

On the heats of formation of trifluoromethyl radical CF₃ and its cation CF₃⁺

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Citation: *The Journal of Chemical Physics* **106**, 210 (1997); doi: 10.1063/1.473982View online: <http://dx.doi.org/10.1063/1.473982>View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/106/1?ver=pdfcov>Published by the [AIP Publishing](#)

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

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(Received 6 August 1996; accepted 24 September 1996)

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 $\text{AP}_0(\text{CF}_3^+/\text{C}_2\text{F}_4)=13.721\pm0.005$ eV and $\text{AP}_0(\text{CF}^+/\text{C}_2\text{F}_4)=13.777\pm0.005$ eV and an accurate difference in ionization potentials, $\text{IP}(\text{CF})-\text{IP}(\text{CF}_3)=0.055\pm0.003$ eV. With the existing photoelectron value $\text{IP}(\text{CF})=9.11\pm0.01$ eV, this produces $\text{IP}(\text{CF}_3)=9.055\pm0.011$ 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 $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Cl})<12.867\pm0.008$ eV has been found to be only an upper limit. The analogous CF_3^+ fragment yield curves from CF_3Br and CF_3I produce $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Br})=12.095\pm0.005$ eV and $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{I})=11.384\pm0.005$ eV, leading to $D_0(\text{CF}_3-\text{Br})=70.1\pm0.3$ kcal/mol (70.8 ± 0.3 kcal/mol at 298 K) and $D_0(\text{CF}_3-\text{I})=53.7\pm0.3$ kcal/mol (54.3 ± 0.3 kcal/mol at 298 K). Based on tabulated values for $\Delta H_f^\circ(\text{CF}_3\text{Br})$ and $\Delta H_f^\circ(\text{CF}_3\text{I})$, which appear to be inconsistent by ~ 1 kcal/mol, a compromise value of $\Delta H_f^\circ(\text{CF}_3)=-111.4\pm0.9$ kcal/mol (-110.7 ± 0.9 kcal/mol at 0 K) is selected, resulting in $\Delta H_f^\circ(\text{CF}_3^+) = 97.4\pm0.9$ kcal/mol (98.1 ± 0.9 kcal/mol at 0 K). Additionally, $\text{IP}(\text{CF}_4)\equiv\text{AP}_0(\text{CF}_3^+/\text{CF}_4)=14.67\pm0.04$ eV can be inferred. From data on C_2F_4 , $\Delta H_f^\circ(\text{CF})=62.5\pm1.1$ kcal/mol (61.7 ± 1.1 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 $\Delta H_f^\circ(\text{CF}_3^+)$ and/or $\text{IP}(\text{CF}_3)$ 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, $\Delta H_f^\circ(\text{CF}_3)$, and its ionization potential, $\text{IP}(\text{CF}_3)$ are still not known accurately.

JANAF⁶ lists $\Delta H_f^\circ(\text{CF}_3)=-112.4\pm1.0$ kcal/mol, originally derived by Syverud⁷ "from least squares, simultaneous adjustment of the enthalpies of formation of CF_3 , CF_3X ($\text{X}=\text{H}, \text{Cl}, \text{Br}, \text{I}, \text{CF}_3$), and C_2F_4 ." The analogous least-squares adjustment of $\Delta H_f^\circ(\text{CF}_3\text{X})$ by Gurvich *et al.*⁸ does not include either C_2F_4 or CF_3 . Rather, they obtain $\Delta H_f^\circ(\text{CF}_3)=-112.8\pm1.2$ kcal/mol as the mean of seven determinations based on various kinetic measurements of $D_0(\text{CF}_3-\text{X})$. McMillen and Golden⁹ recommend a slightly higher value of $\Delta H_f^\circ(\text{CF}_3)=-111.7\pm3.6$ kcal/mol. The compilation by Lias *et al.*¹⁰ prefers the still higher value of Tsang,¹¹ $\Delta H_f^\circ(\text{CF}_3)=-110.0\pm1.0$ kcal/mol (see Table I).

