The Ionization Energy of CF$_3$: When Does Entropy Matter in Gas-Phase Reactions?

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Abstract: A minor controversy has emerged recently over the value of the ionization energy of the trifluoromethyl radical, CF$_3$. Solid evidence appears to support both high values, IE$_a$ ≈ 9.05 eV, and low values, IE$_a$ ≈ 8.65 eV. Examining the assumptions made in the analysis of the various experimental results shows that the root of the discrepancy is the role of entropy in low-pressure, gas-phase ion chemistry. The proper treatment of entropy has, itself, been a more fundamental controversy for a long time. In the zero-pressure limit, conservation of energy (ΔE) in a molecular collision is the primary consideration, but at the high-pressure limit, the free energy (ΔG) dictates the outcome of a reaction: what pressures qualify as "high"? (Henchman, M.; et al. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, The Netherlands, 1987, pp 381−399). The present paper does not achieve any fundamental resolution of the entropy question. However, it does demonstrate that many discrepancies involving CF$_3$ are eliminated (in favor of the higher values of the ionization energy) when the free energy model is used. This result suggests that entropy remains important at lower pressures than many investigators now presume.

Introduction

The adiabatic ionization energy (IE$_a$) of the CF$_3$ radical is very difficult to measure directly because of the large change in geometry that occurs when the pyramidal radical is ionized to the planar cation. About two dozen measurements have been made over three decades, but no consensus value has been reached. The severe disagreement among the measurements was recently highlighted by Jarvis and Tuckett, who measured the energy required to produce CF$_3^+$ from perfluoropropane. Their value limits the adiabatic ionization energy of the CF$_3$ radical to IE$_a$(CF$_3$) ≤ 8.8 ± 0.2 eV (1 eV = 96.485 kJ/mol).[2,3] They reviewed much of the relevant literature and cited several earlier papers that support this limit.[4] Two are ion drift tube studies of reactions 1[5] and 2,[6] whose rate constants were used to infer upper limits to the corresponding reaction endothermicities.

$$HCl^+ + CF_4 \rightarrow CF_3^+ + HF + Cl \quad (1)$$

$$HCN^+ + CF_4 \rightarrow CF_3^+ + HF + CN \quad (2)$$
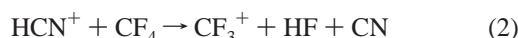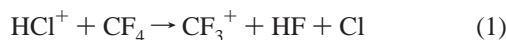
Consequently, IE$_a$(CF$_3$) ≤ 8.68 eV (reaction 1) and IE$_a$(CF$_3$) ≤

8.73 eV (reaction 2). A guided ion beam study of reaction 3 yielded an energetic threshold of 0.24 ± 0.07 eV, which implies IE$_a$(CF$_3$) ≤ 8.73 ± 0.07 eV.[7] Furthermore, photoionization

$$Kr^+(^2P_{3/2}) + CF_4 \rightarrow CF_3^+ + F + Kr \quad (3)$$
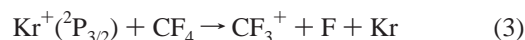
threshold measurements of the appearance energy of CF$_3^+$ from jet-cooled CF$_3$Br[8] and from thermal CF$_3$I[9] imply IE$_a$(CF$_3$) = 8.55 ± 0.08 eV and IE$_a$(CF$_3$) ≤ 8.62 eV, respectively.[3]

However, Jarvis and Tuckett also noted the very different value obtained by Asher and Ruscic,[10] who measured the photoionization appearance energies for CF$_3^+$ and for CF$^+$ from tetrafluoroethylene, reaction 4. From the difference between the

$$h\nu + C_2F_4 \rightarrow CF_3^+ + CF + e^-$$
$$\text{or} \qquad \rightarrow CF_3 + CF^+ + e^- \quad (4)$$
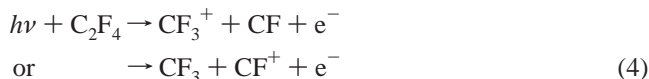
two thresholds and the well-established ionization energy of CF there followed IE$_a$(CF$_3$) = 9.055 ± 0.011 eV. However, as pointed out by Jarvis and Tuckett, this conclusion requires that there be no difference in activation energy for the two branches of reaction 4, which need not be true. Finally, Jarvis and Tuckett noted without comment that the higher value is supported by an ab initio prediction that IE$_a$(CF$_3$) = 8.98 ± 0.05 eV.[11]

The paper by Asher and Ruscic[10] includes an extensive review of earlier measurements of CF$_3^+$ appearance energies, mostly from trifluoromethyl halide precursors, CF$_3$X. The previously reported appearance energies do not agree, spanning ranges of

(1) Henchman, M.; Meot-Ner (Mautner), M.; Lias, S. G.; Fernandez, M. T.; Jennings, K. R.; Mason, R. S.; Stone, J. A.; Squires, R. R.; Hierl, P. M.; Paulson, J. F.; Ahrens, A. F.; Viggiano, A. A. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, The Netherlands, 1987; pp 381−399.

(2) Jarvis, G. K.; Boyle, K. J.; Mayhew, C. A.; Tuckett, R. P. *J. Phys. Chem. A* **1998**, *102*, 3219−3229.

(3) Jarvis, G. K.; Tuckett, R. P. *Chem. Phys. Lett.* **1998**, *295*, 145−151.

(4) Some of the cited studies do not characterize the uncertainty of their measurements. In such cases, the error bar is arbitrarily assumed to represent twice the combined Type B standard uncertainty (see NIST Technical Note 1297 for definitions), denoted here as 2σ for simplicity.

(5) Tichy, M.; Javahery, G.; Twiddy, N. D.; Ferguson, E. E. *Int. J. Mass Spectrom. Ion Processes* **1987**, *79*, 231−235.

(6) Hansel, A.; Scheiring, C.; Glantschnig, M.; Lindinger, W.; Ferguson, E. E. *J. Chem. Phys.* **1998**, *109*, 1748−1750.

