The Structure and Stability of the 10-F-2 Trifluoride Ion, a Compound of a Hypervalent First Row Element[1]

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Abstract: Well correlated ab initio electronic structure calculations have been used to investigate the structure of the trifluoride ion. It is calculated to be stable with respect to F^- and F_2 by about 11 kcal/mol. While this represents a relatively weak bonding of F^- to F_2 to form F_3^-, a significant interaction is evidenced by a 0.3-Å lengthening of the F_2 bond (from 1.41 to 1.70 Å) upon forming the $D_{\infty h}$ F_3^-. This lengthening of the F–F bond distance decreases the repulsive π-type interactions of the unshared electron pairs of the fluorines of F_2, and it is postulated that this provides a major stabilizing influence on the symmetrical trifluoride ion. The calculated centrosymmetric equilibrium structure, along with the calculated vibrational constants, is generally consistent with matrix isolation experiments reported earlier by Ault and Andrews. The nature of the bonding in this unique main group hypervalent molecule is discussed.

The dsp³ hybridization scheme has traditionally been invoked to rationalize the bonding in electron-rich compounds of the main group elements which formally violate G. N. Lewis' octet rule, e.g., PF_5, SF_4, ClF_3, and XeF_2.[2,3] Although molecular structures are usually reliably predicted with this model, estimated electron distributions are inconsistent with NQR[4] and Mossbauer[5] data for several such species that have been studied. In addition, ab initio calculations of the electronic structures of many of these molecules indicate that d-orbitals are not populated to the extent that the hybridization schemes imply.[6] We consider the widely accepted 3-center 4-electron (3c-4e) bond model of Rundle[7] and Pimentel[8] to be a better approximate description of the electronic structure of these molecules. Musher[9] termed these molecules *hypervalent* in order to distinguish them from molecules of the main group elements which have either electron deficient 3-center 2-electron bonds or simple electron pair bonds.

The term "hypervalent" has been redefined several times, most recently through the use of ab initio methods which attempt to calculate a valence for each atom in a molecule based on the calculated population of orbitals centered on the atom.[10] The approximation which we use for the bonding scheme for hypervalent species with a linear 3c-4e bond involves a σ-delocalized bond as in the LCAO–MO diagrams pictured below for the 4-H-2 bifluoride anion and the 10-F-2 trifluoride ion. Both involve σ-delocalized bonds which are σ analogues to the 3c-4e π-bond of the allyl anion. The formal valence shell expansion of the hydrogen of the bifluoride anion and of the central fluorine in the trifluoride ion represented in this way involves the ψ_2 orbital which places two electrons in an orbital essentially localized on the apical ligands. A hypervalent species is one in which this symmetrical structure is an energy minimum. Our definition,[11] which remains

$$[F \!-\! H \!-\! F]^- \qquad [F \!-\!\!-\! F \!-\!\!-\! F]^- \qquad [H_2C \!-\! \underset{H}{C} \!-\! CH_2]^-$$
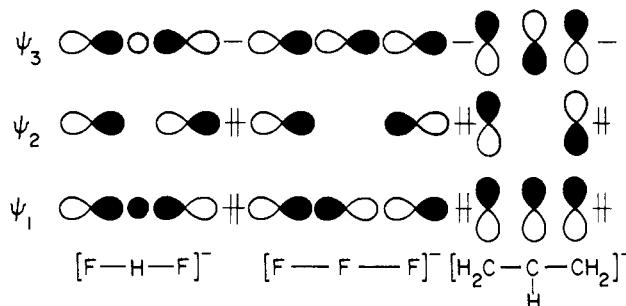
close to Musher's original definition of the term,[14] provides a useful classification scheme rather than a strict statement of the number of electrons assigned to a given atom. It defines hypervalence in terms of a "formal" valence shell expansion. Our definition avoids many of the disadvantages of definitions based on electronic structure calculations, e.g., ambiguities associated with basis set size, completeness, and balance, with the method applied (SCF, CISD, etc.), or with the arbitrary definitions by which electrons are assigned to specific atoms.

