2p\pi$ -orbital and to a deterioration of the $2p\pi$ - $3p\pi$ -overlap between C and Cl such that a net reduction of the CCl double bond character results.

Incorporation of another F atom as in **13** or **55** increases the RBSO value slightly due to σ -electron withdrawal and subsequent π -back donation from two rather than one F atom. Contrary to **48** (having two electron withdrawing groups; RBSO: 1.822), this leads to a slight increase of the double bond character for **55** (from 1.994 to 2.052). For three rather than two halogen substituents, as in **15** or **57**, the result is a slight decrease in the first case [RBSO(**15**): from 1.654 to 1.621] and a significant decrease in the second case [RBSO(**57**): 1.738], which again is a result of $2p\pi$ (C)-orbital contraction due to a larger positive charge at C and the subsequent decrease in π -overlap.

This suggests that the π -character of the CX bond in carbenium ions is a sensitive detector of hyperconjugative and conjugative effects as well as σ -electron withdrawal and orbital contraction where the sensitivity is larger for the CCl than for the CF bonds.

Bonding in halonium ions

Halonium ions were first proposed by Roberts and Kimball^[52] to explain the stereospecificity of bromine addition to alkenes. Olah et al.^[53,54] generated bridged halonium ions in superacid solutions and characterized them by spectroscopic methods. Many experimental and computational studies have been published, which provide a good account of their properties.^[53–59] Dimethylhalonium ions with X = Cl, Br, I are useful methylation agents in synthesis.^[60,61] They also react with a base via proton transfer leading to dialkylhalonium ylides, which in turn generate carbenes and alkenes. Accordingly, dialkylhalonium ylides could be key intermediates in the catalyzed formation of alkenes from halomethanes.^[62] Therefore, the study of halonium ions often includes a comparative study of their ylides,^[63,64] which, however, were not investigated in this work.

Halonium ions play an important role in electrophilic reactions involving CX bonds. Olah's work from the 70s on gives ample evidence for this aspect of halonium ion chemistry.^[53,54] There are also recent examples reflecting the constant interest in the chemistry of halonium ions of which only a few can be

mentioned here. Ohta et al.^[65] demonstrated the decisive role of intermediate bridged halonium ions when adding SO₂ to halocarbenium ions where the halonium ion intermediate decides on the stereochemistry and the mechanism of the reaction.

Stoyanov et al.^[66] succeeded in determining the X-ray structures of the dimethyl and diethyl chloronium ion as carborane salts. They obtained CCl bond lengths of 1.810 and 1.840 Å and were able to measure some typical vibrational frequencies: the CCIC stretching frequencies at 636 (asym) and 596 cm⁻¹ (sym) are close to our calculated values of 650 and 603 cm⁻¹ and also close to the local CCl stretching frequency of 648 cm⁻¹ (anharmonically corrected; Table 2). Bonding in dimethylhalonium ions and their ylides has been investigated by Jubert et al.^[64] using the atoms in molecules analysis of the molecular electron density distribution, the electron localization function analysis, and calculated Natural Bond Order (NBO) charges. The authors come to the conclusion that the CX bonds in halonium ions are of weak covalent character.

The halonium molecules (ions **20–23** and **62–65**) formally can be described as charged halogen derivatives where each halogen establishes two single bonds (see Fig. 1). This might imply that an F⁺ or Cl⁺ ion is present, which is not the case as these ions possess such a high electronegativity that they withdraw negative charge from their bonding partners to adopt a noble gas configuration.

There have been both experimental and computational studies of fluoronium and chloronium ions,^[24,62,66,67] which all describe CX bonds as weak and the stability of halonium ions as low. This is confirmed by the CX stretching force constants k^a and RBSO values n obtained in this work. The RBSO values of the fluoronium ions indicate that only fractional CF bonds ($n < 1$) are established. For **20**, a CF RBSO value of 0.260 is obtained, which confirms that conjugation labializes rather than stabilizes the $\sigma(\text{CF})$ -bonds. Therefore, a bridged fluoronium ion is more stable although the energy difference between the classical structure **20** and the bridged form is just 0.9 kcal/mol (G3 calculations). For the chloronium ion **62** and the bridged form, the energy difference is 15.4 kcal/mol (G3 calculations) indicating that Cl⁺ can establish stronger covalent bonds to the ethene base.