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(8) Clay, J. T.; Walters, E. A.; Grover, J. R.; Willcox, M. V. *J. Chem. Phys.* **1994**, *101*, 2069−2080.

(9) Noutary, C. J. *J. Res. Natl. Bur. Stand.* **1968**, *72A*, 479−485.

(10) Asher, R. L.; Ruscic, B. *J. Chem. Phys.* **1997**, *106*, 210−221.

(11) Horn, M.; Oswald, M.; Oswald, R.; Botschwina, P. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 323−331.

Table 1. Auxiliary Data at 0 and 298.15 K (Ion Convention[54])[a]

species	$\Delta_f H°_0$ (kJ/mol)	$H°(298 \text{ K}) - H°(0)$ (kJ/mol)	$S°_{298}$ (J mol^{-1} K^{-1})
CF_3	-462.8 ± 2.1^b	11.48^c	264.56^c
HF	-273.25 ± 0.70^c	8.60^c	173.78^c
CF_4	-927.23 ± 0.75^c	12.73^c	261.45^c
Br	117.93 ± 0.12^c	6.20^c	175.02^c
HBr^+	1097.23 ± 0.16^d	8.68^e	204.71^e
CF_3^+	[at issue]	11.07^f	250.18^f
SF_6	-1207.7 ± 0.3^g	16.94^c	291.67^c
SF_5^+	84.1 ± 6.0^h	16.51^i	302.90^h
Cl	119.620 ± 0.006^c	6.27^c	165.19^c
CN	437 ± 5^c	8.67^c	202.64^c
HCl^+	1137.66 ± 0.10^j	9.00^e	194.47^e
HCN^+	1445.0 ± 4.0^k	9.32^l	213.79^l
F	77.28 ± 0.30^c	6.52^c	158.75^c
Kr^+	1350.757 ± 0.001^c	6.20^c	175.61^c

[a] Uncertainties are believed to represent approximately 2σ.[4] [b] Reference 24. [c] Reference 35. [d] From $\Delta_f H°_0(HBr) = -28.44 \pm 0.16$ kJ/mol in ref 35 and $IE_a(HBr) = 11.6668 \pm 0.0001$ eV in ref 55. [e] Computed using the RRHO model and data from ref 14. [f] Computed using the RRHO model and data from ref 56. [g] From combining the 298.15 K value from ref 57 with thermal corrections from ref 35. [h] Value from ref 58; uncertainty is estimated. [i] Computed using the RRHO model and parameters computed at the B3LYP/6-31G* level; the value from the polynomial of ref 58 appears to be about 5 times too large. [j] From $\Delta_f H°_0(HCl) = -92.13 \pm 0.10$ kJ/mol in ref 35 and $IE(HCl) = 12.74593 \pm 0.00025$ eV in ref 59. [k] From $\Delta_f H°_0(HCN) = 132.4 \pm 4.0$ kJ/mol in ref 35 and $IE(HCN) = 13.6042 \pm 0.0002$ eV from ref 60. [l] Computed using the rigid rotor model and vibronic levels from ref 60.

0.82, 0.24, 0.36, and 0.47 eV for X = F, Cl, Br, and I, respectively. Asher and Ruscic remeasured these quantities for X = Cl, Br, and I and showed that the combined results of their study were consistent with accepted bond strengths D_0-(CF_3-X). The lower appearance energies obtained by many earlier workers were deemed erroneous and attributed to thermal energy content in the precursor molecules and to incorrect threshold analysis.

There are a few studies that were not discussed by Jarvis and Tuckett or Asher and Ruscic. The same research group that studied reaction 1 also measured the rate constant for the similar reaction 5. If one assumes that there is no kinetic barrier in

$$HBr^+ + CF_4 \rightarrow CF_3^+ + HF + Br \qquad (5)$$
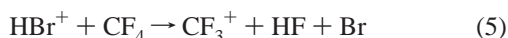
excess of the endothermicity, as is usual for ion−molecule reactions,[12] then one can estimate $\Delta_5 H°_{298} = -RT \ln(k_5/k_{coll}) \le 15.0$ kJ/mol, where k_{coll} is the expected collision rate ($k_{coll} = 6.05 \times 10^{-10}$ cm^3 s^{-1}, Langevin calculation in ref 13). Combined with the auxiliary data collected in Table 1 (which are not particularly controversial), this leads to $\Delta_5 H°_0 \le 10.5$ kJ/mol and $IE_a(CF_3) \le 8.28 \pm 0.02$ eV. This is the same procedure that was used to analyze reaction 1.[5] However, the resulting value for the ionization energy is certainly too low. Indeed, the ion source produced "substantial yields" of HBr^+ in its excited spin−orbit level,[13] $^2\Pi_{1/2}$, which lies 31.7 kJ/mol (0.33 eV) above the ground $^2\Pi_{3/2}$ level.[14] If all the observed extent of reaction 5 is attributed to the excited HBr^+, and if one assumes (to minimize the upper limit) that half the HBr^+ is excited, it follows that $\Delta_5 H°_{298} \le 45.0$ kJ/mol and $IE_a(CF_3) \le 8.59 \pm 0.02$ eV.

(12) Talrose, V. L.; Vinogradov, P. S.; Larin, I. K. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, pp 305−347.
(13) Tichy, M.; Javahery, G.; Twiddy, N. D. *Int. J. Mass Spectrom. Ion Processes* **1990**, *97*, 211−218.
(14) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules*; van Nostrand Reinhold: New York, 1979.

Table 2. Auxiliary Data at 570 K (Ion Convention[54])

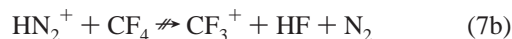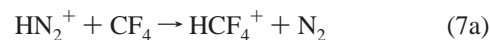| species	$H°(570 \text{ K}) - H°(0)$ (kJ/mol)	$S°_{570}$ (J mol^{-1} K^{-1})
CF_4	33.10^a	308.85^a
CF_3^+	26.03^b	285.30^b
SF_6	49.45^a	367.39^a
SF_5^+	44.00^c	368.06^d

[a] Reference 35. [b] Computed using the RRHO model and data from ref 56. [c] Computed using the RRHO model and parameters computed at the B3LYP/6-31G* level. [d] Reference 58.

