The First Direct Observation of the Trifluoride Anion (F$_3^-$) in the Gas Phase

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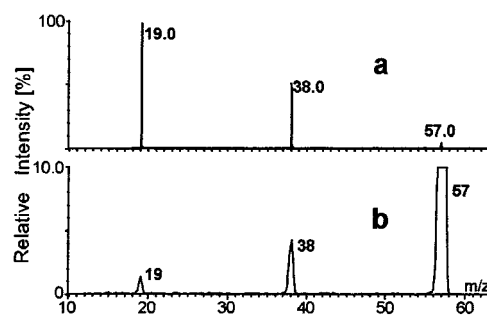*Department of Chemistry, University of Tennessee*
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Numerous theoretical calculations[1−11] predict that F_3^- is a stable anion; however, there has been no reported observation of this species in the gas phase. We now report the formation and detection of F_3^- by electron-capture mass spectrometry, suggest a mechanism for its formation, and present a preliminary investigation of its collision-induced dissociation (CID).

The trihalide anions X_3^- (X = F, Cl, Br, I) are widely discussed in inorganic textbooks and are of considerable practical interest in the fields of polymer science,[12] superconductivity,[13−15] and organic synthesis.[16,17] For X = Cl, Br, and I, Sunderlin's group has prepared X_3^- in a flowing afterglow mass spectrometer and determined the X_2-X^- bond energy by means of energy-resolved CID experiments.[18,19]

In contrast to the extensive measurements conducted on Cl_3^-, Br_3^-, and I_3^-, very little experimental evidence exists concerning F_3^-. The only recorded observations of this species resulted from the spectroscopy of its alkali salts generated in situ within solid argon matrixes.[20−22] The existence of linear F_3^- (with $D_{\infty h}$ symmetry) was inferred from the infrared/Raman mutual-exclusion characteristics displayed in the F_3^- vibrational spectra recorded at 15 K.[20,21]

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Figure 1. (a) Electron capture mass spectrum of F_2, showing peaks at m/z 19 (F$^-$), 38 (F$_2^-$), and 57 (F$_3^-$). (b) *Q*-scan (CID) spectra of precursor ion m/z 57 at 25 eV laboratory frame collision energy with argon. Structure assignments as for (a) above. The intensity of the precursor ion (m/z 57) is normalized to 100%.

Despite the paucity of experimental data on F_3^-, theoretical studies of this anion abound in the literature.[1−11] These quantum chemical studies largely focus on gas-phase F_3^-, although some theoretical investigations include the effects of an associated metal ion[10] or solvent.[11] The validity of any given computational approach has typically been judged by comparing the theoretically predicted vibrational frequencies of singlet F_3^- with those observed by Ault and Andrews[20,21] in the solid argon matrix. It is now well established that F_3^- has substantial multireference character in its singlet electronic state, and an accurate treatment of singlet F_3^- requires the use of either coupled cluster methods with approximate inclusion of triple excitations[4] or genuine multireference techniques.[9]

All theoretical studies agree that F_3^- should be stable with respect to dissociation into F^- and F_2. The most accurate theoretical treatments[4,9] estimate the F_2-F^- bond energy to be 1.14−1.22 eV. Nevertheless, the gas-phase trifluoride anion has not been observed to date. Exhaustive attempts to synthesize the Cs, Na, Ca, and R_4N trifluoride salts (in the absence of an argon matrix) were unsuccessful,[23,24] even though fluorination of various organic substrates is markedly affected by the presence of fluoride salts (see, e.g., ref 25), suggesting formation of F_3^- or a similar transient species. We are now able to generate and detect F_3^- in the gas phase by electron-capture mass spectrometry.

Figure 1a shows the negative-ion mass spectrum of F_2 obtained on a ZAB-EQ instrument (VG-Analytical, Manchester, England) modified with a purpose-built ion source and a dedicated fluorine gas inlet system. (These modifications will be described in detail elsewhere.) The ion source is relatively gastight, allowing a high pressure differential between the ion cavity and the source housing. The source was operated at ambient temperature, and the pressure of pure fluorine within the ion source is estimated to be $10^{-2}-10^{-1}$ mB (direct pressure measurement within the source block is not supported). An electron beam of nominally 70 eV and 1 mA emission current afforded the signals seen in Figure 1a. (The 70-eV electron beam is quickly attenuated within the source block by collisions with the F_2 gas and resulting ionization processes.[26]) Structure assignments are m/z 19 = F$^-$, m/z 38 = F_2^-, and m/z 57 = F_3^-.

The identity of m/z 57 was proven by its CID spectrum, shown in Figure 1b. The ZAB-EQ is a hybrid magnetic-sector/quadrupole mass spectrometer of *BEqQ* geometry; i.e., it comprises a double-focusing magnetic-sector instrument (MS1 = the *B* and *E* sectors),

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followed by a collision quadrupole (q) and an analyzer quadrupole (Q). Figure 1b is obtained by selecting the m/z 57 ions in MS1, decelerating them from the 8 keV kinetic energy used in MS1 to 25 eV, colliding them with Ar ($\sim 5 \times 10^{-4}$ mB) within q, and analyzing the resulting fragments in Q. Clearly, the masses 19 and 38 Da make up the m/z 57 signal, thus firmly establishing its identity as F_3^-.