Cremer and Kraka^[68] showed that bridged fluoronium ions correspond to a π -complex with T-structure. The local mode analysis leads to a CF stretching force constant $k^a = 1.814$ mdyn/Å, a stretching frequency $\omega^a = 647$ cm⁻¹, and a RBSO value $n = 0.520$, which indicates stronger CF bonding than in the case of **20** ($n = 0.260$; $\omega^a = 384$ cm⁻¹, $k^a = 0.639$ mdyn/Å, Table 1). The differences are even larger for the chloronium derivative **62** and its bridged analog: in the latter ion, the CCl bonds are characterized by $k^a = 2.020$ mdyn/Å, $\omega^a = 619$ cm⁻¹, and $n = 0.737$, which are clearly larger than the corresponding values for **62**: $k^a = 1.591$ mdyn/Å, $\omega^a = 550$ cm⁻¹, and $n = 0.606$. These results show that bridged halonium ions are more stable and have stronger CX bonds than their classical analogs.

The less electronegative and more polarizable Cl is better suited for halonium bonding than the F atom. Similar observa-

tions can be made for the methyl halonium ions **21**, **23**, **63**, and **65**. Electron donation via one or two methyl groups as in **21** or **23** leads to significant stabilization (RBSO: 0.434 and 0.606 for X = F; 0.678 and 0.792 for C = Cl; Tables 1 and 2). We conclude that chloronium ions possess more stable CX bonds than fluoronium ions and that electron donating groups can stabilize CX bonding in halonium ions. Bonding can be described as effective electron-deficient bonding because of the high electronegativity of the halogen atom.

This general conclusion seems not to be applicable for the dications **22** and **64** where the allyl cation, that is, an electron withdrawing group, is bonded to the ⁺XH group (see Fig. 2). Strong charge repulsion should hinder the formation of a covalent CX bond; however by 90°-rotation of the ⁺XH group, the positively charged $p\pi$ -orbital can interact with the π -CC bonds via hyperconjugation. A surprisingly strong CX bond is established in this way: F: $n = 0.492$; Cl: $n = 0.777$. A confirmation for this bonding mechanism is provided by the corresponding chalcogen analogs **42** and **84** where the EH groups (E = O or S) do not carry a positive charge. Hence, $p\pi$ -lone pair donation into the empty $2p\pi$ orbital at the central C atom is most effective in a planar form. A partial C=E double bond is established ($n = 1.652$ and 1.697) with the effect that the terminal CH₂ groups obtain some $p\pi$ -radical character, which lead to instability. The molecule counteracts by CH₂ rotation and the formation of a CC bond (r is reduced from 2.343 to 1.559 (E = O) and 2.331 to 1.520 Å (E = S) and the energy is lowered by 9.12 and 15.41 kcal/mol, respectively).

Fractional CX bonding observed for the halonium ions with divalent halogen is characterized by a rapid increase of the bond strength with the stretching force constant than normal CX bonding (see Fig. 3). However, this is of lower relevance in view of the weakness of the RBSO values of the halonium bonds, which is in line with the calculated BDE values ranging from 13 to 47 kcal/mol (Table 1) and 28 to 65 kcal/mol (Table 2) and bond lengths between 1.34 and 1.52 (F) or 1.82 and 1.85 Å (Cl). The latter comparison confirms that bond lengths can largely mislead when analyzing the the actual strength of the targeted bond.

CE bonding

For the C=E bonds, similar trends are found in this work as for the corresponding CX bonds, only that the variation in the double bond character is smaller. Hyperconjugation and conjugation with electron-donating groups lower the double bond character from 2.000 to 1.848 (E = O; **34**, Table 1) and 1.709 (E = S; **70**, Table 2), respectively, thus indicating that the C=S bond is more sensitive to substituent effects because of its larger polarizability. RBSO values larger than 2.00 are obtained for the F-substituted formaldehyde and acetaldehyde (**35**: 2.111, **36**: 2.072, **37**: 2.168) because the electronegative F withdraws σ -electron density from C and enforces thereby a stronger in-plane lone-pair(O) donation into the $\sigma^*(\text{CF})$ -orbital in the sense of an anomeric delocalization. For E = S, anomeric delocalization is less pronounced because of the longer C=S bond and the more diffuse $3p\pi$ -lone pair orbital ($n = 2.030$, 1.833, 1.975 for **77**, **78**, and **79**).