Reaction 6 has been studied by the flowing afterglow method, and $\Delta_6 G°_{298} = 21.2 \pm 1.0$ kJ/mol was deduced from apparent equilibria.[15] This implies $\Delta_6 H°_0 = 13.3 \pm 1.0$ kJ/mol and IE_a-

$$SF_5^+ + CF_4 \rightarrow CF_3^+ + SF_6 \qquad (6)$$
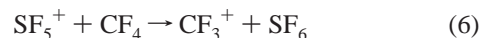
(CF_3) = 8.71 ± 0.07 eV. However, subsequent ion beam[7] and high-pressure mass spectrometry[16] studies concluded that reaction 6 did not actually reach equilibrium in the flowing afterglow experiment. In particular, Sieck and Ausloos inferred the limit $K_6 \le 1/9400$ at the temperature 570 K, or $\Delta_6 G°_{570} \ge 43.4$ kJ/mol. Auxiliary data from Table 2 lead to $\Delta_6 H°_0 \ge 31.2$ kJ/mol and $IE_a(CF_3) \ge 8.90 \pm 0.07$ eV. The ion beam experiments provided an energy threshold of 1.15 ± 0.11 eV (2σ) for reaction 6, which implies $\Delta_f H°_0(CF_3^+) \le 476 \pm 12$ kJ/mol and IE_a-(CF_3) $\le 9.73 \pm 0.13$ eV. However, the authors caution that thresholds for similar charge-transfer reactions are often higher than the corresponding thermodynamic limits, so the measurement for reaction 6 may be a high upper limit.[7]

In elegant free-jet experiments, Latimer and Smith studied reactions 7 and 8 at 5 K, where entropic effects are negligible.

$$HN_2^+ + CF_4 \rightarrow HCF_4^+ + N_2 \qquad (7a)$$

$$HN_2^+ + CF_4 \nrightarrow CF_3^+ + HF + N_2 \qquad (7b)$$

$$H_3^+ + CF_4 \rightarrow CF_3^+ + HF + H_2 \qquad (8)$$

This indicates that $\Delta_8 H°_0 \approx \Delta_8 G°_5 \lesssim 0$, and, unless there is a barrier for the addition of HF to CF_3^+, $\Delta_{7b} H°_0 \approx \Delta_{7b} G°_5 \gtrsim 0$. Combining the most recent recommendations for proton affinity values[17] with ab initio thermal functions [computed using the rigid rotor/harmonic oscillator (RRHO) model and B3LYP/6-31G* molecular parameters] yields $\Delta_f H°_0(H_3^+) = 1110.5 \pm 8$ kJ/mol and $\Delta_f H°_0(HN_2^+) = 1039.8 \pm 8$ kJ/mol. This, in turn, provides $385.8 \pm 8.1 \lesssim \Delta_f H°_0(CF_3^+) \lesssim 456.5 \pm 8.1$ kJ/mol, or $8.80 \pm 0.09 \lesssim IE_a(CF_3) \lesssim 9.53 \pm 0.09$ eV.

Reaction 9 was also studied by guided ion beam mass spectrometry.[7] The measured threshold of 6.38 ± 0.10 eV was

$$CF_3^+ + Xe \rightarrow CF_2^+ + F + Xe \qquad (9)$$
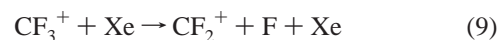
combined with a literature value $\Delta_f H°(CF_2^+) = 9.28 \pm 0.13$ eV (temperature unspecified) to obtain an appearance energy, $AE(CF_3^+/CF_4) = 14.22 \pm 0.16$ eV. Equivalently, $\Delta_f H°_0(CF_3^+) \le 395 \pm 16$ kJ/mol, which implies $IE_a(CF_3) \le 8.52 \pm 0.17$ eV.

Critique of the Above Analysis

The results summarized above are incompatible and cannot all be correct. Barring laboratory problems, the major cause of

(15) Babcock, L. M.; Streit, G. E. *J. Chem. Phys.* **1981**, *74*, 5700−5706.
(16) Sieck, L. W.; Ausloos, P. J. *J. Chem. Phys.* **1990**, *93*, 8374−8378.
(17) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413−656.

the discrepancies is incorrect data analysis; that is, the wrong conclusions were drawn from at least some of the observations. Many of the results cited above are discussed critically in this section.

There are many photoionization threshold measurements, and the corresponding conclusions vary widely. Most of the authors cite rather small uncertainties for the appearance energies that they derive. However, the values obtained depend strongly (well beyond the stated uncertainties) upon the technique chosen for extrapolating the data to the threshold. Practitioners do not yet agree about the proper method of data analysis; Asher and Ruscic mention three very different methods in their paper.[10] This lack of consensus indicates that photoionization threshold measurements must be treated circumspectly when the process of interest has a gradual onset.

Nonetheless, the relatively complicated treatment used by Asher and Ruscic does fit the data over the entire threshold region and not just over a limited portion of it, e.g., over the linear part. The high quality of the fit suggests, but does not prove, that this method of data analysis should be preferred. The most important difference between the experiment reported by Asher and Ruscic and the other photoionization measurements is the choice of precursor molecule, which leads to close competition between the two branches of reaction 4. The reference value of $IE_a(CF)$ provides an internal standard, which is lacking in the absolute appearance energy measurements and which is expected to compensate for most of the systematic error. Formally, this is similar to the mass spectrometric "kinetic method" of measuring the relative energetics of competing ion–molecule reactions.[18,19] In that context, it would be interesting to see the data of ref 10 plotted and analyzed as a branching ratio. Another alternative analysis method would be in terms of competing kinetic processes, as described recently for the collision-induced dissociation of multiply ligated ions.[20]

Jarvis and Tuckett pointed out that Asher and Ruscic's analysis depends on the lack of differential reverse activation barrier for the two branches of reaction 4. This is a common assumption in gas-phase ion chemistry, since the electrostatic attraction between an ion and a polarizable molecule often compensates for any barrier.[12] To test this assumption, ab initio calculations were carried out to determine the corresponding transition-state energies (see Computational Methods section for details). Two transition structures were found lying at quite different energies but below the energies of their respective products. This indicates that the observed branching ratio will, indeed, reflect the asymptotic energetics, supporting Asher and Ruscic's assumption.