Tsang's selection¹¹ for $\Delta H_f^\circ(\text{CF}_3)$ is based on his $D_{300}(\text{CF}_3-\text{Br})=70.5\pm1.0$ kcal/mol (69.8 ± 1.0 kcal/mol at 0 K), yielding $\Delta H_f^\circ(\text{CF}_3)=-111.3\pm1.7$ 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 $D_0(\text{CF}_3-\text{I})=55.0$ kcal/mol (55.6 kcal/mol at 298 K), which implies $\Delta H_f^\circ(\text{CF}_3)=-110.7$ kcal/mol, and therefore supports Tsang's value for $\Delta H_f^\circ(\text{CF}_3)$. In a subsequent paper, Kumaran *et al.*¹⁵ report $D_0(\text{CF}_3-\text{Cl})=89.0\pm1.5$ kcal/mol (89.9 ± 1.5 kcal/mol at 298

K), significantly higher than their previous inference^{6,16} of 84.8 kcal/mol, and implying $\Delta H_f^\circ(\text{CF}_3)=-108.3\pm1.7$ 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 $D_0(\text{CF}_3-\text{Cl})$ fits very well in the trends for the remaining experimental bond strengths, the JANAF⁶ value for $\Delta H_f^\circ(\text{CF}_3)$ 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 $\Delta H_f^\circ(\text{CF}_3)$ 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 $D_0(\text{CF}_3-\text{X})=\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{X})-\text{IP}(\text{CF}_3)$.

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 Chupka¹⁷ 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 unpublished¹⁹ data on CF_3I , CF_3Br , and CF_3Cl . JANAF⁶ adopts the same $\text{IP}(\text{CF}_3)$, while Lias *et al.*¹⁰ prefer the esti-

TABLE I. An overview of various experimental values for the heats of formation of CF₃ and CF₃⁺, and a selection of CF₃-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
$\Delta H_f^\circ(\text{CF}_3)$	-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 <i>et al.</i> ^b
	-110.0 ± 1.0 kcal/mol	$\{-109.3 \pm 1.0$ kcal/mol $\}$	Tsang ^c
	-111.3 ± 1.7 kcal/mol	$\{-110.6 \pm 1.7$ kcal/mol $\}$	Tsang ^d
	-111.7 ± 3.6 kcal/mol	$\{-111.0 \pm 3.6$ kcal/mol $\}$	McMillen and Golden ^e
	$\{-110.7$ kcal/mol $\}$	-110.0 kcal/mol	Kumaran <i>et al.</i> ^f
	$[-108.3$ kcal/mol $]$	$[-107.6$ kcal/mol $]$	Kumaran <i>et al.</i> ^g
	97.4 ± 0.9 kcal/mol	98.1 ± 0.9 kcal/mol	This work
	≤ 86.6 kcal/mol	$\{\leq 87.3$ kcal/mol $\}$	Noutary ^h
$\Delta H_f^\circ(\text{CF}_3^+)$	$[\leq 99 \pm 7$ kcal/mol $]$	$[\leq 99 \pm 7$ kcal/mol $]$	Powis ⁱ
	$[86.4 \pm 1.6$ kcal/mol $]$	$[87.1 \pm 1.6$ kcal/mol $]$	Fisher and Armentrout ^j
	93.5 kcal/mol	98.8 kcal/mol	Ajello <i>et al.</i> ^k
	$\{85.9 \pm 1.1$ kcal/mol $\}$	86.6 ± 1.1 kcal/mol	Clay <i>et al.</i> ^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 <i>et al.</i> ⁿ
	$< 88.8 \pm 0.3$ kcal/mol	$< 87.9 \pm 0.3$ kcal/mol	This work
	85.8 ± 1.3 kcal/mol	84.9 ± 1.3 kcal/mol	JANAF ^a
	$\{89.9 \pm 1.5$ kcal/mol $\}$	89.0 ± 1.5 kcal/mol	Kumaran <i>et al.</i> ^g
	$\{88.4$ kcal/mol $\}$	87.5 kcal/mol	Kumaran <i>et al.</i> ^o
$D_0(\text{CF}_3\text{-Cl})$	$[88.2 \pm 1.3$ kcal/mol $]$	$[87.3 \pm 1.3$ kcal/mol $]$	Tsang ^c
	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
	$[71.8 \pm 1.2$ kcal/mol $]$	$[71.1 \pm 1.2$ kcal/mol $]$	Tsang ^c
	70.5 ± 1.0 kcal/mol	$\{69.8 \pm 1.0$ kcal/mol $\}$	Tsang ^d
$D_0(\text{CF}_3\text{-Br})$	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 <i>et al.</i> ^f
	$[56.3 \pm 1.3$ kcal/mol $]$	$[55.7 \pm 1.3$ kcal/mol $]$	Tsang ^c

