On the heats of formation of trifluoromethyl radical CF_3 and its cation CF_3^+

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The CF^+ and CF_3^+ fragment ion yield curves from C_2F_4 have been remeasured by photoionization mass spectrometry. Fits with appropriate model curves yield the appearance potentials $AP_0(CF_3^+/C_2F_4)=13.721\pm0.005$ eV and $AP_0(CF^+/C_2F_4)=13.777\pm0.005$ eV and an accurate difference in ionization potentials, $IP(CF)-IP(CF_3)=0.055\pm0.003$ eV. With the existing photoelectron value $IP(CF)=9.11\pm0.01$ eV, this produces $IP(CF_3)=9.05_5\pm0.01_1$ eV. The CF_3^+ fragments from CF_3Cl, CF_3Br, and CF_3I have also been remeasured, and their ion yield curves fitted with model functions. The experimentally derived $AP_0(CF_3^+/CF_3Cl)<12.867\pm0.008$ eV has been found to be only an upper limit. The analogous CF_3^+ fragment yield curves from CF_3Br and CF_3I produce $AP_0(CF_3^+/CF_3Br)=12.095\pm0.005$ eV and $AP_0(CF_3^+/CF_3I)=11.384\pm0.005$ eV, leading to $D_0(CF_3-Br)=70.1\pm0.3$ kcal/mol (70.8\pm0.3 kcal/mol at 298 K) and $D_0(CF_3-I)=53.7\pm0.3$ kcal/mol (54.3\pm0.3 kcal/mol at 298 K). Based on tabulated values for $\Delta H_f^\circ(CF_3Br)$ and $\Delta H_f^\circ(CF_3I)$, which appear to be inconsistent by ~ 1 kcal/mol, a compromise value of $\Delta H_{f\ 298}^\circ(CF_3)=-111.4\pm0.9$ kcal/mol (-110.7 ± 0.9 kcal/mol at 0 K) is selected, resulting in $\Delta H_{f\ 298}^\circ(CF_3^+)=97.4\pm0.9$ kcal/mol (98.1\pm0.9 kcal/mol at 0 K). Additionally, $IP(CF_4)\equiv AP_0(CF_3^+/CF_4)=14.67\pm0.04$ eV can be inferred. From data on C_2F_4, $\Delta H_{f\ 298}^\circ(CF)=62.5\pm1.1$ kcal/mol (61.7\pm1.1 kcal/mol at 0 K) can be deduced. Many earlier literature values for appearance potentials of CF_3^+ from CF_3X, leading to very low $\Delta H_f^\circ(CF_3^+)$ and/or $IP(CF_3)$ values, are demonstrated to be in error. © *1997 American Institute of Physics.* [S0021-9606(97)01601-2]

I. INTRODUCTION

The CF_3 radical has attracted recent attention because of its relevance in the atmospheric chemistry associated with oxidative degradation of fluorocarbons and hydrofluorocarbons.[1–5] It is thus surprising to find that its heat of formation, $\Delta H_f^\circ(CF_3)$, and its ionization potential, $IP(CF_3)$ are still not known accurately.

JANAF[6] lists $\Delta H_{f\ 298}^\circ(CF_3)=-112.4\pm1.0$ kcal/mol, originally derived by Syverud[7] "from least squares, simultaneous adjustment of the enthalpies of formation of CF_3, CF_3X (X=H,Cl,Br,I,CF_3), and C_2F_4." The analogous least-squares adjustment of $\Delta H_f^\circ(CF_3X)$ by Gurvich *et al.*[8] does not include either C_2F_4 or CF_3. Rather, they obtain $\Delta H_{f\ 298}^\circ(CF_3)=-112.8\pm1.2$ kcal/mol as the mean of seven determinations based on various kinetic measurements of $D_0(CF_3-X)$. McMillen and Golden[9] recommend a slightly higher value of $\Delta H_{f\ 298}^\circ(CF_3)=-111.7\pm3.6$ kcal/mol. The compilation by Lias *et al.*[10] prefers the still higher value of Tsang,[11] $\Delta H_{f\ 300}^\circ(CF_3)=-110.0\pm1.0$ kcal/mol (see Table I).

Tsang's selection[11] for $\Delta H_f^\circ(CF_3)$ is based on his $D_{300}(CF_3-Br)=70.5\pm1.0$ kcal/mol (69.8\pm1.0 kcal/mol at 0 K), yielding $\Delta H_{f\ 300}^\circ(CF_3)=-111.3\pm1.7$ kcal/mol, which was then fine tuned to -110.0 ± 1.0 kcal/mol using tabulated kinetic data[12,13] involving CHF_3 and C_2H_6. Recently, Kumaran *et al.*[14] inferred $D_0(CF_3-I)=55.0$ kcal/mol (55.6 kcal/mol at 298 K), which implies $\Delta H_{f\ 298}^\circ(CF_3)=-110.7$ kcal/mol, and therefore supports Tsang's value for $\Delta H_f^\circ(CF_3)$. In a subsequent paper, Kumaran *et al.*[15] report $D_0(CF_3-Cl)=89.0\pm1.5$ kcal/mol (89.9\pm1.5 kcal/mol at 298

K), significantly higher than their previous inference[6,16] of 84.8 kcal/mol, and implying $\Delta H_{f\ 298}^\circ(CF_3)=-108.3\pm1.7$ kcal/mol. However, after elaborate comparison with data on other halomethanes and high-quality *ab initio* calculations, Kumaran *et al.*[15] conclude that although the experimental $D_0(CF_3-Cl)$ fits very well in the trends for the remaining experimental bond strengths, the JANAF[6] value for $\Delta H_f^\circ(CF_3)$ is nevertheless probably correct, and that most inconsistencies can be resolved by attaching error bars which are somewhat larger than those originally quoted.

The determinations of $\Delta H_f^\circ(CF_3)$ discussed above are based primarily on measurements of CF_3-X bond energies by kinetic methods. At least in principle, an alternative approach is provided by photoionization mass spectrometry, which can yield accurate appearance potentials (AP) of the CF_3^+ fragment from various CF_3X parent molecules. Together with the ionization potential (IP) of CF_3, these APs lead to the desired bond energies through $D_0(CF_3-X)=AP_0(CF_3^+/CF_3X)-IP(CF_3)$.

Unfortunately, direct measurements of the adiabatic IP of CF_3 are quite difficult, since the ionization threshold is dominated by very unfavorable Franck–Condon factors, reflecting the change in geometry from pyramidal CF_3 to planar CF_3^+. Thus, from photoionization measurements of the CF_3 radical, Lifshitz and Chupka[17] concluded early on that the adiabatic IP is "probably" 9.25 ± 0.04 eV. Subsequently, Walter *et al.*[18] suggested 9.17 ± 0.08 eV as a "weighted average of 9.25 and 9.11 eV," the latter based on unpublished[19] data on CF_3I, CF_3Br, and CF_3Cl. JANAF[6] adopts the same $IP(CF_3)$, while Lias *et al.*[10] prefer the esti-

TABLE I. An overview of various experimental values for the heats of formation of CF_3 and CF_3^+, and a selection of CF_3–X (X=Cl, Br, and I) bond energies relevant to present work. The currently recommended values are underlined. Unless stated otherwise, values in brackets have been inferred using standard heats of formation (see Ref. 50). Values obtained by conversion between 0 K and 298 K are in braces.