The threshold energy measured by Jarvis and Tuckett also depends on certain assumptions. An erroneously low value could be obtained through incorrect data analysis, as described above. If abundant CF₃ radicals are formed by photodissociation, they would be photoionized at low energy, obscuring the desired process. A kinetic shift of the threshold to higher energy will occur if the precursor ion is metastable, with a long lifetime compared to the experimental flight time. In the case of C_3F_8, the ground electronic state of the molecular ion is thought to be repulsive, which implies a very short lifetime.[3] Indeed, CF_3^+ is the base peak in the electron-impact mass spectrum of C_3F_8[21]

and accounts for half the total ion signal in threshold photoionization of C_3F_8.[2] Thus, no kinetic shift is expected. A more likely problem with Jarvis and Tuckett's synchrotron experiment is a contribution from high-energy photons diffracted in second order from the grating. Although the investigators were aware of this possibility, they did not attempt to forestall it because they did not expect C_3F_8 to exhibit a peak at 26 eV in the threshold photoelectron spectrum.[2] To test this assumption, ab initio calculations were performed to predict the vertical ionization peaks for C_3F_8 and also for C_2F_6 (see Computational Methods section for details). The predictions agree well with the experimental spectra,[2] although they tend to be a little too high at the higher energies. The predicted peak energies and assignments are listed in the Supporting Information. For C_3F_8, states are predicted at 25.6 and 27.8 eV, which should probably be corrected to ∼25.1 and ∼27.2 eV. Since the observed peaks are as broad as ∼2 eV at half-height, ionization is very likely at 26 eV, contradicting Jarvis and Tuckett's assumption. Also note that uncertainties were combined linearly in the analysis of the CF_3^+ thermochemistry.[3] When uncertainties are instead combined quadratically, as is appropriate for uncorrelated Gaussian uncertainties,[22] Jarvis and Tuckett's measured threshold corresponds to $IE_a(CF_3) \leq 8.83 \pm 0.14$ eV instead of $\leq 8.83 \pm 0.25$ eV.

All appearance energy measurements rely upon auxiliary thermochemical data to derive quantitative information about fragment ions. For photoionization of trifluoromethyl halides, CF_3X (X = F, Cl, Br, I), into CF_3^+ and X, the enthalpies of formation of CF_3X and atomic X are required. The enthalpies of formation of gaseous halogen atoms are very well established and have uncertainties less than 0.01 eV.[23] A recent combined theoretical study and literature evaluation recommends only small adjustments (<0.05 eV) to accepted values for CF_3X.[24] Such small changes have a negligible effect on the credibility of the early photoionization experiments. The same study also suggests that the experimental enthalpy of formation for C_2F_4 is too high by up to 0.11 eV.[24] Fortunately, Asher and Ruscic's experiment provides the difference between two thresholds; it relies upon the ionization energy of CF and not upon the thermochemistry of the C_2F_4 precursor. The former quantity was measured by photoelectron spectroscopy to be $IE_a(CF) = 9.11 \pm 0.01$ eV.[25] This value is supported by the present ab initio calculations (9.08 ± 0.05 eV, see below), by G3 calculations[26] (9.14 eV, see below), and by extrapolated calculations (9.12 eV, derived from calculated[27] bond strengths). Jarvis and Tuckett's experiment relies upon the thermochemistry of C_3F_8 and of C_2F_5. Jarvis and Tuckett adopted $\Delta_fH°_{298}(C_3F_8) = -1783 \pm 7$ kJ/mol and $\Delta_fH°_{298}(C_2F_5) = -893 \pm 4$ kJ/mol. A more recent value for C_3F_8 is essentially equal, -1784.7 ± 8.8 kJ/mol.[21] For C_2F_5, empirically corrected ab initio calculations have provided $\Delta_fH°_{298}(C_2F_5) = -907.6 \pm 6.7$ kJ/mol,[28] which is lower than the value used by Jarvis and Tuckett and would raise their limit significantly, to $IE_a(CF_3) \leq 8.98 \pm 0.15$ eV. However, the authors of those calculations indicated that additional,

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(26) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764−7776.
(27) Ricca, A. *J. Phys. Chem. A* **1999**, *103*, 1876−1879.
(28) Zachariah, M. R.; Westmoreland, P. R.; Burgess, D. R., Jr.; Tsang, W.; Melius, C. F. *J. Phys. Chem.* **1996**, *100*, 8737−8747.

unquantified uncertainties arise from the choice of reference compound and from the large number of C–F bonds in this radical. Thus, the calculations do not appear reliable enough to supplant the earlier experimental value. Additional calculations were therefore done to assess the reliability of the experimental value. $\Delta_f H°_{298}(C_2F_5)$ was determined using an isodesmic, isogyric reaction scheme and estimated CCSD(T)/cc-pVTZ energies; details are given in the Computational Methods section. The result, $\Delta_f H°_{298}(C_2F_5) = -896 \pm 7$ kJ/mol, supports the experimental value adopted by Jarvis and Tuckett.