The concept of dsp³ hybridization has inhibited attempts to synthesize hypervalent derivatives of the first row elements despite the fact that hypervalent hydrogen compounds, e.g., HF_2^-, have long been known. The preparation of hypervalent boron[15] and carbon[16] species has provided convincing grounds for deemphasizing the traditional dsp³ hybridization scheme for hypervalent species. Evidence for the existence of the trifluoride ion, F_3^-, was first reported in 1976.[17,18] The trifluoride structure was proposed on the basis of infrared and Raman spectroscopic analysis of the products obtained by codeposition of F_2 and M^+F^- ($M^+ = Cs^+$, Rb^+, K^+) with argon at 15 K. On the basis of mutually exclusive Raman and IR lines, it was assigned a linear symmetric ($D_{\infty h}$)

(1) The *N-X-L* nomenclature is used to classify compounds of the main group elements, where *N* represents the number of electrons involved in bonding *L* ligands to a central atom X. In general, hypervalent compounds are those compounds with *N* > 8. For a complete description, see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753-7759. Current address for J.C.M.: Vanderbilt University, Box 1822, Station B, Nashville, TN 37235.

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(3) In addition, the d²sp³ hybridization scheme has been employed in the description of 12-electron species, e.g., SF_6, ClF_5, and XeF_4.

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(5) Jones, C. W. *J. Chem. Phys.* **1975**, *62*, 4343-4349 and references therein.

(6) Keil, F.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1975**, *97*, 3623-3632.

(7) Rundle, R. E. *Surv. Prog. Chem.* **1963**, *1*, 81-131.

(8) Pimentel, G. C. *J. Chem. Phys.* **1951**, *19*, 446-448.

(9) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54-68.

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(11) The unique characteristic of all hypervalent molecules is the presence of at least one occupied high-energy molecular orbital which is σ rather than π in symmetry with respect to a central atom to ligand bond, and which has virtually no overlap with the valence orbitals on a central atom. For metallic cage species,[12] including species such as CLi_5 and CLi_6,[13] in which a non-metal is surrounded by more than four metal atoms, ambiguities exist which make any applications of the term hypervalent difficult to justify.

(12) Tachikawa, M.; Muetterties, E. L. In "Progress in Inorganic Chemistry"; Lippard, S. J., Ed.; Wiley: New York, 1981; Vol. 28, p 203-238.

(13) Schleyer, P. v. R.; Wurthwein, E.-U.; Kaufmann, E.; Clark, T.; Pople, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5930-5932.

(14) Our definition of "hypervalent" also includes the 12-electron molecules, such as SF_6, IF_5, and XeF_4, which Musher termed "supervalent". In addition, molecules with strongly unsymmetrical 3c-4e bonds may be described as having hypervalent character. We do not use the term hypervalent to describe electron-rich molecules such as SO_2 or O_3 in which the highest energy occupied orbitals are not of σ symmetry.

(15) Lee, D. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 5745-5746.

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(17) Ault, B. S.; Andrews, L. *J. Am. Chem. Soc.* **1976**, *98*, 1591-1593.

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Table I. Electronic Energy and Stability of Fluoride, Molecular Fluorine, and the Trifluoride Ion

calculational level	R_{F-F}, Å	energy, au	energy relative to F^- and F_2, kcal/mol
F_3^-, DZP/ACCD	1.711	-298.15650[a]	-26.1
F_3^-, TZP/SCF	1.669	-298.20308[a]	+10.0
F_3^-, TZP/ACCD	1.701	-298.85770	-10.7
F^-, TZP/ACCD		-99.67174	
F_2, TZP/ACCD	1.421	-199.16889	

[a] Constrained to $D_{\infty h}$ geometry.

structure. The ion was stable up to at least 42 K.