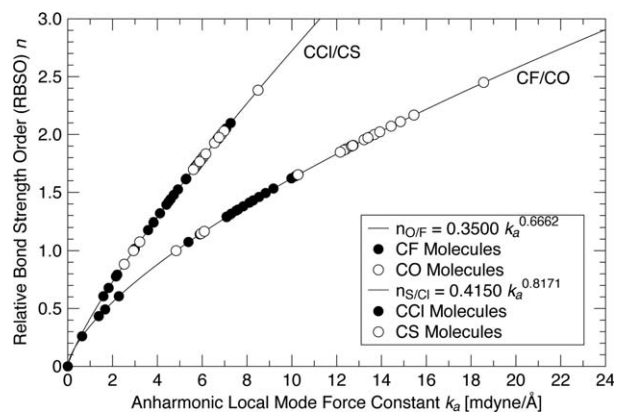


Figure 8. RBSOs n are given as a function of anharmonically corrected local stretching force constants k^a for all molecules studied. The second (O/F) and third (S/Cl) period molecules have unique $n(k^a)$ power relationships due to the definition of two sets of reference bonds: $\text{H}_3\text{C}-\text{OH}$ and $\text{H}_2\text{C}=\text{O}$; $\text{H}_3\text{C}-\text{SH}$ and $\text{H}_2\text{C}=\text{S}$. (M06-2X/cc-pVTZ calculations).

Relative strength of CX and CE bonds

The local stretching force constants directly provide a quantitative measure for the relative strength of the CX and CE bonds. Hence, one could argue to determine RBSO values for all bonds investigated with just one power relationship $n=f(k^a)$ using methanol and formaldehyde as reference. According to such a description, the CS bond in thioformaldehyde **66** would no longer be a double bond (the same conclusions could be drawn comparing the BDE values of **24** and **66**: 177.8 and 130.4 kcal/mol). This would be against chemical convention, which assigns a fully developed double bond to thioformaldehyde **66** in line with the two valences of S and the MO description leading to $\sigma-\pi$ -bonding situation. We have chosen the reference bonds for CCl and CS in this spirit. However, this requires some caveats for the interpretation of their bond strength.

In Figure 8, $n=f(k^a)$ curves based on anharmonicity calculations are shown for both CF/CO and CCl/CS bonds. The steeper increase of the RBSO values with the stretching force constant k^a for CCl/CS is a direct consequence of the choice of the reference bonds. It implies a larger variation in the RBSO values with k^a . If a single power relationship were defined for all bonds, the larger variation in bonding would be found for the second rather than the third period partners of C as the stretching force constants of the latter stretch over 8.5 rather than 18.5 mdyn/Å (see Fig. 8).

The presentation in Figure 8, clarifies that there is a substantially larger k -variation for CO than CF bonding (although bond types such as halonium ylide bonding, oxonium bonding, and so forth, were not investigated in this work). In the third period, there is also a larger k -variation for CS than CCl bonding, but the differences becomes smaller, which is due to the fact that partial triple bond character is somewhat less developed in CS ($n = 2.383$) than in CO ($n = 2.450$). In general, it is true that a systematic analysis of CX and CE bonding reveals a large variety, which cannot be accounted for by simple electron pair, orbital, or electron density models.

Conclusions

This work has demonstrated that vibrational spectroscopy is an excellent tool to unravel electronic effects and their impacts on bonding. For this purpose, one has to extract from the normal vibrational modes the corresponding local vibrational modes. A reliable bond strength descriptor is the local stretching force constant and the RBSO n derived from it by using suitable reference bonds with well-defined bond orders. For the description of carbon-halogen bonds, we utilized the extended Badger rule and suitable CO or CS reference bonds to set up RBSO-force constant power relationships, which are used to describe C-X ($X = \text{F}$ or Cl) bonding. The following conclusions can be drawn from our investigation.