The above considerations suggest that the most reliable value from photoionization experiments is that obtained by Asher and Ruscic, $IE_a(CF_3) = 9.055 \pm 0.011$ eV. Asher and Ruscic cited an ab initio value of 8.98 ± 0.05 eV for support.[11] This was a very high-level calculation and included variational zero-point energy (ZPE), which is more accurate than the usual harmonic oscillator approximation. However, the basis sets were not augmented with diffuse functions. Diffuse functions are important when there is significant charge separation within a molecule, as found in CF_3 but not as much in CF_3^+. Diffuse functions will therefore stabilize neutral CF_3 more than CF_3^+, raising the computed ionization energy. Indeed, frozen-core CCSD(T)/aug-cc-pVTZ calculations (184 contracted basis functions) lead to an IE_a value 0.208 eV higher than the corresponding cc-pVTZ calculations. This difference is even larger than that obtained in ref 11, with a comparable increase in the size of the basis set in the valence region. Thus, the value in ref 11 should be revised to $IE_a(CF_3) = 9.04 \pm 0.05$ eV, which is in remarkably close agreement with the value obtained experimentally by Asher and Ruscic. For comparison, similar calculations on the CF radical lead to $IE_a(CF) = 9.08 \pm 0.05$ eV, in good agreement with the experimental value of 9.11 ± 0.01 eV measured directly by photoelectron spectroscopy.[25] Note that the more approximate G3 protocol[26] predicts $IE_a(CF_3) = 9.08$ eV[24] and $IE_a(CF) = 9.14$ eV.

Very recently, Ricca has reported CCSD(T) calculations on CF_n and CF_n^+ that were extrapolated to the limit of an infinitely large basis set.[27] Combining those calculated bond dissociation energies with the ionization energy of the carbon atom, $IE(C) = 11.26030$ eV,[21] leads to the prediction that $IE_a(CF_3) = 9.04$ eV. This agrees with the CCSD(T) result obtained above, although its uncertainty should be smaller, near ± 0.03 eV.

Even if one were to dismiss all the photoionization results, many conflicting measurements remain. Several of these rely upon ion–molecule reactions, which are usually supposed to be exothermic when they are observed to occur. This supposition has been ascribed to pragmatic decisions made in the early days of gas-phase ion chemistry.[1] However, reactions 1–3 and 5 are unusual because three product molecules are produced instead of only two. Such a change in molecularity is associated with large positive reaction enthalpies. The flow tube experiments were conducted at temperatures near 298 K and probably at pressures between 10^2 and 10^3 Pa.[29] As stated in the Abstract, it is not evident a priori whether one should apply conservation of energy or standard high-pressure thermochemistry. Reactions 1, 2, and 5 were interpreted in terms of conservation of energy, with $\Delta_r H° \lesssim 0$ for a spontaneous reaction. Considering spontaneity to indicate, instead, that the free energy is negative, $\Delta_r G° \lesssim 0$, leads to quite different implications for the energetics of CF_3^+, as shown below.

For reaction 1, the computed entropy change is $\Delta_1 S°_{298} = 133.2$ J mol^{-1} K^{-1} (Table 1), so the enthalpy change differs

from the free energy change by $T\Delta S = 39.7$ kJ/mol. If the reaction rate is interpreted to indicate that $\Delta_1 G°_{298}$ (and not ΔH) ≤ 0.06 eV,[5] then $\Delta G + T\Delta S = \Delta_1 H°_{298} \leq 45.5$ kJ/mol, $\Delta_1 H°_{298} - [H°_{298} - H°_0]$(reaction 1) $= \Delta_1 H°_0 \leq 41.3$ kJ/mol, and $\Delta_f H°_0$-$(CF_3^+) \leq 405.4 \pm 1.0$ kJ/mol. This leads to $IE_a(CF_3) \leq 9.00 \pm 0.02$ eV, with the correct value probably close to the upper limit.[5] This reinterpreted value is now in acceptable agreement with the photoionization and ab initio results. Note that the paper reporting reaction 1 also included a result for SF_5^+ that requires the same reinterpretation to bring it into conformity with more compelling observations.[30]

For reaction 2, the computed entropy change is $\Delta_2 S°_{298} = 151.4$ J mol^{-1} K^{-1} and $T\Delta S = 45.1$ kJ/mol. The reported rate constant[6] can be interpreted to imply that $\Delta_2 G°_{298} \leq 0.13$ eV, which leads to $\Delta_f H°_0(CF_3^+) \leq 405.4 \pm 6.5$ kJ/mol and IE_a-$(CF_3) \leq 9.00 \pm 0.07$ eV. The correct value would again be expected to lie close to the upper limit unless there is a kinetic barrier. This reinterpretation again removes the discrepancy with the higher ionization energy preferred here.

For reaction 5, $\Delta_5 S°_{298} = 132.8$ J mol^{-1} K^{-1} and $T\Delta S = 39.6$ kJ/mol. Two alternative chemical interpretations were described in the Introduction section. Attributing all reactivity to thermalized HBr^+ suggests $\Delta_5 G°_{298} \leq 15.0$ kJ/mol, which implies $\Delta_f H°_0(CF_3^+) \leq 375.5 \pm 1.1$ kJ/mol and $IE_a(CF_3) \leq 8.69 \pm 0.02$ eV, with equality if there are no kinetic barriers. Attributing the reactivity to abundant, excited $HBr^+(^2\Pi_{1/2})$, as above, leads to $IE_a(CF_3) \leq 9.00 \pm 0.02$ eV. The distribution of internal energy in the HBr^+ reactant was not well characterized in the experiment, but the authors determined that some excited HBr^+ was present.[13] Thus, the free energy interpretation again supports the higher value.

Reactions 1, 2, and 5 were studied in flow tubes. In contrast, reaction 3 was studied using guided ion beam mass spectrometry, in which an ion beam of controlled kinetic energy strikes a thermal (ca. 300 K), neutral gas. Pressures are typically kept between 4 and 100 mPa, so that reaction cross sections are measured under single-collision conditions.[31] Energy thresholds are derived by using an empirical function to fit the dependence of the cross section upon impact energy.[31,20] Note that $D_0(KrF)$ is probably between 0.013 and 0.035 eV,[32] so the identity of the neutral products of reaction 3 actually makes little difference in the enthalpy change. Since these are single-collision experiments, one would expect conservation of energy, and not free energy, to dictate the reactivity. The fitted threshold for reaction 3 is 0.24 ± 0.07 eV,[7] corresponding to $IE_a(CF_3) \leq 8.73 \pm 0.07$ eV. If the higher value for the ionization energy is actually correct, e.g., 9.055 ± 0.011 eV, then the threshold for reaction 3 should be 0.67 ± 0.03 eV at 0 K (Table 1). The ideal-gas heat content of the reactants equals the difference, 0.43 ± 0.08 eV (41 ± 8 kJ/mol), at a temperature of 530 ± 80 K. This is clearly too high for an ambient temperature, so thermal excitation cannot explain the discrepancy. Other possibilities are (1) the presence of $Kr^+(^2P_{1/2})$ (excitation energy = 0.666 eV[33]) in the beam or (2) incorrect data analysis, as in apparently most of the photoionization threshold measurements.