Quantity	298 K	0 K	Source
$\Delta H_f^\circ(CF_3)$	-111.4 ± 0.9 kcal/mol	-110.7 ± 0.9 kcal/mol	This work
	-112.4 ± 1.0 kcal/mol	-111.7 ± 1.0 kcal/mol	JANAF[a]
	-112.8 ± 1.2 kcal/mol	-112.1 ± 1.2 kcal/mol	Gurvich et al.[b]
	-110.0 ± 1.0 kcal/mol	$\{-109.3\pm1.0$ kcal/mol$\}$	Tsang[c]
	-111.3 ± 1.7 kcal/mol	$\{-110.6\pm1.7$ kcal/mol$\}$	Tsang[d]
	-111.7 ± 3.6 kcal/mol	$\{-111.0\pm3.6$ kcal/mol$\}$	McMillen and Golden[e]
	$\{-110.7$ kcal/mol$\}$	-110.0 kcal/mol	Kumaran et al.[f]
	$[-108.3$ kcal/mol$]$	$[-107.6$ kcal/mol$]$	Kumaran et al.[g]
$\Delta H_f^\circ(CF_3^+)$	97.4 ± 0.9 kcal/mol	98.1 ± 0.9 kcal/mol	This work
	$\leqslant86.6$ kcal/mol	$\{\leqslant87.3$ kcal/mol$\}$	Noutary[h]
	$[\leqslant99\pm7$ kcal/mol$]$	$[\leqslant99\pm7$ kcal/mol$]$	Powis[i]
	$[86.4\pm1.6$ kcal/mol$]$	$[87.1\pm1.6$ kcal/mol$]$	Fisher and Armentrout[j]
	93.5 kcal/mol	98.8 kcal/mol	Ajello et al.[k]
	$\{85.9\pm1.1$ kcal/mol$\}$	86.6 ± 1.1 kcal/mol	Clay et al.[l]
	97.6 kcal/mol	98.3 kcal/mol	Berman and Beauchamp[m]
	95.4 ± 1.2 kcal/mol	96.1 ± 1.2 kcal/mol	Bombach et al.[n]
$D_0(CF_3\text{-}Cl)$	$<88.8\pm0.3$ kcal/mol	$<87.9\pm0.3$ kcal/mol	This work
	85.8 ± 1.3 kcal/mol	84.9 ± 1.3 kcal/mol	JANAF[a]
	$\{89.9\pm1.5$ kcal/mol$\}$	89.0 ± 1.5 kcal/mol	Kumaran et al.[g]
	$\{88.4$ kcal/mol$\}$	87.5 kcal/mol	Kumaran et al.[o]
	$[88.2\pm1.3$ kcal/mol$]$	$[87.3\pm1.3$ kcal/mol$]$	Tsang[c]
$D_0(CF_3\text{-}Br)$	70.8 ± 0.3 kcal/mol	70.1 ± 0.3 kcal/mol	This work
	69.4 ± 1.2 kcal/mol	68.7 ± 1.2 kcal/mol	JANAF[a]
	$[71.8\pm1.2$ kcal/mol$]$	$[71.1\pm1.2$ kcal/mol$]$	Tsang[c]
	70.5 ± 1.0 kcal/mol	$\{69.8\pm1.0$ kcal/mol$\}$	Tsang[d]
$D_0(CF_3\text{-}I)$	54.3 ± 0.3 kcal/mol	53.7 ± 0.3 kcal/mol	This work
	53.9 ± 1.3 kcal/mol	53.3 ± 1.3 kcal/mol	JANAF[a]
	$\{55.6$ kcal/mol$\}$	55.0 kcal/mol	Kumaran et al.[f]
	$[56.3\pm1.3$ kcal/mol$]$	$[55.7\pm1.3$ kcal/mol$]$	Tsang[c]

[a]Reference 6.
[b]Reference 8.
[c]Reference 11, final recommendation for $\Delta H_f^\circ(CF_3)$, adopted by Lias et al. (Ref. 10).
[d]Reference 11, experimental determination of $D_0(CF_3\text{-}Br)$.
[e]Reference 9.
[f]Reference 14, experimental determination of $D_0(CF_3\text{-}I)$.
[g]Reference 15, experimental determination of $D_0(CF_3\text{-}Cl)$.
[h]Reference 24.
[i]Reference 29, from the upper limit to $AP(CF_3^+/CF_4)$.
[j]Reference 33.
[k]Reference 34.
[l]Reference 37.
[m]Reference 38.
[n]Reference 39, listed as suggested value in Lias et al. (Ref. 10).
[o]Reference 15, the value for $D_0(CF_3\text{-}Cl)$ from Troe/Lennard-Jones and RRKM/Gorin models.

mated IP(CF_3)$\leqslant$8.9 eV of Loguinov et al.[20] (see Table II).

Recent calculations by Horn et al.[21] suggest that it is genuinely difficult to obtain a reliable value for the adiabatic IP(CF_3) by direct photoionization or photoelectron measurements. Their calculated Franck–Condon envelope shows that the vertical transition occurs at $v'=20$ of the umbrella motion, and that, as one progresses toward the threshold, at $v'=8$ the intensity has already fallen to less than 1%. Thus, determining the position of $v'=0$ by direct methods may be, in words of Horn et al., "a formidable problem."

Consequently, one is encouraged to find alternative paths to IP(CF_3). An excellent succedaneum is offered through photoionization of C_2F_4. Walter et al.[18] observed and measured both of the following two fragmentation processes:

$$C_2F_4 + h\nu \rightarrow CF^+ + CF_3 + e^-,$$

$$C_2F_4 + h\nu \rightarrow CF + CF_3^+ + e^-.$$

If small enough, the energy gap between the two thresholds corresponds to the difference between the IPs of CF_3 and CF, i.e., $AP(CF^+/C_2F_4) - AP(CF_3^+/C_2F_4) = IP(CF) - IP(CF_3)$. Walter et al.[18] report $AP_0(CF_3^+/C_2F_4) = 13.70\pm0.02$ eV, $AP_0(CF^+/C_2F_4) = 13.76\pm0.01$ eV, and also $AP(CF^+/C_2F_4) - AP(CF_3^+/C_2F_4) = 0.06\pm0.01$ eV. At the time, IP(CF) was known even less precisely than IP(CF_3) and hence Walter et al. used their suggested IP(CF_3)$=9.17\pm0.08$ eV and the gap value to obtain IP(CF)$=9.23\pm0.08$ eV. Since then, IP(CF)$=9.11\pm0.01$ eV has been firmly established by

TABLE II. Experimentally derived ionization potentials and appearance potentials relevant to present work. The currently recommended values are underlined. Unless stated otherwise, values in brackets have been inferred using standard heats of formation (see Ref. 50). Values obtained by conversion between 0 K and 298 K are in braces.

Quantity	298 K	0 K	Source
IP(CF_3)	9.05$_5$±0.01$_1$ eV		This work
	9.25±0.04 eV		Lifshitz and Chupka[a]
	9.17±0.08 eV		Walter et al.[b]
	9.11 eV		Walter et al.[c]
	≤8.9 eV		Loguinov et al.[d]
	[9.05±0.02 eV]		Walter et al.; Dyke et al.[e]
	<8.62 eV		Noutary[f]
	[≤9.2±0.3 eV]		Powis[g]
	[8.62±0.08 eV]		Fisher and Armentrout[h]
	[8.9 eV or 9.1 eV]		Ajello et al.[i]
	[8.60±0.06 eV]		Clay et al.[j]
	[9.11±0.06 eV]		Berman and Beauchamp[k]
	[9.01±0.07 eV]		Bombach et al.[l]
AP(CF_3^+/C_2F_4)	13.616±0.005 eV	13.721±0.005 eV	This work
	{13.60±0.02 eV}	13.70±0.02 eV	Walter et al.[b]
AP(CF^+/C_2F_4)	13.672±0.005 eV	13.777+0.005 eV	This work
	{13.66±0.01 eV}	13.76±0.01 eV	Walter et al.[b]
IP(CF)-IP(CF_3)	0.055±0.003 eV		This work
	0.06±0.01 eV		Walter et al.[b]
AP(CF_3^+/CF_4)	⋯	[14.67±0.04 eV]	This work[m]
	⋯	15.52 eV	Noutary[f,m]
	⋯	≤15.35 eV	Walter et al.[b,m]
	⋯	≤14.7 eV	Rosenstock et al.[m,n]
	⋯	≤14.7±0.3 eV	Powis[m,g]
	14.2±0.1 eV	⋯	Tichy et al.[o,p]
	14.24±0.07 eV	⋯	Fisher and Armentrout[h,p]
AP(CF_3^+/CF_3Cl)	<12.788±0.008 eV	<12.867+0.008 eV	This work
	⋯	12.57 eV	Noutary[f,q]
	12.65±0.04 eV	12.81±0.04 eV	Ajello et al.[i,q]
	12.55 eV	⋯	Jochims et al.[r]
	⋯	12.75±0.05 eV	Creasey et al.[q,s]
AP(CF_3^+/CF_3Br)	12.009±0.005 eV	12.095±0.005 eV	This work
	⋯	11.84 eV	Noutary[f,q]
	⋯	11.92±0.02 eV	Creasey et al.[q,s]
	⋯	11.56±0.02 eV	Clay et al.[j,q]
AP(CF_3^+/CF_3I)	11.293±0.005 eV	11.384±0.005 eV	This work
	⋯	10.89 eV	Noutary[f,q]
	11.27±0.02 eV	11.36±0.02 eV	Berman and Beauchamp[k]
	11.13±0.1 eV	11.26±0.05 eV	Bombach et al.[l]