Two competing CID pathways are discernible in Figure 1b:

$$F_3^- \rightarrow F^- + F_2 \qquad \text{(fragment ion } m/z \text{ 19)} \qquad (1)$$

$$F_3^- \rightarrow F + F_2^- \qquad \text{(fragment ion } m/z \text{ 38)} \qquad (2)$$

Reaction 2 is not unprecedented in the literature; I_2^- and Br_2^- compete with I^- and Br^- as minor ($<10\%$) CID products of the respective X_3^- anions.[18,19] The prominence of F_2^- in Figure 1b is nevertheless surprising. Reaction 1 is energetically favored by the difference in the electron affinities (EA) of F and F_2, which are 3.40 and 3.08 eV, respectively.[27] For a thermodynamically controlled reaction at ambient temperature, this 0.32-eV energy difference would dictate a preference for reaction 1 over reaction 2 by a factor greater than 10^5. Instead, reaction 2 predominates by a factor of roughly 3, as seen in Figure 1b.[28]
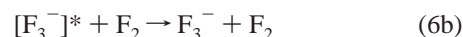
Alternatively, for a kinetically controlled fragmentation, the electronic configuration of F_3^- will play a central role in determining the distribution of the final products. Ab initio calculations of singlet F_3^- predict a ground-state electronic structure with significant electron deficiency at the central fluorine and excess electron density at the terminal fluorines, resembling a fluorine cation flanked by two fluorine anions.[9] Fragmentation starting from such a configuration would also be expected to favor reaction 1.

However, the ab initio treatment of F_3^- presented by Wright and Lee examined the possibility of triplet electronic states apparently not considered by other investigators.[7] These authors found that, at the CISD/6-31G* level of theory, the lowest energy triplet state of linear F_3^- was only slightly higher in energy than the lowest energy singlet state. Furthermore, at the ROHF/6-31G* level of theory, the triplet state of linear F_3^- possessed an electronic structure, described as "...essentially a F^- with two F atoms at either end...". Fragmentation initiated from such a state would be compatible with the observation in Figure 1b of a preference for reaction 2 over reaction 1, and the triplet surface may play an important role in the CID of F_3^-. Unfortunately, the calculations in ref 7 employ small basis sets and are based on a single reference approach, now known to be inadequate for the description of singlet F_3^-; higher level calculations are needed to estimate the F_3^- singlet–triplet energy gap and elucidate the role of the triplet state in the CID of F_3^-. Such calculations are being undertaken in this laboratory.

The following reaction scheme is proposed to rationalize the observations of F^-, F_2^-, and F_3^- shown in Figure 1a:

$$F_2 + e \rightarrow F^- + F \qquad (3)$$

$$F^- + F_2 \rightarrow F_2^- + F \qquad (4)$$

$$F_2^- + F_2 \rightarrow F_3^- + F \qquad (5)$$

$$F^- + F_2 \rightleftharpoons [F_3^-]^* \qquad (6a)$$

$$[F_3^-]^* + F_2 \rightarrow F_3^- + F_2 \qquad (6b)$$

where $[F_3^-]^*$ denotes a vibrationally excited transient intermediate. F_2 is known to undergo dissociative attachment of low-energy electrons to form F^- with a large cross section.[29] The kinetic energy of F^- formed in reaction 3 is 0.9 eV for incident electrons with zero kinetic energy; i.e., the difference between the bond energy of F_2 (1.60 eV[30]) and the EA of F (3.40 eV[27]) divided between F^- and F. For 1-eV electrons, this kinetic energy becomes 1.4 eV.[29] Collisions between F_2 and translationally hot F^- anions will produce stable F_2^- via reaction 4 because the reactants' center-of-mass kinetic energy (two-thirds of the F^- kinetic energy) is above the 0.32-eV charge-transfer threshold [the difference between the EAs of F (3.40 eV[27]) and F_2 (3.08 eV[31])]. F_2^- anions formed in reaction 4 can react with ambient F_2 to produce F_3^- via reaction 5; an analogous reaction was invoked by Hogness and Harkness to explain their observation of I_3^-.[32] Using the estimated[4,9] range of F_2–F^- bond energies (1.14–1.22 eV), the bond energy of F_2, and the EAs of F and F_2 (all of which are known and listed above), reaction 5 is endothermic by between 0.14 and 0.06 eV. Vibrational and kinetic energies of the thermally excited reactants could readily overcome this small energy deficit. Alternatively, slower F^- anions may form a long-lived collision complex with F_2 which can be relaxed by subsequent collisions with F_2 to form stable F_3^- via reactions 6. A final possibility is the formation of weakly bound F^-:$(F_2)_n$ van der Waals cluster anions (ion–induced dipole binding) with $n = 1$. The formation mechanism again would be three-body collision stabilization (i.e., reactions 6a and 6b). However, the result from the collision-induced dissociation experiment (intensity $F_2^- > F^-$) argues against this possibility. Experiments to determine the pressure dependence of the F^-, F_2^-, and F_3^- signals in Figure 1a and the collision energy dependence of reactions 1 and 2 are ongoing.

Detection of F_3^- in the gas phase concludes the series of nonradioactive trihalide anion observations: I_3^- (first reported in 1928[32]), Cl_3^- (1958[33]), and Br_3^- (1976[34]).

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