Although it is speculative, a third alternative is to treat the ion beam reaction as a free energy process. As noted in the experimental report, the temperature is not well defined.[7] One

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Table 3. Results for the Adiabatic Ionization Energy of CF$_3$ (Denoted Here as *I*) When Experiments Are Interpreted in Terms of Energy (Column Labeled ΔE) or When Reinterpreted in Terms of Free Energy (Column Labeled ΔG)[a]

reaction	ΔE	ΔG
1	$I \leq 8.68$ eV	$I \leq 9.00 \pm 0.02$
2	$I \leq 8.73$	$I \leq 9.00 \pm 0.07$
3	$I \leq 8.73 \pm 0.07$	$I \leq 9.02 \pm 0.07$
4	$I = 9.055 \pm 0.011$	
5	$I \leq 8.59 \pm 0.02$	$I \leq 9.00 \pm 0.02$
6		$8.90 \pm 0.07 \leq I$
7 and 8	$8.80 \pm 0.09 \leq I \leq 9.53 \pm 0.09$	
ab initio	$I = 9.04 \pm 0.05$	

[a] Unit is eV (1 eV = 96.485 kJ/mol). Uncertainties are believed to represent approximately 2σ.[4]

may estimate a crude effective temperature at threshold as the value corresponding to the internal energy in the collision complex. Assuming an ambient temperature of 298 K, the average internal energy at threshold is then $(H_{298} - H_0)[Kr^+ + CF_4] + 0.24$ eV $- 2.5RT = 36$ kJ/mol, where the last term in the sum approximately represents translational enthalpy that is unavailable for reaction.[34] Integrated ideal-gas heat capacity data for Kr$^+$ and CF$_4$[35] then imply an effective temperature of about 480 K. For reaction 3, we then compute $\Delta_3 S°_{480} = 138$ J mol^{-1} K^{-1} and $T_{eff}\Delta S = 66$ kJ/mol. At threshold, one can speculate that $\Delta_r G°_{480} \leq 0 \pm 0.07$ eV, so that $\Delta_r H^0_{480} \leq 66 \pm 7$ kJ/mol. Since $(H_{480} - H_0)$[reaction 3] = 5.5 kJ/mol, one computes $\Delta_r H°_0 \leq 60.5 \pm 7$ kJ/mol and $\Delta_f H°_0(CF_3^+) \leq 407 \pm 7$ kJ/mol. This corresponds to IE$_a$(CF$_3$) $\leq 9.02 \pm 0.07$ eV, which agrees with the value preferred here. It is hard to accept that data from guided ion beam mass spectrometry should be interpreted in this way; a comparative study of widely different ΔS may be illuminating.

The failure to observe reaction 7b only indicates endoergicity if there is no barrier to the reverse reaction. This assumption was verified by using ab initio calculations (see the Computational Methods section for details).

Reaction 9 was studied using guided ion beam mass spectrometry.[7] The measured threshold was 6.38 ± 0.11 eV (616 $\pm$ 11 kJ/mol). As noted by the authors of that study, this energy should equal the dissociation energy $D_0(CF_2^+-F)$. This quantity has been calculated recently by Ricca at the CCSD(T) level with basis set extrapolation. The result is $D_0(CF_2^+-F) = 579$ kJ/mol,[27] with a probable uncertainty of about 3 kJ/mol (i.e., $D_0 = 6.00 \pm 0.03$ eV). Thus, the measured threshold is probably too high by 0.38 ± 0.11 eV. If this reaction were treated as a free energy process, the enthalpic threshold would be shifted even higher, increasing the discrepancy. An activation barrier could explain the discrepancy but is very unlikely for a simple bond fission reaction in an ion. A more likely explanation is that conversion of translational energy to internal energy is incompletely efficient at collision energies as high as 6 eV, shifting the observed threshold above the thermodynamic limit.[36]
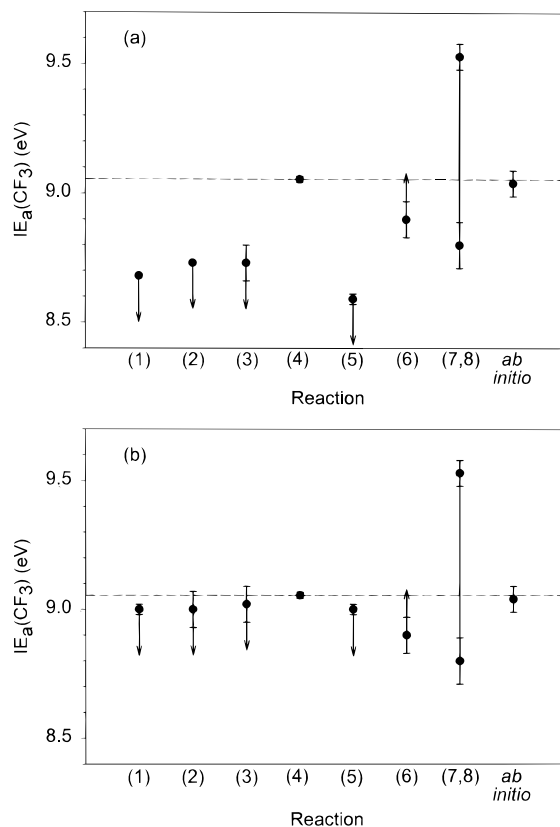
Summary and Conclusions