[a]Reference 17.
[b]Reference 18.
[c]Reference 19.
[d]Reference 20, adopted by Lias et al. (Ref. 10).
[e]Estimated using IP(CF)-IP(CF_3) from Walter et al. (Ref. 18) and IP(CF) from Dyke et al. (Ref. 22).
[f]Reference 24.
[g]Reference 29.
[h]Reference 33.
[i]Reference 34.
[j]Reference 37.
[k]Reference 38.
[l]Reference 39.
[m]The onset of CF_3^+ from CF_4 has to be interpreted in terms of parent ionization rather than fragmentation (see text for details).
[n]IP(CF_4), as estimated in Ref. 23.
[o]Reference 32.
[p]The reported value is determined as an enthalpy of reaction for $CF_4 \rightarrow CF_3^+ + F + e^-$ at some unknown temperature, tacitly assumed to be 298 K.
[q]Threshold value picked as "first onset;" it is not clear how to convert from 0 K to 298 K or vice versa.
[r]Reference 35.
[s]Reference 36.

photoelectron spectroscopy.[22] With the 0.06±0.01 eV gap of Walter *et al.*,[18] one derives IP(CF$_3$)=9.05±0.02 eV, which is, in our opinion, the best currently available experimental value for this quantity, in reasonably good agreement with the latest calculated[21] IP of 8.98±0.05 eV.

Besides IP(CF$_3$), the key to determining D_0(CF$_3$–X) by photoionization methods are accurate values for AP(CF$_3^+$/CF$_3$X). Older determinations by electron impact and other methods are conveniently tabulated by Rosenstock *et al.*[23] One of the earliest photoionization measurement of various CF$_3$X species was performed by Noutary.[24] *Inter alia*, he reports AP$_0$(CF$_3^+$/CF$_3$X)=15.52 eV, 12.57 eV, 11.84 eV, 10.89 eV, and 14.14 eV for X=F, Cl, Br, I, and H, respectively. However, these "AP$_0$" values were produced by selecting the first discernible onset of the CF$_3^+$ fragment in the ion yield curve, far into the thermal tail. Such selection is contrary to modern understanding of fragmentation thresholds and, in general, will result in values that are too low. Thus, Noutary concluded that IP(CF$_3$)⩽8.62 eV and consequently $\Delta H_{f\ 0}^{\circ}$(CF$_3^+$)⩽87.3 kcal/mol. He also noted that the CF$_3^+$ fragment is generated with "large amounts of excess energy." Undoubtedly, this inference was partly induced by the inclusion of examples which were later found to be pathological cases, such as CF$_4$ (for which Noutary found the largest excess energy, 31 kcal/mol), and which do not produce simply interpretable CF$_3^+$ fragment thresholds.

The ground state of CF$_4^+$ is repulsive and fragments to CF$_3^+$+F on a timescale significantly shorter than the instrumental residence time.[18,25–27] Except for special circumstances,[28] the parent CF$_4^+$ is not observed. Instead, the CF$_3^+$ fragment appears and assumes the role of a pseudoparent. Thus, the CF$_3^+$ onset from CF$_4$ is shaped essentially by the underlying Franck–Condon factors for parent ionization,[18] rather than by the fragmentation rate. Because of this, the CF$_3^+$ threshold should be interpreted in terms of parent ionization and it becomes not only justifiable, but necessary to look close to the first onset of the ion signal. In fact, the difference between the adiabatic IP(CF$_4$) and AP$_0$(CF$_3^+$/CF$_4$) is semantic, since both correspond to the same transition, from the ground state of CF$_4$ directly to the CF$_3^+$+F dissociation asymptote.

Since Noutary's work, there has been a number of attempts to clarify the fragmentation of CF$_4^+$ by various methods.[18,25,29–33] Recognizing it as an upper limit, Walter *et al.*[18] report AP(CF$_3^+$/CF$_4$)⩽15.35 eV. More recently, Powis[29] derived an improved limit of ⩽14.7±0.3 eV from energy release coincidence measurements. Using ion/molecule reaction techniques, Tichy *et al.*[32] obtained AP(CF$_3^+$/CF$_4$)=14.2±0.1 eV, later refined by Fisher and Armentrout[33] to 14.24±0.07 eV. (Here, "AP" is actually the room-temperature enthalpy of the reaction CF$_4$→CF$_3^+$+F, which differs from the related room-temperature photoionization appearance potential.) The value of Fisher and Armentrout[33] yields $\Delta H_{f\ 298}^{\circ}$(CF$_3^+$)=86.4±1.6 kcal/mol, while the upper limit of Powis[29] implies ⩽99±7 kcal/mol. Coupling these values to ΔH_f°(CF$_3$) from JANAF,[6] one obtains IP(CF$_3$)⩽9.2±0.3 eV from Powis,[29] but 8.62±0.08 eV from Fisher and Armentrout.[33]

After Noutary,[24] the appearance potentials of the CF$_3^+$ fragment from CF$_3$Cl, CF$_3$Br, and CF$_3$I have been revisited several times by photoionization mass spectrometry. Ajello *et al.*[34] reported AP$_{300}$(CF$_3^+$/CF$_3$Cl)=12.65±0.04 eV and AP$_0$ of 12.81±0.04 eV. On closer scrutiny, one discovers that their AP$_0$, or "estimated value," was determined by linear extrapolation of the threshold region, resembling contemporary approaches to obtain a room-temperature AP, while their AP$_{300}$, or "observed value," corresponds to the first measurable onset in the tail region. From AP$_{300}$, Ajello *et al.* list $\Delta H_{f\ 300}^{\circ}$(CF$_3^+$)=93.5 kcal/mol in a table, while in the text they use AP$_0$ to obtain $\Delta H_{f\ 0}^{\circ}$(CF$_3^+$)=98.8 kcal/mol. The two values are inconsistent by ∼4.6 kcal/mol. Remarking that the value is probably too low and thus refraining from using it to infer ΔH_f°(CF$_3^+$), Jochims *et al.*[35] report an appearance potential of CF$_3^+$ from CF$_3$Cl of 12.55 eV, "in agreement with Noutary's value." Very recently, Creasey *et al.*[36] examined CF$_3$Cl and report "a sharp threshold" of CF$_3^+$ at 12.75±0.05 eV, which really corresponds to the first onset, since they "define and determine a threshold energy to be that value of the energy where the yield of a particular ion, within experimental error, lies above the background level."

Creasey *et al.*[36] also examined CF$_3$Br, for which they report an appearance potential for CF$_3^+$ of 11.92±0.02 eV, noting that their value is higher than that of Clay *et al.*[37] for reasons of instrumental sensitivity. Clay *et al.*,[37] on the other hand, report AP$_0$(CF$_3^+$/CF$_3$Br)=11.56±0.02 eV and derive $\Delta H_{f\ 0}^{\circ}$(CF$_3^+$)=86.6±1.1 kcal/mol, implying IP(CF$_3$)=8.60 eV. Their threshold selection also essentially corresponds to the first detectable departure of the ion signal from background. However, they imply that such a selection is justified, since their source is cold (reportedly with a rotational temperature of 30 K, although not necessarily in a Boltzmann equilibrium with vibrations). The selected threshold corresponds to the onset of a very weak tail, which Clay *et al.* claim to be able to detect solely because of the high intensity of their synchrotron light source.

The appearance of the CF$_3^+$ fragment from CF$_3$I has been studied by Berman and Beauchamp.[38] From the photoion fragment yield curve they obtain AP$_{298}$(CF$_3^+$/CF$_3$I)=11.27 eV, and after correcting for the available internal energy, they derive AP$_0$(CF$_3^+$/CF$_3$I)=11.36±0.02 eV, and hence $\Delta H_{f\ 0}^{\circ}$(CF$_3^+$)=98.3 kcal/mol. A subsequent paper from the same group[39] reexamines this threshold by coincidence techniques and selects a somewhat lower AP$_0$(CF$_3^+$/CF$_3$I)=11.26±0.05 eV, yielding $\Delta H_{f\ 0}^{\circ}$(CF$_3^+$)=96.1±1.2 kcal/mol. These two values of ΔH_f°(CF$_3^+$) imply IP(CF$_3$)≈9.1–9.0 eV.