There is no spectroscopic or electronic structure data on F_3^- in the isolated molecule limit. The important questions of the stability of the trifluoride and the nature of bonding in this first row, hypervalent fluorine compound have not been addressed, so we have undertaken large basis set, well correlated, ab initio calculations on the electronic structure of F_3^-. These first reported large scale correlated calculations on any hypervalent compound more complex than hydrogen bonded molecules support the assigned symmetrical structure of F_3^-.

Theoretical Approach and Results

Two basis sets were used in the calculations, a polarized double-ζ (DZP) set and a polarized triple-ζ (TZP) set. The valence sets were Dunning contracted Huzinaga sets of Cartesian, Gaussian functions[19] and the polarization functions were uncontracted 3d Gaussian functions with exponent 0.9. In addition to self-consistent-field (SCF) molecular orbital calculations, better wave functions and more reliable electronic energies were also obtained via the inclusion of electron correlation effects. The method used was a direct, matrix-formulated approach[20] to coupled cluster wave functions with double substitutions.[21-25] This type of wave function accounts for not only the primary pair correlations but also the higher order correlation effects that result from the inclusion of quadruple substitutions, hextuple substitutions, and so forth. These higher-order substitutions enter the coupled cluster wave function with expansion coefficients given by products of the expansion coefficients of the doubly substituted configurations or pair excitations. In this way, the coupled cluster wave functions and energies are size–extensive which is to say that they necessarily go to the proper separated electron pair limit. This is an important feature for studying the dissociation energy of F_3^- into the closed-shell F^- and F_2 species. A computationally advantageous neglect of certain small Hamiltonian matrix elements that nearly cancel, an approach designated ACCD,[26,27] was used throughout. Fluorine 1s atomic-core electrons were not correlated.

The equilibrium structure of F_3^- was calculated at two levels, and in both cases the molecule was found to be linear with equivalent bonds. At the DZP/ACCD level, the F–F bond length in F_3^- was 1.711 Å, while at the TZP/ACCD level it was 1.701 Å. This is substantially longer than the bond length of F_2, which is found to be 1.421 Å at the TZP/ACCD level, closely comparable to the spectroscopically determined value of 1.412 Å.[28]

Table II. Vibrational Frequencies of the Trihalide Ions

ion	ν_1 (cm^{-1})	ν_3 (cm^{-1})	f_r (mdyn/Å)	f_{rr}	ref
F_3^- exptl	461	550	1.76	0.63	17
F_3^- calcd	472	228	1.41	1.21	
Cl_3^- exptl	268	242	0.96	0.55	35
Br_3^- exptl	168	187	0.94	0.39	36
I_3^- exptl	113	135	0.70	0.25	36

The stability of F_3^- at different levels of calculation is shown in Table I. At the most complete level of treatment, it is calculated to be stable by 11 kcal/mol with respect to F^- and F_2. At the SCF level, bonding is not evidenced and the potential is slightly repulsive. The TZP/SCF structure of F_3^- used for this energy comparison was accomplished by constraining the system to $D_{\infty h}$ symmetry and finding the lowest energy bond distance. Though this is not a true equilibrium on the full TZP/SCF potential energy surface, the energy at this structure, when compared with correlated energies, does serve to illustrate that correlation effects are very important. The DZP/ACCD stability favors F_3^- by 17 kcal/mol more than does the TZP/ACCD result. Most of this difference arises because the DZ valence set is very deficient for describing F^-, making it too high in energy. The flexibility of our TZ set corrects this problem quite well: tests of further basis set enlargement showed much smaller changes in the total electronic energy of F^-. Around the F_3^- equilibrium, the differences between DZP and TZP relative energies are not so important. Thus, DZP/ACCD calculations were used to search for a bent structure.[29] This search established that the $D_{\infty h}$ structure was a global minimum and that the symmetric geometry is the equilibrium.