Table 3 summarizes the agreement among different results when interpreted in terms of energy or enthalpy (ΔE or ΔH) and when reinterpreted in terms of free energy (ΔG). For

Figure 1. Comparison of various results for the adiabatic ionization energy of CF$_3$ before (a) and after (b) reinterpretation of several experiments with entropic considerations included. Dashed lines mark the best experimental value IE$_a$(CF$_3$) = 9.055 ± 0.011 eV. The error bars represent 2σ.[4]

reaction 4, no free energy analysis was attempted because the experiment was collisionless. For reaction 6, the measured constraint on the equilibrium constant was only interpreted in terms of free energy because equilibrium conditions are always interpreted in terms of free energy. For reactions 7 and 8, the experiment was done at 5 K, where $T\Delta S \approx 0$ and the difference between the two interpretations is negligible. Although most of the entries in Table 3 indicate upper limits for IE$_a$(CF$_3$), it is likely in all cases that there are no kinetic barriers and that the equality holds. Figure 1 shows clearly that the various observations are much more consistent if entropy is considered in their analyses. This suggests that entropy is important in the flow tube experiments. It also suggests that entropy (i.e., density of states) is important in the guided ion beam experiment (reaction 3). However, since that is a single-collision experiment, it is more plausible that some other problem is responsible for the discrepancy between it and the other measurements. It would be instructive to examine other guided ion beam measurements for evidence of entropic effects.

Accepting Asher and Ruscic's value, IE(CF$_3$) = 9.055 ± 0.011 eV,[10] implies $\Delta_f H°_0(CF_3^+) = 410.9 \pm 2.4$ kJ/mol. Table 4 summarizes the corresponding energy changes and free energy changes for reactions 1−3, 5, and 7b at 298.15 and 400 K. Studies of other chemical reactions by Abboud and co-workers suggest that entropy remains important at pressures as low as 0.1 mPa.[37−39] It would be interesting to compare Table 4 with

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Table 4. Changes in Internal Energy [$\Delta U = \Delta H - \Delta(PV) = \Delta H - RT$] and Free Energy ($\Delta G = \Delta H - T\Delta S$) for Selected Reactions at 298.15 and 400 K[a]

reaction	$\Delta_r U^\circ_{298}$	$\Delta_r G^\circ_{298}$	$\Delta_r U^\circ_{400}$	$\Delta_r G^\circ_{400}$	uncertainty
1	48.6	11.3	47.9	−2.3	2.6
2	60.7	18.0	60.9	2.4	6.9
3	67.0	29.0	66.8	15.0	2.5
5	87.6	50.4	87.1	36.8	2.6
7b	28.9	−13.8	28.4	−29.3	8.4

[a] Uncertainty represents 2σ.[4] Units are kJ/mol.

Table 5. Frozen-Core, Spin-Unrestricted CCSD(T)//UMP2/ 6-311+G* Energies of $C_2F_4^+$, CF_3^+, CF, CF_3, CF^+, and the Two Transition Structures for Reaction 4[a]

species	E_0 (hartree)
$C_2F_4^+$	−474.293014
CF_3^+	−336.641097
CF	−137.528095
TS1	−474.208317
CF_3	−336.970604
CF^+	−137.201351
TS2	−474.177229

[a] ZPE is at the ROHF/6-31G* level and has been scaled by 0.91.[50]

observations made in an ion cyclotron resonance (FTMS) spectrometer at even lower pressures. FTMS is typically operated at pressures between 10^{-4} and 1 mPa and with time scales between 10^{-2} and 10^3 s. Comparison with the flow tube results (ΔG columns in Table 4) might reveal how low the pressure must be to suppress entropic effects.

Computational Methods[40]

Miscellaneous calculations were done at the B3LYP/6-31G* level (hybrid density functional) to determine molecular geometries and harmonic vibrational frequencies for purposes of computing the molecular partition function.[34] These calculations were done using the Gaussian 98 program package.[41]

Transition structures for the two branches of reaction 4 were computed at the ROHF/6-31G* level. Mulliken population analysis confirmed that the charge and spin densities corresponded to the desired transition states. IRC calculations[42] verified that the transition structures connected the reactant with the desired products. The transition structures were then refined at the frozen-core UMP2/6-311+G* level. Single-point frozen-core UCCSD(T)/6-311+G*//UMP2 energies for the various species are listed in Table 5. Geometries and harmonic vibrational spectra are available as Supporting Information. Two very different transition states were found. TS1 leads to the more stable products $CF_3^+ + CF$, while TS2 leads to $CF_3 + CF^+$. The C−C distances are 1.487 Å for TS1 and 2.785 Å for TS2, and they lie at

different energies, 222 and 304 kJ/mol (including ZPE) above $C_2F_4^+$, respectively. They do lie 103 and 14 kJ/mol below their respective products, indicating that there are no barriers to the reverse of reactions 4 and supporting the interpretation by Asher and Ruscic. Furthermore, the surfaces for the two electronic states cross each other (and also cross at least one other surface) during the reaction (C_1 symmetry). Thus, vibronic mixing would tend to average the two diabatic curves together. These results were obtained using the GAMESS,[43] Gaussian 98,[41] and ACES II[44] program packages.

Vertical ionization energies (IE_v) of C_3F_8 and C_2F_6 were computed at optimized B3LYP/6-31G* geometries using the frozen-core, outer-valence Green's function method (OVGF)[45,46] and 6-311+G* basis sets. Values of IE_v (see Supporting Information for tables) correspond to the ionic states accessible by removing a single valence electron from the neutral molecule. Pole strengths are all ≥ 0.89, suggesting that the OVGF results are reliable.[46] Comparisons with Figures 1 and 2 of ref 2 indicate that the calculations overbind slightly, with the error increasing with increasing binding energy. At 24 eV, the errors are approximately 0.4 eV for C_2F_6 and 0.5 eV for C_3F_8. These calculations were done using the Gaussian 98[41] program package.