At this point one should mention several pertinent spectroscopic details which may influence the shape of the CF$_3^+$ fragmentation threshold. In CF$_3$X$^+$, there are two low-lying dissociation asymptotes to CF$_3^+$+X, reflecting the $^2P_{3/2}$-$^2P_{1/2}$ spin-orbit splitting in the ground state of the halogen atom X. The splitting increases with the atomic number, and amounts to 0.0501 eV, 0.1094 eV, 0.4569 eV, and 0.9427 eV for F, Cl, Br, and I, respectively.[40] The ground state (^2E) of CF$_3$X$^+$ is also split, into $^2E_{3/2}$ and $^2E_{1/2}$

components, either by the Jahn–Teller distortion or by spin-orbit effects. The two effects compete, and the Jahn–Teller distortion dominates in lighter members, while heavier members primarily undergo spin-orbit splitting. Both components of the ground state configuration of CF_3X^+ connect to the lower asymptote, $CF_3^+(^1A_1') + X(^2P_{3/2})$.

Recently it has been suggested[37] that CF_3Br^+ $(^2E_{3/2})$ fragments significantly more slowly than CF_3Br^+ $(^2E_{1/2})$, and hence the thermodynamic threshold for CF_3^+ is expected to be very weak, presumably gaining significantly in intensity after the onset of CF_3Br^+ $(^2E_{1/2})$. Clay *et al.*[37] report $IP(CF_3Br) = 11.404$ eV; using the Landé interval rule, one estimates the location of CF_3Br^+ $(^2E_{1/2})$ as 11.709 eV. Accepting the very low $IP(CF_3) = 8.6$ eV, which corresponds to $\Delta H_{f\ 0}^{\circ}(CF_3^+) = 86.6$ kcal/mol, locates[37] the $CF_3^+ + Br(^2P_{3/2})$ asymptote at 11.56 eV, ~0.15 eV below the $^2E_{1/2}$ state. However, the more plausible $IP(CF_3) = 9.05$ eV, together with the existing range of literature values for $\Delta H_f^{\circ}(CF_3)$, leads to an estimated threshold of ~12.01–12.13 eV, significantly above the onset of CF_3Br^+ $(^2E_{1/2})$. In CF_3I, the possibly slow dissociation of the $^2E_{3/2}$ state is even less of a concern. With $IP(CF_3I) = 10.32 \pm 0.03$ eV from Berman *et al.*[38] and Landé interval rule, the estimated onset of CF_3X^+ $(^2E_{1/2})$ is 10.95 eV, while $IP(CF_3I) = 10.23$ eV from Lias *et al.*[10] places the $^2E_{1/2}$ state even lower, at 10.86 eV. Even with the low $\Delta H_{f\ 0}^{\circ}(CF_3^+) = 86.6$ kcal/mol, the CF_3^+ fragmentation asymptote is located at 10.91 eV, approximately at, or only slightly below the onset of CF_3X^+ $(^2E_{1/2})$. With $IP(CF_3) = 9.05$ eV, the expected position of the fragmentation asymptote is significantly higher, ~11.34–11.46 eV.

The CF_3I molecule has the best chance of providing a correct CF_3^+ fragmentation threshold from yet another standpoint. Since the earliest photoionization work on CF_3X molecules, it has been noticed that the gap between $IP(CF_3X)$ and $AP(CF_3^+/CF_3X)$, corresponding to the CF_3-X bond energy in the ion, increases with the atomic number of the halogen. This has been recently discussed by Morris *et al.*[41] and again by Clay *et al.*[37] The point that we would like to make here is that a small gap between $IP(CF_3X)$ and $AP(CF_3^+/CF_3X)$ may mean that the threshold region of the CF_3^+ fragment ion yield curve is bottlenecked not by an inherently slow fragmentation rate, but by a low total ionization cross section (or energy deposition function) resulting from unfavorable Franck–Condon factors for accessing the parent. The extreme example is CF_4 (*vide supra*), where the IP and AP coincide, and the CF_3^+ fragment onset is entirely dominated by the Franck–Condon envelope. As the energy range in which the parent ion is stable increases with the atomic number of the halogen atom, the threshold region of the CF_3^+ fragment moves into a more favorable domain of the total ionization cross section and its shape becomes more truly determined by the fragmentation rate. Extrapolating the trend from CF_4 to CF_3I, one can predict that in CF_3Cl some bottlenecking by Franck–Condon factors may still be encountered, but that by the time CF_3I is reached, any such effects should be negligible.

The literature values reviewed above and systematized in Tables I and II suggest that there is an uncertainty of ~2–4 kcal/mol in $\Delta H_f^{\circ}(CF_3)$ and ~10–15 kcal/mol in $\Delta H_f^{\circ}(CF_3^+)$. The former reflects discrepancies in determinations of $D_0(CF_3-X)$ by kinetic methods, while the latter results from the enormous disparity in the reported APs. Although some of the APs appear to have been determined by the generally accepted method[42] of linear extrapolation of the onset with subsequent correction to 0 K by the available internal energy, others have been determined by choosing the point of ''first departure from the background level,'' and subsequently used either as AP_0 or AP_{298}. At present, it is difficult to attach thermodynamical significance to thresholds obtained by the ''first departure'' approach, since it generally leads to a selection of some arbitrary point in the exponentially decaying tail caused by thermally excited parent molecules. Such ''threshold'' is primarily determined by the instrumental sensitivity and the level of background noise. Although the thermal tail is expected to be greatly reduced if the sample is relatively cold, as it is in a molecular beam effusing from a jet,[37] other factors, such as background corrections and various secondary processes that contribute to the tail region (collisions, field effects, etc.), may complicate the situation. Even the generally accepted approach of linear or quasilinear extrapolation of the fragmentation onset[42] may suffer from a certain degree of subjectivity in selecting the threshold value.

Recently, we have developed a procedure[43] for obtaining appearance potentials from fragment photoion yield curves, which helps eliminate, or at least greatly reduce, the subjective component. The approach produces an appearance potential by a least-squares fit of the threshold region with a model function obtained by convoluting a kernel function (i.e., the idealized 0 K threshold shape) with an internal energy distribution function. Full details and background of this technique are given elsewhere.[43(f)]

The main goal of this paper is to reexamine by photoionization mass spectrometry the threshold regions of the CF_3^+ fragment from CF_3Cl, CF_3Br, and CF_3I, and shed light on the correct value of $\Delta H_f^{\circ}(CF_3^+)$. Our fitting procedure should readily detect possible complications such as retarded (i.e., slow) fragmentation or bottlenecking by poor Franck–Condon factors for parent ionization. Additionally, since $IP(CF_3)$ is the crucial link between $\Delta H_f^{\circ}(CF_3^+)$ and $\Delta H_f^{\circ}(CF_3)$, we shall remeasure and fit the thresholds of CF_3^+ and CF^+ from C_2F_4, and redetermine more accurately the value for the energy gap $AP(CF^+/C_2F_4)$-$AP(CF_3^+/C_2F_4)$ given originally by Walter *et al.*[18]

II. EXPERIMENTAL ARRANGEMENT

The photoionization apparatus utilized in this study was recently described in more detail elsewhere.[43(f)] Both the He Hopfield continuum and the many-line pseudo-continuum of H_2 were utilized as light sources in the experiments described here. Throughout the experiments, the nominal photon resolution was kept at 0.83 Å (FWHM). The wavelength scale was calibrated by internal standards consisting of sparse impurity lines[44] (Ne I, N II, and H I) in the He
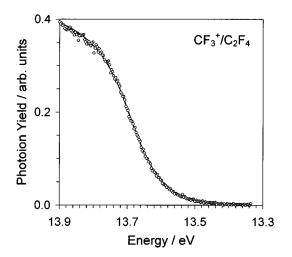
FIG. 1. The expanded threshold region of the CF$_3^+$ fragment ion yield curve from C$_2$F$_4$. The solid line is a least-square fit with the appropriate model function, as described in the text, and yields AP$_0$(CF$_3^+$/C$_2$F$_4$)=13.721±0.005 eV.
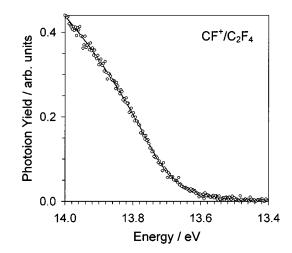

FIG. 2. The expanded threshold region of the CF$^+$ fragment ion yield curve from C$_2$F$_4$. The solid line is a least-square fit with the appropriate model function, and yields AP$_0$(CF$^+$/C$_2$F$_4$)=13.777±0.005 eV. Together with AP$_0$(CF$_3^+$/C$_2$F$_4$), it leads to IP(CF)−IP(CF$_3$)=0.055±0.003 eV.