1. Compared to RBSO values based on measured vibrational frequencies, those based on anharmonicity corrections are equally reliable as was shown in previous work.^[17] In this work, we have demonstrated that RBSO values based on harmonic local modes slightly differ from those obtained when anharmonicity corrections are included. However, the differences are not significant and RBSO values based either on the harmonic or anharmonic approach describe the same trends.
2. Comparison of RBSO values obtained from local stretching force constants with the corresponding bond lengths r or the corresponding BDE values reveals that both r and BDE are not reliable bond strength descriptors. There is a variation of the covalent radius with the charge, the atomic polarizability, and the number of core shells, which directly affects the bond lengths irrespective of the bond strength. In the case of the BDE, relaxation of the geometry and the electron density distribution of the dissociation fragments obscure the bond strength (Figs. 4–7).
3. Chloro-substituted carbenium ions can have a fully developed CCl double bond provided the carbenium C atom is not bonded to electron-donating groups. Fluoro-substituted carbenium ions can form only partial CF double bonds ($n = 1.64$ or smaller). This is a result of the reduced electronegativity, the larger polarizability, and the stronger π -donor ability of Cl compared to F.
4. In view of the electronegativity of F and Cl, a fully developed CX triple bond is not possible. RBSO values of 1.98 and 2.10 for CF^+ and CCl^+ confirm a double rather than a triple bond contrary to previous claims.^[34]
5. π -Bonding in F- or Cl-substituted carbenium ions is highly sensitive to hyperconjugative and conjugative effects of the carbenium ion substituents. In this regard, halogenocarbenium ions can be used as sensitive probes for quantitatively assessing the electron donating (withdrawing) ability of a substituent via the relevant local stretching force constants.
6. CCl contrary to CF bonding in X-substituted carbenium ions is sensitive to orbital contraction effects, which are caused by electron-withdrawing substituents and an increase of the positive charge at C. Overlap between $3p\pi(\text{Cl})$ and $2p\pi(\text{C})$ orbitals is reduced and the bond

strength is lowered as reflected by the smaller RBSO and local stretching force constant values.

7. Halonium ions with divalent halogen possess fractional covalent bonds, which can be characterized as electron-deficient $2e-3c$ bonds due to the reluctance of F or Cl to donate an electron lone pair for establishing fully developed C—X single bonds.
8. Bridged halonium ions with $2e-3c$ bonds form significantly stronger CX bonds than the isomeric alkyl halonium hydride. Methyl or other donating groups stabilize the electron deficient CX bonds in halonium ions. Cl is more suited for halonium bonding, which explains the experimental isolation of dialkyl chloronium ions. A halonium dication in the form of 22 or 64 is surprisingly stable because of a rotation of the XH group into a position perpendicular to the allyl cation plane.
9. C=E double bonds show a similar dependence on substituent effects as the corresponding partial CX double bonds. However, the variation in the bond strength is much smaller due to a π -bond, which is better shared between carbon and chalcogen than carbon and halogen. A CE triple bond is not realized for E = O and S as documented by RBSO values of 2.45 and 2.38, respectively.
10. The variation in the bond strength is larger for CO than CF bonds and larger for CS than CCl bonds. The range of calculated force constants is much smaller for CS and CCl than CO and CF bonds. This has to be considered when, via a common chemical definition of the CS double bond in thioformaldehyde with $n = 2.00$, the sensitivity of the RBSO on k^a is artificially increased as reflected by the $n=f(k^a)$ curves of Figure 8.


In future work, we will extend this investigation to an systematic analysis of fourth and fifth period bonds.

Acknowledgment

The authors thank Southern Methodist University for providing computational resources.

Keywords: carbon halogen bonds · carbon chalcogen bonds · local mode analysis · relative bond strength order · halonium ions

How to cite this article: R. Kalescky, E. Kraka, D. Cremer. *Int. J. Quantum Chem.* **2014**, *114*, 1060–1072. DOI: 10.1002/qua.24626

 Additional Supporting Information may be found in the online version of this article.