For the direct calculation of the ionization energy of CF_3, CEPA-1/cc-pVQZ-g geometries were taken from ref 11. Neglecting vibrational zero-point energy (ZPE), the result from frozen-core CCSD(T)/cc-pVTZ calculations [$E_e(CF_3) = -337.172974$ and $E_e(CF_3^+) = -336.850175$ hartree (1 hartree = 27.2114 eV = 2625.5 kJ/mol)] is $IE_e(CF_3) = 8.784$ eV. For the same calculation, Horn et al. reported $IE_a = 8.834$ eV;[11] the difference reflects anharmonic ZPE. Adding diffuse functions, the CCSD(T)/aug-cc-pVTZ result [$E_e(CF_3) = -337.201152$ and $E_e(CF_3^+) = -336.870692$ hartree] is $IE_e(CF_3) = 8.992$ eV, 0.208 eV higher than the cc-pVTZ result. When the valence saturation is instead increased to cc-pVQZ (with g-functions deleted), the resulting $IE_a = 8.977$ eV is 0.143 eV higher than the cc-pVTZ result.[11] The largest t_2 amplitudes in the aug-cc-pVTZ calculations were 0.018 for CF_3 and 0.039 for CF_3^+. These values are small and indicate that CCSD(T) theory will probably give very reliable results.

For the ionization energy of CF, geometries were computed at the frozen-core CCSD(T)/cc-pVTZ level and were $r = 1.2779$ and 1.1617 Å for CF and CF^+, respectively (1 Å = 10^{-10} m). The potential energy curves were computed at the same level, and vibrational levels were computed variationally using the Fourier grid Hamiltonian procedure,[47] leading to ZPE = 658 cm^{-1}, $\omega_e = 1319$ cm^{-1}, and $\omega_e x_e = 10.0$ cm^{-1} for CF, which may be compared with experimental values $\omega_e = 1308.1$ cm^{-1} and $\omega_e x_e = 11.10$ cm^{-1}.[14] The corresponding results for CF^+ are ZPE = 891 cm^{-1}, $\omega_e = 1786$ cm^{-1}, and $\omega_e x_e = 12.4$ cm^{-1}. At the frozen-core CCSD(T) level, the cc-pVTZ basis sets then yield $IE_a(CF) = 8.981$ eV. Aug-cc-pVTZ, cc-pVQZ (g-functions included), and aug-cc-pVQZ give 9.076, 9.049, and 9.087 eV, respectively. The largest t_2 amplitudes in the aug-cc-pVTZ calculations were 0.054 for CF and 0.100 for CF^+, suggesting that CCSD(T) will work well but not as reliably as for CF_3 and CF_3^+. The calculations on CF_3^+ and CF^+ were done using the ACES II,[44,48] Gaussian 94,[49] and Gaussian 98[41] program packages. Open-shell calculations were spin-unrestricted.

The Gaussian-3 (G3) calculations for CF and CF^+ were computed according to the published procedure[26] and using the Gaussian 94[49]

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program package. The resulting G3 energies are -137.721113 and -137.385192 hartree for CF and CF$^+$, respectively.

To seek a barrier for the reverse of reaction 7b, the geometry of CF$_4$H$^+$, which is a product of reaction 7a, was first optimized at the HF/6-31G* level. The resulting structure is a complex between CF$_3^+$ and HF, with an F$_3$C$^+\cdots$FH distance of 2.211 Å. The F$_3$C$^+\cdots$FH distance was incrementally increased to 10.211 Å, with all other coordinates relaxed. The energy along this adiabatic potential energy curve increases monotonically; there is no reverse barrier at the HF/6-31G* level. This supports the assumption made in the critique section regarding reaction 7b. These calculations were done using the Gaussian 98[41] program package.

The enthalpy of formation of C$_2$F$_5$ radical was estimated using reaction 10, which is isodesmic and isogyric. Auxiliary data were taken

$$C_2F_5 + CF_4 \rightarrow C_2F_6 + CF_3 \qquad (10)$$

from ref 24: $\Delta_fH°_{298}(CF_4) = -933.2 \pm 0.8$ kJ/mol, $\Delta_fH°_{298}(C_2F_6) = -1344.3 \pm 3.3$ kJ/mol, and $\Delta_fH°_{298}(CF_3) = -465.7 \pm 2.1$ kJ/mol. Geometries and vibrational frequencies were computed at the B3LYP/6-31G* level. Vibrational zero-point energies were computed using a scaling factor of 0.9806.[50] Enthalpy increments ($H°_{298} - H°_0$) were computed using the rigid rotor/harmonic oscillator model and unscaled vibrational frequencies.[34] Energies were estimated assuming basis set additivity (as in Gaussian-3 and related protocols[26]) as $\Delta_rH°_{298}$[CCSD-(T)/cc-pVTZ] $\approx \Delta_rH°_{298}$[CCSD(T)/cc-pVDZ] $- \Delta_rH°_{298}$[MP2/cc-pVDZ] $+ \Delta_rH°_{298}$[MP2/cc-pVTZ] $= (22.0-20.2 + 17.5)$ kJ/mol $= 19.3$ kJ/mol, using Dunning's correlation-consistent basis sets.[51] Com-

bining the experimental uncertainties with an estimated calculational uncertainty of 6 kJ/mol leads to $\Delta_fH°_{298}(C_2F_5) = -896.1 \pm 7.2$ kJ/mol. These calculations were done using the Gaussian 98[41] program package.

Visualization tasks were done using the MOLDEN[52] and XMol[53] programs. Calculations were done on Cray C90, IBM RS/6000, and Intel PentiumII-based computers.

Supporting Information Available: Tables of molecular geometries and harmonic vibrational spectra computed at the ROHF/6-31G* level, molecular geometries computed at the frozen-core (U)MP2/6-311+G* level, and outer valence vertical ionization energies computed at the frozen-core ROVGF/6-311+G*//B3LYP/6-31G* level (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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