Hopfield continuum or H$_2$ emission lines of known positions.[45] The mass selected ions were pulse counted, while the light intensity was concomitantly recorded by monitoring the fluorescence of a sodium salicylate coated window. All samples used in these experiments were of commercial origin (C$_2$F$_4$ and CF$_3$Br from AGA, CF$_3$Cl and CF$_3$I from Aldrich) and highest purity available (99+%). As some of these substances seemed to linger in the inlet system and on the cryogenic traps even after their introduction into the system was terminated, we took particular care to avoid cross contamination. Before introducing a new sample, the inlet system was subjected to prolonged purging and pumping, while the cryogenic traps and the main chamber were thoroughly outgassed, until we were able to ascertain that there are no discernible signals from the previous sample. For the purpose of thermodynamic treatment, all samples were assumed to be thermally equilibrated at room temperature (298 K).

III. RESULTS AND THEIR INTERPRETATION

A. CF$^+$ and CF$_3^+$ fragments from C$_2$F$_4$

The photoionization of C$_2$F$_4$ has been studied extensively at room temperature and at 140 K by Walter et al.,[18] who have shown that CF$_3^+$ and CF$^+$ are the first two fragments. Here we will present only the corresponding threshold regions (CF$_3^+$ in Fig. 1 and CF$^+$ in Fig. 2). Except for the discrimination factor of the quadrupole mass filter, the relative intensities of the two fragments, denoted by the ordinates, are meaningful.

The solid lines in Figs. 1 and 2 are the least-squares fits of our model functions to the experimental points. In both cases a kernel of the general form $\{1-\exp[-B(h\nu-E_T)]\}$ was convoluted with an internal energy distribution function of the form $E^\eta \exp(-aE)$, where $h\nu$ is the photon energy, E_T is the fragmentation threshold, and B, η and a are adjustable parameters.[43(f)] The internal energy distribution function

was predetermined with the aid of Haarhoff's[46] approximate expression for the density of states, calculated numerically in the range of interest by using known frequencies for C$_2$F$_4$.[6,8] The calculated distribution was utilized to determine which parameter η best reproduces its overall shape, while parameter a was obtained by imposing the requirement that the function corresponds to the correct amount of average internal energy (4.086 kT at 298 K).[6,8,47] During the fits to the experimental data, the internal energy function was kept fixed at its predetermined form, and only the kernel position and shape were allowed to change.

Figures 1 and 2 show that the quality of both fits is excellent. The fitted thresholds are AP$_0$(CF$_3^+$/C$_2$F$_4$)=13.721±0.005 eV and AP$_0$(CF$^+$/C$_2$F$_4$)=13.777±0.005 eV, while the gap between them is 0.055±0.003 eV. The appearance potentials by Walter et al.[18] are in good accord (within ±0.02 eV) with ours, while their gap is, perhaps fortuitously, in excellent agreement with the current determination.

B. CF$_3^+$ fragment from CF$_3$Cl

Figure 3 provides an overview of the photoion yield curves of the parent CF$_3$Cl$^+$ and its principal fragments. The relative intensities of the ion yield curves reflect the actual abundances as measured through our quadrupole filter, with the natural isotopic composition of Cl taken into account. The overall picture is congruent with previous findings.[30,34,35,48] CF$_3^+$ corresponds to the first fragment and is the most abundant species in the spectrum. The CF$_3$Cl$^+$ parent is relatively small, but readily detectable. Its ionization onset is characterized by slow growth, reflecting an extended Franck–Condon region. About 0.3 eV later, at the onset of the CF$_3^+$ fragment, the parent levels off rather abruptly and remains roughly constant toward higher energies. Such behavior is often interpreted as a sign that quasi-equilibrium theory is fully applicable.
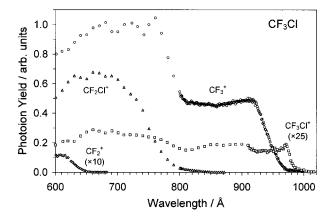
FIG. 3. An overview of the photoion yield curves of the parent CF$_3$Cl$^+$ and its principal fragments, with only sparse points at shorter wavelengths. The CF$_3^+$ fragment corresponds to the first fragmentation process and is the most abundant species in the spectrum. The gap between the onset of the parent and that of the fragment is relatively small, only ~0.3 eV.

FIG. 5. An overview of the photoion yield curves of the parent CF$_3$Br$^+$ and its principal fragments. At shorter wavelength points have been recorded at larger intervals. The gap between the onset of the parent and that of the fragment is ~0.5 eV, which allows the parent CF$_3$Br$^+$ to attain a significantly higher abundance than in the chloro analog.

Figure 4 displays the threshold region of the CF$_3^+$ fragment in more detail. The solid line is a least-squares fit with our model function, which has been determined as outlined in Sec. III A. The internal energy function used in the convolution corresponds to 3.059 $kT \equiv 0.0786$ eV (at 298 K) of available average internal energy.[6,8,47] The 0 K threshold implied by the fit is 12.917 eV. Unfortunately, the fit is not perfect and misses some of the roundness in the tail region. We tried to improve the function by including two kernels spaced by 0.1094 eV, hoping that this will adequately model the two spin-orbit split dissociation asymptotes. The quality
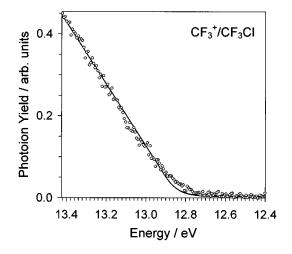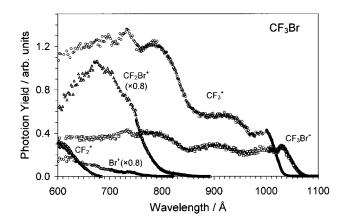

FIG. 4. The expanded threshold region of the CF$_3^+$ fragment from CF$_3$Cl. The solid line is the least-squares fit with a single-kernel model function, and it misses some of the roundness in the tail region. A fit with a model function that includes two kernels with a fixed gap of 0.1094 eV between their thresholds, which should reflect more appropriately the existence of two spin-orbit split asymptotes, CF$_3^+$($^1A_1'$)+Cl($^2P_{3/2}$) and CF$_3^+$($^1A_1'$)+Cl($^2P_{1/2}$) in the region of interest, brings only a marginal improvement. As discussed in the text, the possible culprit is subtle bottlenecking by unfavorable Franck–Condon factors for parent ionization. The experimentally derived AP$_0$(CF$_3^+$/CF$_3$Cl)<12.867±0.008 eV, is only an upper limit to the true threshold.

of the fit improved only marginally, resulting in a 0 K threshold of 12.867±0.008 eV for the lower asymptote. Substantial improvement was achieved only when the gap between the two kernels was allowed to be a free parameter. In that case, the lower of the two thresholds became 12.851 eV, but the splitting increased to 0.240 eV. Although it could be argued that the observed splitting is enhanced by a kinetic shift of the higher threshold, this is only a very remote possibility, in light of the fact that the two asymptotes are thermodynamically only 0.11 eV apart. Thus, we conclude that the model function describing a normal fragmentation is not entirely adequate and that the threshold shape is rendered complex by some other factors.

It is not clear that slow dissociation from the $^2E_{3/2}$ state is able to explain the distortion of the threshold. Creasey et al.[36] report IP(CF$_3$Cl)=12.52±0.05 eV; in order to relate to the observations, the $^2E_{3/2}$-$^2E_{1/2}^-$ splitting would have to be >0.2–0.3 eV. Perhaps a more likely explanation is that the threshold shape is subtly modulated by Franck–Condon factors for parent ionization, as suggested by the fact that the fragmentation onset is located ~0.2 eV below the vertical IP of the first photoelectron band (13.08 eV, unresolved ^2E configuration[49]). This, of course, does not rule out the possibility of additional effects resulting from a hypothetical slower fragmentation of CF$_3$Cl$^+$ ($^2E_{3/2}$).