We performed a limited analysis of the vibrations of F_3^- and also a vibrational analysis of F_2 for comparison. At the TZP/ACCD level, a potential curve from 1.2 to about 1.5 Å was generated for F_2 and fit to a sixth order polynomial. An exact Cooley–Numerov vibration wave function calculation[30] was performed by using this potential. With the F_2 vibrational state energies obtained in this way, $\omega_{0\rightarrow1}$ was calculated to be 939 cm^{-1} compared to the experimental value of 892 cm^{-1}.[31] The very good agreement is due in large part to the completeness of the coupled cluster treatment of electron correlation, which has been shown to give good calculated values of vibrational constants of other diatomic, polyatomic,[32] and hydrogen bonded[33] molecules. The CEPA approximation to coupled cluster wave functions was used by Ahlrichs et al.[34] to obtain an equally good value of the harmonic frequency of F_2.

With the use of four potential energy surface grid points around the equilibrium point, stretching force constants were obtained. With these, normal mode frequencies were calculated, and the values are given in Table II along with experimental values. The agreement for ν_1 is excellent, but the observed and calculated values of ν_3 differ greatly. Since this is a comparison of harmonic or equilibrium frequencies with transition frequencies, some error is expected, particularly where there is sizable anharmonicity. For

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(28) Huber, K. P.; Herzberg, G. "Molecular Spectra and Molecular Structure"; Van Nostrand Reinhold: New York, 1979; Vol. 4, pp 214-217.

(29) The DZP/ACCD energy of F_3^- at an F-F distance of 1.72 Å increases from -298.73411 to -298.73262 hartrees upon bending the ion from a linear geometry to an F-F-F angle of 170°. When normal mode analysis is used, this corresponds to a bending force constant of 0.144 mdyn/Å and a frequency of 277 cm^{-1}. (For comparison, the corresponding values for KrF_2 and XeF_2 are 0.21 and 232.6; 0.20 and 213.2: Claassen, H. H.; Goodman, G. L.; Malm, J. G.; Schreiner, F. *J. Chem. Phys.* **1965**, *42*, 1229-1232.) The actual bending frequency is expected to be lower than this value because of factors not included in the normal mode analysis (anharmonicity, stretch/bend mixing). No lines in the spectrum of F_3^- were assigned to a bending vibration.

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ν_3, this is quite pronounced. In this case, the stretch corresponds to moving the central fluorine back and forth between the two apical fluorines, and for this motion the potential is very flat. Movement of the central fluorine by 0.04 Å toward one fluorine and away from the other gave an increase of only 40 cal/mol from the minimum energy. Thus, the physical significance or quantitative usefulness of these normal mode frequencies is quite limited for the F_3^- species.

It has been established for some time that one means of obtaining a correct dissociation energy for F_2 is the use of a multi-configuration reference wave function. If limited configuration expansions are to be used, they should be built on such a reference.[37] This adequately describes the spin coupling and electron pair formation of the unpaired electrons on each fluorine atom and is not a consequence of dynamical correlation. Our calculations used a single configuration reference with a very extensive treatment of the dynamical correlation effects because we sought to obtain the stability of F_3^- with respect to two closed-shell species, F^- and F_2. What is important is that we can describe the change in the electronic structure of F_2 when it weakly attaches an F^-, especially in view of the bond elongation that is found. In fact, the good agreement with experiment for the F_2 vibrational analysis indicates that the level of calculation performed is suitable for describing the system even when it is distorted as significantly as it is in F_3^-. The fact that the bonding is weak is an indication that dynamical correlation effects must be treated fully. The results in Table I show, for example, that SCF results are much different. Were it necessary to more completely describe this system, an approximate Breuckner orbital treatment with the ACCD wave function could be used since it has been shown to treat single bond breaking accurately.[38] In many ways, this orbital improvement process accomplishes a description similar to that obtained with the use of a multi-configuration reference. We carried out these types of calculations for the elongation of the F_2 bond away from its equilibrium value, and the effect on the vibrational energy curve was slight. For these several reasons, we believe the correlation treatment to be adequate for an assessment of the viability of F_3^- as a species in the isolated molecule limit and for the determination of its equilibrium structure. At the same time, the flatness of the potential energy surface means that refinements in the incorporation of the correlation effects or in the basis set could produce some noticeable changes in certain of the calculated values. The 17 kcal/mol stability difference between the DZP/ACCD and TZP/ACCD results (Table I), for example, is large enough to anticipate at least some lingering basis set effects on this energy. Given the flexibility of the TZP basis and the extensiveness of the ACCD correlation treatment, however, it is not anticipated that still higher level calculations would affect the conclusion that F_3^- is a bound species. Similarly, the centrosymmetry of the equilibrium structure is a conclusion that is meaningful to the extent that if the structure should actually be asymmetric, the centrosymmetric "barrier" must be quite low in energy, probably lower than the zero point virational energy.