^aReference 6.

^bReference 8.

^cReference 11, final recommendation for $\Delta H_f^\circ(\text{CF}_3)$, adopted by Lias *et al.* (Ref. 10).

^dReference 11, experimental determination of $D_0(\text{CF}_3\text{-Br})$.

^eReference 9.

^fReference 14, experimental determination of $D_0(\text{CF}_3\text{-I})$.

^gReference 15, experimental determination of $D_0(\text{CF}_3\text{-Cl})$.

^hReference 24.

ⁱReference 29, from the upper limit to $\text{AP}(\text{CF}_3^+/\text{CF}_4)$.

^jReference 33.

^kReference 34.

^lReference 37.

^mReference 38.

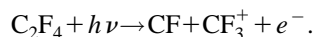
ⁿReference 39, listed as suggested value in Lias *et al.* (Ref. 10).

^oReference 15, the value for $D_0(\text{CF}_3\text{-Cl})$ from Troe/Lennard-Jones and RRKM/Gorin models.

mated $\text{IP}(\text{CF}_3) \leq 8.9$ 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 $\text{IP}(\text{CF}_3)$ 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 $\text{IP}(\text{CF}_3)$. 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:



If small enough, the energy gap between the two thresholds corresponds to the difference between the IPs of CF₃ and CF, i.e., $\text{AP}(\text{CF}^+/\text{C}_2\text{F}_4) - \text{AP}(\text{CF}_3^+/\text{C}_2\text{F}_4) = \text{IP}(\text{CF}) - \text{IP}(\text{CF}_3)$. Walter *et al.*¹⁸ report $\text{AP}_0(\text{CF}_3^+/\text{C}_2\text{F}_4) = 13.70 \pm 0.02$ eV, $\text{AP}_0(\text{CF}^+/\text{C}_2\text{F}_4) = 13.76 \pm 0.01$ eV, and also $\text{AP}(\text{CF}^+/\text{C}_2\text{F}_4) - \text{AP}(\text{CF}_3^+/\text{C}_2\text{F}_4) = 0.06 \pm 0.01$ eV. At the time, $\text{IP}(\text{CF})$ was known even less precisely than $\text{IP}(\text{CF}_3)$ and hence Walter *et al.* used their suggested $\text{IP}(\text{CF}_3) = 9.17 \pm 0.08$ eV and the gap value to obtain $\text{IP}(\text{CF}) = 9.23 \pm 0.08$ eV. Since then, $\text{IP}(\text{CF}) = 9.11 \pm 0.01$ 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)	<u>9.05 ± 0.01 eV</u>		This work
	9.25 ± 0.04 eV		Lifshitz and Chupka ^a
	9.17 ± 0.08 eV		Walter <i>et al.</i> ^b
	9.11 eV		Walter <i>et al.</i> ^c
	≤ 8.9 eV		Loguinov <i>et al.</i> ^d
	$[9.05 \pm 0.02 \text{ eV}]$		Walter <i>et al.</i> ; Dyke <i>et al.</i> ^e
	< 8.62 eV		Noutary ^f
	$[\leq 9.2 \pm 0.3 \text{ eV}]$		Powis ^g
	$[8.62 \pm 0.08 \text{ eV}]$		Fisher and Armentrout ^h