Regardless of the reason for the imperfect fit, the derived threshold value is only an upper limit, AP$_0$(CF$_3^+$/CF$_3$Cl)<12.867±0.008 eV. It is interesting to note that the AP that would be obtained from a traditional graphical approach is the same as that derived from a fit with a single kernel, 12.917 eV (or 12.838 eV at 298 K), although without giving a clear indication that the onset is complicated by additional factors.

C. CF$_3^+$ fragment from CF$_3$Br

An overview of the photoion yield curves of the parent CF$_3$Br$^+$ and its principal fragments is shown in Fig. 5. The
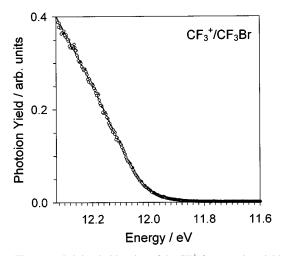
FIG. 6. The expanded threshold region of the CF$_3^+$ fragment ion yield curve from CF$_3$Br. The solid line is a least-square fit with the appropriate model function, as described in the text, and yields AP$_0$(CF$_3^+$/CF$_3$Br)=12.095±0.005 eV. As opposed to the chloro analog, the quality of the threshold fit is excellent. Here there is no need to include the upper spin-orbit split asymptote in the fit, since it is located outside the range of interest.
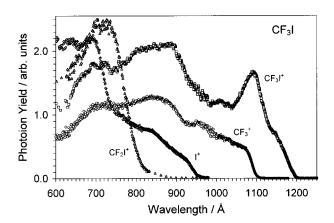

FIG. 7. An overview of the photoion yield curves of the parent CF$_3$I$^+$ and its principal fragments. As opposed to the chloro and bromo analogs, the CF$_3$I$^+$ parent is much more prominent and is the dominant species at least until 800 Å. The gap between the onset of the parent and that of the fragment is significantly larger ($\sim$1.0–1.1 eV) than in the case of lighter analogs.

relative intensities of the ion yield curves are adjusted for the isotopic composition of Br, but not for the mass dependent discrimination factor of the quadrupole filter. The general picture agrees with previously published spectra.[36,37] As in the case of CF$_3$Cl described above, CF$_3^+$ is the first and most abundant fragment (at least until 800 Å), and its onset terminates the growth of the parent. However, the relative abundance of the parent CF$_3$Br$^+$ is significantly higher than in the chloro analog, and the gap between the onsets of the parent ion and the CF$_3^+$ fragment is larger, $\sim$0.5 eV.

Figure 6 provides a more detailed view of the threshold region of the CF$_3^+$ fragment. The solid line is the fit with our model function, obtained by the procedure described in Sec. III A. The average available internal energy implied by the convoluting function is 3.336 kT≡0.0857 eV (298 K), as obtained by standard methods.[6,8,47] As opposed to CF$_3$Cl, the quality of the fit is excellent. The resulting threshold is AP$_0$(CF$_3^+$/CF$_3$Br)=12.095±0.005 eV. Clearly, there is no need to include the upper spin-orbit split asymptote in the fit, since it is located completely outside the range of interest, 0.457 eV higher.[40]

Clay *et al.*[37] report IP(CF$_3$Br)=11.40±0.01 eV, while Creasey *et al.*[36] give 11.63±0.05 eV. These lead to estimated onsets for CF$_3$Br$^+$ ($^2E_{1/2}$) of either 11.70 eV or 11.93 eV. Both are significantly below the fragmentation threshold reported here. If the thermodynamic onset of CF$_3^+$ were lower, as claimed by Clay *et al.*,[37] but made extremely weak by slow dissociation from the $^2E_{3/2}$ state of CF$_3$Br, one would expect to see an onset that is related to the position of the $^2E_{1/2}$ state. This definitely does not appear to be the case here. Bottlenecking by Franck–Condon factors is also very unlikely, in light of the high quality of the fit and the fact that the threshold determined here is located close to the vertical IP to the ^2E state (12.08±0.05 eV, from photoelectron spectroscopy[49]).

D. CF$_3^+$ fragment from CF$_3$I

Figure 7 gives an overview of the parent and the most prominent fragment ion yield curves resulting from photoionization of CF$_3$I. As before, the relative intensities are meaningful, apart from the discrimination factors of the quadrupole filter. In contrast to the lighter analogs, the CF$_3$I$^+$ parent is very prominent and is the dominant species until $\sim$800 Å. After the threshold, it exhibits strong growth which ends in a giant autoionization resonance centered at $\sim$1100 Å. The initial rise of the parent displays an inflection at $\sim$1140 Å, most likely corresponding to the onset of the spin-orbit split $^2E_{1/2}$ state. The first fragment corresponds to CF$_3^+$, similar to the case of CF$_3$Cl and CF$_3$Br. However, the gap between the ionization onset and the onset of CF$_3^+$ is significantly larger ($\sim$1.0–1.1 eV) than in the lighter analogs.
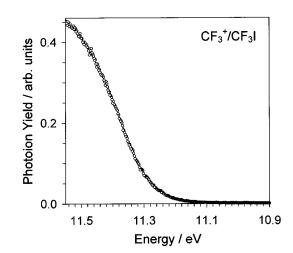
Figure 8 provides a view of the threshold region of the

FIG. 8. The expanded threshold region of the CF$_3^+$ fragment ion yield curve from CF$_3$I. The solid line, barely discernible behind the data points, is a least-square fit with the appropriate model function, as described in the text. The resulting threshold value is AP$_0$(CF$_3^+$/CF$_3$I)=11.384±0.005 eV.

CF_3^+ fragment. The barely discernible solid line is a fit with our model function, derived as outlined in Sec. III A. The convoluting function implies an average internal energy[6,8,47] of 3.554 $kT \equiv 0.0913$ eV (298 K). As in the bromo analog, the quality of the fit is excellent. The resulting threshold $AP_0(CF_3^+/CF_3I) = 11.384 \pm 0.005$ eV is not only well past the onset of CF_3I^+ ($^2E_{1/2}$), but is even past the vertical IP of that state, found to be 11.18 eV by Cvitas et al.[49]

IV. DISCUSSION

A. IP(CF$_3$)

From our refined value for $AP(CF^+/C_2F_4)$ $-AP(CF_3^+/C_2F_4) = 0.055 \pm 0.003$ eV and $IP(CF) = 9.11 \pm 0.01$ eV from Dyke et al.,[22] we obtain $IP(CF_3) = 9.05_5 \pm 0.01_1$ eV, in excellent agreement with the value inferred in the Introduction. One should note that the bulk of the error bar of $IP(CF_3)$ propagates from the uncertainty in IP(CF).

In principle, one could challenge this approach to the IP of CF_3, arguing that the fragmentation thresholds for CF_3^+ and CF^+ from C_2F_4 may be retarded, and that consequently the derived gap is incorrect. This is highly unlikely. CF_3^+ and CF^+ are the first two fragments from C_2F_4, and have rather unremarkable thresholds, as demonstrated by excellent fits (see Figs. 1 and 2). Even if the thresholds were retarded, one would expect them to suffer from comparable kinetic shifts, since the two fragmentation asymptotes differ only in the final location of the charge and the energy gap between them is quite small. If anything, one would expect that the higher energy process will undergo a slightly larger retardation. This means that 0.055 ± 0.003 is technically an *upper limit* to the gap, and 9.05 eV a *lower limit* to the IP of CF_3. The consequence of this deduction is very important, since it immediately rules out the low $IP(CF_3) \approx 8.6$ eV arising from the data of Noutary,[24] Fisher and Armentrout,[33] and Clay et al.,[37] as well as the estimated value of ≤ 8.9 eV by Loguinov et al.[20] (see Table II). The present determination of $9.05_5 \pm 0.01_1$ eV for the $IP(CF_3)$ is quite close to 9.11 eV inferred by Walter et al.[18] from unpublished[19] data on CF_3X, and to IPs in the range ~ 9.0–9.1 eV, implied by the data of Powis,[29] Ajello et al.,[34] Creasey et al.,[36] and Berman and Beauchamp.[38]

B. AP(CF$_3^+$/CF$_3$X) and D$_0$(CF$_3$−X)

In Sec. III B we have shown that photoionization measurements provide only an upper limit to the AP of CF_3^+ from CF_3Cl, $<12.867 \pm 0.008$ eV at 0 K (or $<12.788 \pm 0.008$ eV at 298 K). This threshold is in good agreement with the "estimated" AP_0 of 12.81 ± 0.04 eV by Ajello et al.,[34] which was obtained by linear extrapolation, and should be treated as a room-temperature value. Not surprisingly, their "observed" AP_{300} of 12.65 ± 0.04 eV, selected as the "first onset," is significantly lower, as are the analogous "first onset" of Noutary[24] (12.57 eV), and the value of 12.55 eV reported by Jochims et al.[35] but recognized by them to be too

low. Curiously, the value of 12.75 ± 0.05 eV by Creasey et al.,[36] also defined as a "first departure," is very close to our 298 K value.