Discussion

The results of these calculations are in convincing agreement with the published experimental data on the trifluoride ion. The calculated stability of F_3^- with respect to F^- and F_2 (11 kcal/mol) is consistent with the observed thermal stability of $Cs^+F_3^-$.[39] As expected, this value is less than the gas-phase measured value[40]

of 38 kcal/mol for the stability of Cl_3^- relative to Cl^- and Cl_2. The calculated single minimum potential surface for F_3^- corresponds to an equilibrium F-F bond length of 1.70 Å. This is consistent with the $D_{\infty h}$ geometry assigned to the trifluoride ion on the basis of mutually exclusive infrared and Raman frequencies. The calculated symmetric stretch, (ν_1, 472 cm^{-1}) frequency is only 11 cm^{-1} higher than the observed ν_1 (461 cm^{-1}).[41] The calculated asymmetric stretch (ν_3, 229 cm^{-1}) frequency differs, however, from the observed ν_3 (550 cm^{-1}) by over 300 cm^{-1}. The potential surface for the asymmetric stretch is strongly anharmonic, so this error could be attributed to the limitations of the simple normal mode analysis used. Alternatively, the observed infrared absorption may be due to an overtone or combination transition with ν_3 lying below the range of reported IR frequencies. Another possibility is that this weak deformation mode is strongly affected by nearby matrix atoms or a counterion.

Qualitatively, the bonding in F_3^- can be described as a 3c-4e bond involving only p-orbitals. Consistent with this is the ACCD (correlated) charge distribution in the ion which places -0.51 e on each apical fluorine and +0.03 e on the central fluorine.[42] Because d-orbitals are not qualitatively important (the Mulliken population of the d-orbitals is only 0.05 e), there is no *a priori molecular orbital argument against the formation of* hypervalent compounds of other first row elements. Syntheses of hypervalent compounds of other first-row elements have been reported: one of hypervalent carbon[16] and four of hypervalent boron.[15] Compounds of hypervalent nitrogen or oxygen have not yet been observed.

The importance of including d-type polarization functions in quantitative calculations of hypervalent second row elements has been noted by several authors.[43] It is, however, somewhat misleading to interpret the participation of d-orbitals in hypervalent bonding as evidence for dp hybridization.[44] The d-orbitals are calculated to be only fractionally occupied in the molecules studied and of comparable importance in hypervalent compounds of second row elements and in normal valent compounds of second row elements at the SCF level.[45] A satisfactory interpretation of the calculations is that d-orbitals are required because of the greater polarizability of the second row elements compared to the first row elements, and because d-orbitals of suitable energy are available for a significant level of π-back-bonding with ligand lone pairs. At a correlated level, Pople has recently calculated the heat of reaction of molecular hydrogen and molecular nitrogen to give ammonia and found that even on the normal valent first row element nitrogen, d- and f-orbitals are needed to provide a precise fit to experimental date.[46] The arguments about d-orbital participation in hypervalent molecules may be considered a moot point because all near quantitative ab initio calculations require a polarized basis set. It is also clear that the ligand structure, e.g, chelating ligands, can be more important energetically than the calculated importance of d-orbitals. Interpretations of the calculated percent participation of d-functions are subject to basis set deficiencies and to the type of calculation (SCF, CI, etc.) used. The physical significance of d-functions beyond the polarization