- [1] S. Patai, Z. Rappoport, *The Chemistry of Halides, Pseudo-Halides and Azides*, Supplement D2, Parts 1 and 2; Wiley: New York, **1995**.
- [2] W. M. Haynes, Ed., *Handbook of Chemistry and Physics*, 92nd ed.; CRC Press: Boca Raton, **2011**.
- [3] D. Cremer, A. Wu, A. Larsson, E. Kraka, *J. Mol. Model.* **2000**, *6*, 396.
- [4] J. Decius, *J. Chem. Phys.* **1963**, *38*, 241.
- [5] D. C. McKean, *Chem. Soc. Rev.* **1978**, *7*, 399.
- [6] J. L. Duncan, J. L. Harvie, D. C. McKean, C. Craddock, *J. Mol. Struct.* **1986**, *145*, 225.
- [7] W. F. Murphy, F. Zerbetto, J. L. Duncan, D. C. McKean, *J. Phys. Chem.* **1993**, *97*, 581.
- [8] B. R. Henry, *Acc. Chem. Res.* **1987**, *20*, 429.
- [9] K. Brandhorst, J. Grunenberg, *Chem. Soc. Rev.* **2008**, *37*, 1558.
- [10] M. Vijay Madhav, S. Manogaran, *J. Chem. Phys.* **2009**, *131*, 174112.
- [11] J. Grunenberg, N. Goldberg, *J. Am. Chem. Soc.* **2000**, *122*, 6045.
- [12] K. Brandhorst, J. Grunenberg, *J. Chem. Phys.* **2010**, *132*, 184101.
- [13] A. Espinosa, R. Streubel, *Chem. Eur. J.* **2011**, *17*, 3166.
- [14] E. Kraka, J. A. Larsson, D. Cremer, In: *Computational Spectroscopy: Methods, Experiments and Applications*, J. Grunenberg, Ed., Wiley: New York, **2010**; p. 105.
- [15] Z. Konkoli, D. Cremer, *Int. J. Quant. Chem.* **1998a**, *67*, 1.
- [16] D. Cremer, J. A. Larsson, E. Kraka, In *Theoretical and Computational Chemistry*, Vol. 5, *Theoretical Organic Chemistry*; C. Parkanyi, Ed.; Elsevier: Amsterdam, **1998**; p. 259.
- [17] R. Kalescky, W. Zou, E. Kraka, D. Cremer, *Chem. Phys. Lett.* **2012**, *554*, 243.
- [18] R. Kalescky, E. Kraka, D. Cremer, *Mol. Phys.* **2013a**, *111*, 1497.
- [19] Z. Konkoli, D. Cremer, *Int. J. Quant. Chem.* **1998b**, *67*, 29.
- [20] W. Zou, R. Kalescky, E. Kraka, D. Cremer, *J. Chem. Phys.* **2012a**, *137*, 084114.
- [21] W. Zou, R. Kalescky, E. Kraka, D. Cremer, *J. Mol. Model.* **2012b**, *137*, 084114.
- [22] B. Pein, N. -H. Seong, D. Dlott, *J. Phys. Chem. A* **2010**, *114*, 10500.
- [23] Y. -J. Wu, H. -F. Chen, S. -L. Chou, M. -Y. Lin, B. -M. Cheng, *Chem. Phys. Lett.* **2010**, *497*, 12.
- [24] F. Zunino, F. Liu, C. Berrier, A. Martin-Mingot, S. Thibaudeau, M. -P. Jouannetaud, J. -C. Jacquesy, C. Bachmann, *J. Fluorine Chem.* **2008**, *129*, 775.
- [25] I. S. Han, C. K. Kim, C. K. Sohn, E. K. Ma, H. W. Lee, C. K. Kim, *J. Phys. Chem. A* **2011**, *115*, 1364.
- [26] Y. Pan, Y. Pan, Y. Tang, Y. Tang, R. Wang, R. Wang, *J. of Fluorine Chem.* **2011**, *132*, 15.
- [27] J. Oomens, T. H. Morton, *Int. J. Mass Spect.* **2011**, *308*, 232.
- [28] D. A. Neufeld, M. G. Wolfire, *Astrophys. J.* **2009**, *706*, 1594.
- [29] M. Pérez-Casany, J. Sánchez-Marín, I. Nebot-Gil, *J. Am. Chem. Soc.* **2000**, *122*, 11585.
- [30] P. Kiprof, S. R. Miller, M. A. Frank, *J. Mol. Struct. Theochem* **2006**, *764*, 61.
- [31] I. Raabe, D. Himmel, I. Krossing, *J. Phys. Chem. A* **2007**, *111*, 13209.
- [32] J. Oomens, E. Kraka, M. K. Nguyen, T. H. Morton, *J. Phys. Chem. A* **2008**, *112*, 10774.
- [33] E. Kraka, D. Cremer, *ChemPhysChem* **2009**, *10*, 686.
- [34] P. Pyykkö, S. Riedel, M. Patzschke, *Chem. Eur. J.* **2005**, *11*, 3511.
- [35] R. Kalescky, E. Kraka, D. Cremer, *J. Phys. Chem. A* **2013b**, *117*, 8981.
- [36] D. C. McKean, I. Torto, A. R. Morrisson, *J. Phys. Chem.* **1982**, *86*, 307.
- [37] Z. Konkoli, J. A. Larsson, D. Cremer, *Int. J. Quantum Chem.* **1998a**, *67*, 29.
- [38] Z. Konkoli, J. Larsson, D. Cremer, *Int. J. Quantum Chem.* **1998b**, *67*, 41.
- [39] M. Freindorf, E. Kraka, D. Cremer, *Int. J. Quantum Chem.* **2012**, *112*, 3174.
- [40] E. B. Wilson, J. C. Decius, P. C. Cross, *Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra*; McGraw-Hill: New York, **1955**.
- [41] R. M. Badger, *J. Chem. Phys.* **1934**, *2*, 128.
- [42] D. Cremer, E. Kraka, *Curr. Org. Chem.* **2010**, *14*, 1524.
- [43] D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
- [44] S. Kozuch, J. M. L. Martin, *J. Chem. Theory Comput.* **2013**, *9*, 1918.
- [45] G. L. Borosky, K. K. Laali, *J. Phys. Org. Chem.* **2010**, *23*, 115.
- [46] R. Kendall, T. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.
- [47] V. Barone, *J. Chem. Phys.* **2005**, *122*, 014108.
- [48] L. Curtiss, K. Raghavachari, P. Redfern, V. Rassolov, J. Pople, *J. Chem. Phys.* **1998**, *109*, 7764.
- [49] Y. -R. Luo, *Comprehensive Handbook of Chemical Bond Energies*; Taylor and Francis: Boca Raton, **2007**.
- [50] E. Kraka, M. Filatov, W. Zou, J. Gräfenstein, H. Joo, D. Izotov, J. Gauss, Y. He, A. Wu, V. Polo, L. Olsson, Z. Konkoli, Z. He, D. Cremer, Southern Methodist University: Dallas, TX, **2013**.
- [51] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H.

- Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09 Revision A.01, Gaussian, Inc., Wallingford CT, **2009**.
- [52] I. Roberts, G. E. Kimball, *J. Am. Chem. Soc.* **1937**, *59*, 947.
- [53] G. A. Olah, Halonium Ions; Wiley: New York, **1975**.
- [54] G. A. Olah, K. K. Laali, Q. Wang, G. K. S. Prakash, Onium Ions; Wiley: New York, **1998**.
- [55] T. P. Hamilton, H. F. Schaefer, *J. Am. Chem. Soc.* **1990**, *112*, 8260.
- [56] C. H. Reynolds, *J. Am. Chem. Soc.* **1992**, *114*, 8676.
- [57] C. F. Rodriguez, D. K. Bohme, A. C. Hopkinson, *J. Am. Chem. Soc.* **1993**, *115*, 3263.
- [58] R. Damrauer, M. D. Leavell, C. M. Hadad, *J. Org. Chem.* **1998**, *63*, 9476.
- [59] G. A. Olah, G. Rasul, M. Hachoumy, A. Burcher, G. K. S. Prakash, *J. Am. Chem. Soc.* **2000**, *122*, 2737.
- [60] G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1970**, *92*, 2562.
- [61] G. A. Olah, Y. K. Mo, *J. Am. Chem. Soc.* **1974**, *96*, 3560.
- [62] L. Noronha, T. Judson, J. Dias, L. Santos, M. Eberlin, C. Mota, *J. Org. Chem.* **2006**, *71*, 2625.
- [63] B. Yates, W. Bouma, L. Radom, *J. Am. Chem. Soc.* **1987**, *109*, 2250.
- [64] A. Jubert, N. Okulik, M. Michelini, C. Mota, *J. Phys. Chem. A* **2008**, *112*, 11468.
- [65] B. K. Ohta, T. M. Scupp, T. J. Dudley, *J. Org. Chem.* **2008**, *73*, 7052.
- [66] E. Stoyanov, I. Stoyanova, F. Tham, C. Reed, *J. Am. Chem. Soc.* **2010**, *132*, 4062.
- [67] D. F. Shellhamer, D. C. Gleason, S. J. Rodriguez, V. L. Heasley, J. A. Boatz, J. J. Lehman, *Tetrahedron* **2006**, *62*, 11608.
- [68] D. Cremer, E. Kraka, *J. Am. Chem. Soc.* **1985**, *107*, 3800.

Received: 22 October 2013
Revised: 3 January 2014
Accepted: 14 January 2014
Published online 27 February 2014