$AP_0(CF_3^+/CF_3Cl) < 12.867 \pm 0.008$ eV, with $IP(CF_3) = 9.05_5 \pm 0.01_1$ eV, yields the upper limit $D_0(CF_3-Cl) < 87.9 \pm 0.3$ kcal/mol (or $< 88.8 \pm 0.3$ kcal/mol at 298 K). JANAF[6,50] gives $D_0(CF_3-Cl) = 84.9 \pm 1.3$ kcal/mol (85.8 ± 1.3 kcal/mol at 298 K), well below our upper bound. The recent experimental inference of $D_0(CF_3-Cl) = 89.0 \pm 1.5$ kcal/mol by Kumaran et al.[15] lies nominally above our upper limit. However, their value was selected to encompass three different RRKM fits to their data. While the sophisticated model resulted in 90.5 kcal/mol, which indeed seems too high, two simpler models gave 87.5 kcal/mol. The latter value satisfies our upper limit, and is in close agreement with $D_0(CF_3-Cl) = 87.3 \pm 1.3$ kcal/mol (88.2 ± 1.3 kcal/mol at 298 K), which can be obtained from Tsang's[11] $\Delta H^\circ_{f\ 298}(CF_3) = -110.0 \pm 1.0$ kcal/mol (-109.3 ± 1.0 at 0 K) and auxiliary heats of formation.[50] If a value of $D_0(CF_3-Cl) \sim 87.5$–87.3 kcal/mol were correct, it would imply that the true threshold of CF_3^+ from CF_3Cl is situated only about 0.02–0.03 eV lower than our upper limit, while JANAF's[6] value of 84.9 kcal/mol requires the true threshold to be ~ 0.13 eV lower. Judging from the amount of misfit in Fig. 4 and the conjecture that the likely culprit is a subtle bottlenecking effect by Franck–Condon factors, one can, albeit only qualitatively, conclude that probably the true threshold is not as much as 0.13 eV lower than our upper limit, i.e., $AP_0(CF_3^+ CF_3Cl) > 12.74$ eV.

From our $AP_0(CF_3^+/CF_3Br) = 12.095 \pm 0.005$ eV and $IP(CF_3) = 9.05_5 \pm 0.01_1$ eV, we obtain $D_0(CF_3-Br) = 70.1 \pm 0.3$ kcal/mol (or 70.8 ± 0.3 kcal/mol at 298 K). This is in excellent agreement with the experimental determination of $D_{300}(CF_3-Br) = 70.5 \pm 1.0$ kcal/mol by Tsang,[11] and in reasonably good agreement with the bond energy of 71.1 ± 1.2 kcal/mol (71.8 ± 1.2 kcal/mol at 298 K), which can be obtained from Tsang's recommended[11] value for $\Delta H^\circ_f(CF_3)$ and auxiliary data.[50] JANAF's[6] $\Delta H^\circ_f(CF_3)$ leads to $D_0(CF_3-Br) = 68.7 \pm 1.2$ kcal/mol (69.4 ± 1.2 kcal/mol at 298 K), ~ 1.4 kcal/mol lower than our value, but still overlapping within the combined error bars. In contrast to this, the "first onset" values for $AP(CF_3^+/CF_3Br)$ of 11.84 eV by Noutary[24] and 11.92 ± 0.02 eV by Creasey et al.,[36] when combined with $IP(CF_3) = 9.05_5 \pm 0.01_1$ eV, yield low bond energies of 64.2 kcal/mol and 66.1 ± 0.5 kcal/mol, respectively, while the AP of 11.56 ± 0.02 eV from Clay et al.[37] leads to the extremely low value of 57.7 ± 0.5 kcal/mol.

Combining our $AP_0(CF_3^+/CF_3I) = 11.384 \pm 0.005$ eV with $IP(CF_3)$ gives $D_0(CF_3-I) = 53.7 \pm 0.3$ kcal/mol (or 54.3 ± 0.3 kcal/mol at 298 K). This is in excellent agreement with JANAF's[6] value of 53.3 ± 1.3 kcal/mol (53.9 ± 1.3 kcal/mol at 298 K), but slightly lower than the value of 55.0 kcal/mol (55.6 kcal/mol at 298 K) by Kumaran et al.[14] and the value of 55.7 ± 1.3 kcal/mol (56.3 ± 1.3 kcal/mol at 298 K) derived[50] from Tsang's[11] $\Delta H^\circ_f(CF_3)$. The $AP_0(CF_3^+/CF_3I)$ by Berman and Beauchamp,[38] 11.36 ± 0.02 eV, which is in very good agreement with our AP_0, leads to $D_0(CF_3-I) = 53.2 \pm 0.5$ kcal/mol, while the revised appear-

ance potential of 11.26±0.05 eV by Bombach et al.[39] leads to the considerably lower D_0(CF$_3$–I)=50.8±1.2 kcal/mol.

To reiterate, our AP(CF$_3^+$/CF$_3$Br), AP(CF$_3^+$/CF$_3$I), and IP(CF$_3$) lead to D_0(CF$_3$–Br)=70.1±0.3 kcal/mol and D_0(CF$_3$–I)=53.7±0.3 kcal/mol. The latter bond energy is in excellent agreement with JANAF,[6,50] while the former is in excellent agreement with the measurement of Tsang[11] and, within combined error bars, barely agrees with JANAF.[6,50] Our analysis in terms of bond energies indicates that a considerable number of literature values for AP(CF$_3^+$/CF$_3$X), chiefly obtained by the "first onset" approach, are too low.

C. ΔH_f°(CF$_3$) and ΔH_f°(CF$_3^+$)

Our D_0(CF$_3$–Br)=70.1±0.3 kcal/mol and JANAF's[6,50] ΔH_f°(CF$_3$Br)=−152.2±0.7 kcal/mol gives $\Delta H_{f\ 0}^\circ$(CF$_3$) =−110.3±0.8 kcal/mol, close to one of the values of Tsang.[11] However, our D_0(CF$_3$–I)=53.7±0.3 kcal/mol and JANAF's[6,50] $\Delta H_{f\ 0}^\circ$(CF$_3$I)=−139.4±0.8 kcal/mol, yields $\Delta H_{f\ 0}^\circ$(CF$_3$)=−111.3±0.9 kcal/mol, exactly 1.0 kcal/mol lower, and closer to JANAF's[6] value for ΔH_f°(CF$_3$). Since our two derived values of ΔH_f°(CF$_3$) overlap within their error bars, selecting a weighted average of $\Delta H_{f\ 0}^\circ$(CF$_3$)=−110.7±0.9 kcal/mol or $\Delta H_{f\ 298}^\circ$(CF$_3$) =−111.4±0.9 kcal/mol seems to be a good compromise.