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(39) A referee has pointed out that the reaction $2F_3^- \rightarrow 2F_2^- + F_2$ is nearly thermoneutral if the value for the electron affinity of F_2 is taken to be −71 ± 3 kcal/mol (Chupka, W. A.; Berkowitz, J.; Gutman, D. *J. Chem. Phys.* **1971**, *55*, 2724–2733). There is no published experimental evidence for this reaction in either direction, however. In the IR spectra of the $M^+F_3^-$ salts formed from M^+F^- and F_2 no lines that were previously assigned to ν_2 of $M^+F_2^-$ were observed. In addition, the reported UV data on $Cs^+F_3^-$ did not indicate a long wavelength absorption that could be attributed to F_2^-. The reverse reaction may occur during the formation of $M^+F_2^-$, but the F_3^- produced may simply be formed from F_2 and M^+F^- (which is also formed in the reaction). (Howard, W. F., Jr.; Andrews, L. *Inorg. Chem.* **1975**, *14*, 409–413.)

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(41) The observed ν_1 (symmetric stretch) for the trihalide ions F_3^-, Cl_3^-, Br_3^-, and I_3^- are all within a few wavenumbers of the ν_1 vibrations of the corresponding X_2^- species as would be expected if the harmonic force constants for the X_2 stretching and for ν_1 stretching in X_3^- were of comparable size.

(42) The calculated Mulliken populations change somewhat upon the inclusion of electron correlation. The charge on the central fluorine drops from the SCF value of +0.14 e to only +0.03 e and the charge on each apical fluorine drops from −0.57 e to −0.51 e. The calculated charge distribution for F_3^- is nearly the same as that estimated for Cl_3^- and I_3^- by NQR and Mossbauer experiments.[5]

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of charge and their involvement in back-bonding in unclear.

In the calculation of well correlated wave functions, polarization functions allow the electrons to more adequately correlate with each other because, for example, d-functions introduce additional angular nodes into the wave function. In molecules with vicinal lone pairs, multiple bonds, or σ delocalized electron deficient bonds (e.g., B_2H_6) correlation effects are especially important. The ACCD (approximate coupled clusters with double substitutions) method was used in our calculations to compute accurately the correlation energies. It is instructive to compare the trifluoride ion, formed from F^- and F_2, with the closely analogous $(F^- + CH_3F)$[47] and $(H_2O + CH_3OH_2^+)$[48] systems, both of which have been studied experimentally in the gas phase, as well as with high-level calculations. The potential surfaces for the methyl systems have double minima along the S_N2 reaction coordinate. These minima correspond to charge dipole complexes separated by a symmetrical hypervalent transition state. This is strikingly different from the single minimum calculated for the F_3^- surface. The calculations and experimental results both indicate, however, that even the symmetrical hypervalent transition state can be lower in energy than the separated molecules in some cases.

In judging the stability of hypervalent compounds, normal valent reference compounds are usually chosen. For X_3^-, X^- and X_2 are reference compounds; for XeF_2, Xe and F_2 are, etc. Factors which destabilize reference compounds may contribute, of course, to the thermodynamic stability of the corresponding hypervalent molecule. The trifluoride ion is expected to be stabilized with respect to F^- and F_2 primarily by two factors: (1) relief of lone pair repulsions in F_2 due to bond elongation and (2) charge delocalization upon the formation of a symmetric ion. The dissociation energy of F_2 is only 37 kcal/mol,[31] much less than is expected from extrapolation of the bond energies of the other halogens. The bond in F_2 is destabilized by strong repulsive forces between the vicinal lone pairs.[49] Bond elongation (1.42 Å in F_2 to 1.70 Å in F_3^-) decreases these repulsions and therefore favors the F_3^- ion. Furthermore, the fluoride ion is destabilized because a full negative charge is placed on a very small atom. Although the fluorine atom is more electronegative than chlorine, its electron affinity is lower than that of chlorine (78.4 vs. 83.4 kcal/mol).[50] Charge delocalization in the trifluoride ion is therefore favored.[51]

The reasons that the symmetrical structure in the $(F^- + CH_3F)$ system is a transition state as opposed to a potential minimum may be attributed to the absence of the lone pair repulsions in CH_3F. In calculations of $CH_3F_2^-$ constrained to the D_{3h} potential surface, the surface is markedly flat and has a minimum near a C–F distance of 1.85 Å[52] —much longer than the value of 1.70 Å we calculated for the trifluoride ion, longer by an amount essentially the same as that predicted from the difference between covalent radii of carbon and fluorine in normal valent species (0.1

Å). We have inspected SCF wave functions for the symmetrical $[F–CH_3–F]^-$ system and compared them to similar wave function for F_3^-. Although many differences are noted, no particular orbital or orbitals seemed to play a dominant role in deterimining the differences between the two systems.

The barriers for S_N2 reactions at carbon is the gas phase are generally small. e.g. 10–15 kcal/mol if the carbon atom is in a methyl group or a mono-substituted methyl group and a good nucleophile is used.[53] Small changes in the ligand environment around carbon or in the character of the nucleophile may lead to an observable hypervalent carbon species in the gas phase. In the only hypervalent carbon species which has been observed (in solution) the combination of chelating five-membered rings, electronegative apical ligands, and relatively electropositive π-acceptor equatorial ligands is thought to have eliminated the barrier entirely, converting the energy maximum characteristic of the trigonal-bipyramidal (TBP) geometry of a 10-C-5 species into an energy minimum.[16] A similar conclusion has been reached with hypervalent boron species. Because boron is less electronegative than carbon, it should be (and is) easier to include in a ligand system which renders it hypervalent. The inclusion of strongly electron withdrawing groups in a chelating tridentate ligand has enabled the direct observation of both 10-B-5 and 12-B-6 species.[15] Charge delocalization is apparently very important in the stabilization of several hypervalent ions. Electrically neutral analogues of the anionic [10-X-2] trihalide series, the neutral [9-X-2] trihalogen radicals, have not been observed except for Cl_3· (which was observed in a matrix at low temperature).[54] Much of this difference in stability relative to the trihalide ions is attributable to the delocalization of the extra negative charge in the anion because the additional electron goes into a nonbonding (or slightly antibonding) orbital.

The trifluoride anion has never been observed in the gas phase.

Conclusions

The trifluoride anion is calculated to be a linear centrosymmetric $(D_{\infty h})$ ion bound by 11 kcal/mol with respect to F^- and F_2. The dissociation to give F^- and two fluorine atoms requires 48 kcal. This is an average F–F bond energy of 24 kcal/mol and is only 13 kcal/mol lower than the bond dissociation energy of F_2 (37 kcal/mol). The [10-F-2] trifluoride anion is much more stable thermodynamically than the analogous [10-Kr-2] KrF_2 which has an average Kr–F bond strength of only 12 kcal/mol.[55] The bonding in this ion is qualitatively described as a 3-center 4-electron hypervalent bond. The stability of the first row hypervalent compound (relative to fluoride and molecular fluorine) can be explained in terms of relief of the lone pair repulsions in F_2 upon formation of the long F–F bonds in the trifluoride ion (1.70 Å) and the delocalization of charge in the F_3^- compared to F^-.

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