However, one would like to understand the origin of the 1 kcal/mol discrepancy between our two values of ΔH_f°(CF$_3$). One interpretation, nominally similar to the original conclusion of Noutary,[24] is that there is a smooth trend in the APs of the CF$_3^+$ fragment, and that AP(CF$_3^+$/CF$_4$) is the farthest from the thermodynamical threshold, while AP(CF$_3^+$/CF$_3$I) is the closest. This interleaves well with the known aberration in CF$_4$ and perhaps also with our findings on AP(CF$_3^+$/CF$_3$Cl), but it would imply that AP(CF$_3^+$/CF$_3$Br) is retarded by ~1 kcal/mol, or 0.043 eV. In light of the excellent fit (Fig. 6) and analysis in Sec. III C, this seems very unlikely. A more plausible explanation is that there is a basic discrepancy between the tabulated[6,8] heats of formation of halomethanes, and in particular, between ΔH_f°(CF$_3$Br) and ΔH_f°(CF$_3$I). As mentioned in Sec. I, Kumaran et al.[15] have recently noticed some inconsistencies concerning the heats of formation of halomethanes, and concluded that various experimental and theoretical findings can be reconciled only if the error bars are increased beyond their original magnitudes. The problem of consistency between the heats of formation of CF$_3$X has been brought up also by Berman and Beauchamp,[38] who pointed out that ΔH_f°(CF$_3$Cl) and ΔH_f°(CF$_3$Br) were determined relative to ΔH_f°(CF$_3$I), while the latter has been determined relative to ΔH_f°(CF$_3$H). This would make it appear that ΔH_f°(CF$_3$I) is more fundamental than ΔH_f°(CF$_3$Br), and that therefore ΔH_f°(CF$_3$) derived from D_0(CF$_3$I) is to be preferred. However, the least-squares adjustments of Syverud[7] and Gurvich et al.[8] introduce a more complex interdependence of the tabulated[6,8] values for ΔH_f°(CF$_3$X), so that, in fact, ΔH_f°(CF$_3$Br) winds up with a slightly lower error bar than ΔH_f°(CF$_3$I).

The difference AP$_0$(CF$_3^+$/CF$_3$Br)-AP$_0$(CF$_3^+$/CF$_3$I) =0.711±0.007 eV≡16.4±0.2 kcal/mol is a direct measure

of D_0(CF$_3$Br)-D_0(CF$_3$I). This may be equivalently expressed as $\Delta H_{f\ 0}^\circ$(CF$_3$Br)-$\Delta H_{f\ 0}^\circ$(CF$_3$I)=13.8±0.2 kcal/mol, using[50] only ΔH_f°(Br) and ΔH_f°(I) in addition. The tabulated[6,8] heats for formation of CF$_3$Br and CF$_3$I differ by 12.8±1.1 kcal/mol, and imply a 15.4±1.1 kcal/mol difference in bond energies. Thus, our data are suggestive of a discrepancy of ~1 kcal/mol between the tabulated heats of formation of CF$_3$Br and CF$_3$I, which seem to be in need of a careful redetermination.

Taking tentatively the tabulated[6,8,50] value for ΔH_f°(CF$_3$Cl) as correct, our ΔH_f°(CF$_3$) leads to D_0(CF$_3$-Cl) =85.9±1.2 kcal/mol, and with IP(CF$_3$) yields AP$_0$(CF$_3^+$/CF$_3$Cl)=12.78±0.05 eV. The derived appearance potential is within the range of the fitted upper limit and the rough estimate for the lower limit (see Sec. IV B) and indicates that the experimental fragmentation onset is too high by ~0.08 eV. However, nudging down ΔH_f°(CF$_3$Cl) by 0.5–1 kcal/mol, would bring both the derived D_0(CF$_3$-Cl) closer to that of Kumaran et al.,[15] and the derived AP(CF$_3^+$/CF$_3$Cl) closer to our limit.

Using our ΔH_f°(CF$_3$) recommended above and IP(CF$_3$)=9.05$_5$±0.01$_1$ eV, we obtain $\Delta H_{f\ 0}^\circ$(CF$_3^+$) =98.1±0.9 kcal/mol and $\Delta H_{f\ 298}^\circ$(CF$_3^+$)=97.4±0.9 kcal/mol. This is in good agreement with one of the values of Ajello et al.,[34] $\Delta H_{f\ 0}^\circ$(CF$_3^+$)=98.8 kcal/mol, and with $\Delta H_{f\ 0}^\circ$(CF$_3^+$)=98.3 kcal/mol by Berman and Beauchamp.[38] It also agrees well with the limit of ≤99±7 kcal/mol implied by the results of Powis,[29] and is not too far from $\Delta H_{f\ 0}^\circ$(CF$_3^+$)=96.1±1.2 kcal/mol by Bombach et al.[39] However, it is significantly higher than $\Delta H_{f\ 0}^\circ$(CF$_3^+$)≤87.3 kcal/mol of Noutary,[24] $\Delta H_{f\ 298}^\circ$(CF$_3^+$)=86.4±1.6 kcal/mol implied by Fisher and Armentrout,[33] and $\Delta H_{f\ 0}^\circ$(CF$_3^+$) =86.6±1.1 kcal/mol reported by Clay et al.[37]

Our value for ΔH_f°(CF$_3^+$), together with the well established[6,8,50] ΔH_f°(CF$_4$), yields AP$_0$(CF$_3^+$/CF$_4$)=14.67 ±0.04 eV (14.73±0.04 eV for AP$_{298}$ or 339.4±1.0 kcal/mol for $\Delta H_{r\ 298}^\circ$ for the reaction CF$_4$→CF$_3^+$+F) and also IP(CF$_4$)=14.67±0.04 eV, if the ground state of CF$_4^+$ indeed does not have a minimum in the potential well when zero point energy is considered.[26,27] The AP is in very good agreement with the upper limit of Powis[29] but is discordant with the conclusions of Tichy et al.[32] and Fisher and Armentrout.[33] Not surprisingly, the inferred IP is lower than any of the direct observations,[10,18,24] but in remarkably good agreement with the estimate of ~14.7 eV by Rosenstock et al.[23]

The thresholds of the CF$^+$ and CF$_3^+$ fragments from C$_2$F$_4$ present the opportunity to estimate the otherwise poorly established ΔH_f°(CF). From AP$_0$(CF$_3^+$/C$_2$F$_4$)=13.721±0.005 eV and $\Delta H_{f\ 0}^\circ$(CF$_3^+$)=98.1±0.9 kcal/mol, and assuming that JANAF's[6] $\Delta H_{f\ 0}^\circ$(C$_2$F$_4$)=−156.6±0.6 kcal/mol is correct, we obtain $\Delta H_{f\ 0}^\circ$(CF)=61.7±1.1 kcal/mol or $\Delta H_{f\ 298}^\circ$(CF) =62.5±1.1 kcal/mol, implying D_0(CF)=5.50±0.05 eV. This is in reasonable agreement with JANAF's[6] inference of $\Delta H_{f\ 0}^\circ$(CF)=60±2 kcal/mol, and not very far from the selection of Gurvich et al.[8] of 57.5±2.5 kcal/mol.

V. CONCLUSION

Remeasured and accurately fitted photoionization appearance potentials of CF^+ and CF_3^+ from C_2F_4, lead to $IP(CF)-IP(CF_3)=0.055\pm0.003$ eV, and, consequently, $IP(CF_3)=9.05_5\pm0.01_1$ eV. The appearance potential of CF_3^+ from CF_3Cl has been found to be an upper limit to the thermodynamical value, but the analogous appearance potentials from CF_3Br and CF_3I, after careful fitting, lead to $D_0(CF_3\text{-}Br)=70.1\pm0.3$ kcal/mol (70.8±0.3 kcal/mol at 298 K) and $D_0(CF_3\text{-}I)=53.7\pm0.3$ kcal/mol (54.3±0.3 kcal/mol at 298 K). The tabulated[6,8] heats of formation of halomethanes are suspected to be inconsistent by ~1 kcal/mol and probably in need of redetermination. A compromise value of $\Delta H^\circ_{f\,298}(CF_3)=-111.4\pm0.9$ kcal/mol (-110.7 ± 0.9 kcal/mol at 0 K) is selected, based on tabulated values of $\Delta H_f(CF_3Br)$ and $\Delta H_f(CF_3I)$. This leads to $\Delta H^\circ_{f\,298}(CF_3^+)=97.4\pm0.9$ kcal/mol (98.1±0.9 kcal/mol at 0 K). An $IP(CF_4)\equiv AP_0(CF_3^+/CF_4)=14.67\pm0.04$ eV is also inferred. Together with data on C_2F_4, the selected $\Delta H^\circ_f(CF_3)$ leads to $\Delta H^\circ_{f\,298}(CF)=62.5\pm1.1$ kcal/mol (61.7±1.1 kcal/mol at 0 K) or $D_0(CF)=5.50\pm0.05$ eV. Many earlier literature values for appearance potentials of CF_3^+ from CF_3X, which lead to very low $\Delta H^\circ_f(CF_3^+)$ and/or $IP(CF_3)$, are demonstrated to be wrong.

ACKNOWLEDGMENT

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