	$[8.9 \text{ eV or } 9.1 \text{ eV}]$		Ajello <i>et al.</i> ⁱ
	$[8.60 \pm 0.06 \text{ eV}]$		Clay <i>et al.</i> ^j
AP($\text{CF}_3^+/\text{C}_2\text{F}_4$)	<u>13.616 ± 0.005 eV</u>	<u>13.721 ± 0.005 eV</u>	This work
	$\{13.60 \pm 0.02 \text{ eV}\}$	$13.70 \pm 0.02 \text{ eV}$	Walter <i>et al.</i> ^b
AP($\text{CF}^+/\text{C}_2\text{F}_4$)	<u>13.672 ± 0.005 eV</u>	<u>13.777 ± 0.005 eV</u>	This work
	$\{13.66 \pm 0.01 \text{ eV}\}$	$13.76 \pm 0.01 \text{ eV}$	Walter <i>et al.</i> ^b
IP(CF)-IP(CF_3)	<u>0.055 ± 0.003 eV</u>		This work
	$0.06 \pm 0.01 \text{ eV}$		Walter <i>et al.</i> ^b
AP($\text{CF}_3^+/\text{CF}_4$)	...	<u>$[14.67 \pm 0.04 \text{ eV}]$</u>	This work ^m
	...	15.52 eV	Noutary ^{f,m}
	...	$\leq 15.35 \text{ eV}$	Walter <i>et al.</i> ^{b,m}
	...	$\leq 14.7 \text{ eV}$	Rosenstock <i>et al.</i> ^{m,n}
	...	$\leq 14.7 \pm 0.3 \text{ eV}$	Powis ^{m,g}
	$14.2 \pm 0.1 \text{ eV}$...	Tichy <i>et al.</i> ^{o,p}
AP($\text{CF}_3^+/\text{CF}_3\text{Cl}$)	$14.24 \pm 0.07 \text{ eV}$...	Fisher and Armentrout ^{h,p}
	$< 12.788 \pm 0.008 \text{ eV}$	$< 12.867 \pm 0.008 \text{ eV}$	This work
	...	12.57 eV	Noutary ^{f,q}
	$12.65 \pm 0.04 \text{ eV}$	$12.81 \pm 0.04 \text{ eV}$	Ajello <i>et al.</i> ^{i,q}
	12.55 eV	...	Jochims <i>et al.</i> ^r
AP($\text{CF}_3^+/\text{CF}_3\text{Br}$)	...	$12.75 \pm 0.05 \text{ eV}$	Creasey <i>et al.</i> ^{q,s}
	<u>$12.009 \pm 0.005 \text{ eV}$</u>	<u>$12.095 \pm 0.005 \text{ eV}$</u>	This work
	...	11.84 eV	Noutary ^{f,q}
	...	$11.92 \pm 0.02 \text{ eV}$	Creasey <i>et al.</i> ^{q,s}
AP($\text{CF}_3^+/\text{CF}_3\text{I}$)	...	$11.56 \pm 0.02 \text{ eV}$	Clay <i>et al.</i> ^{j,q}
	<u>$11.293 \pm 0.005 \text{ eV}$</u>	<u>$11.384 \pm 0.005 \text{ eV}$</u>	This work
	...	10.89 eV	Noutary ^{f,q}
	$11.27 \pm 0.02 \text{ eV}$	$11.36 \pm 0.02 \text{ eV}$	Berman and Beauchamp ^k
	$11.13 \pm 0.1 \text{ eV}$	$11.26 \pm 0.05 \text{ eV}$	Bombach <i>et al.</i> ^l

^aReference 17.^bReference 18.^cReference 19.^dReference 20, adopted by Lias *et al.* (Ref. 10).^eEstimated using IP(CF)-IP(CF_3) from Walter *et al.* (Ref. 18) and IP(CF) from Dyke *et al.* (Ref. 22).^fReference 24.^gReference 29.^hReference 33.ⁱReference 34.^jReference 37.^kReference 38.^lReference 39.^mThe onset of CF_3^+ from CF_4 has to be interpreted in terms of parent ionization rather than fragmentation (see text for details).ⁿIP(CF_4), as estimated in Ref. 23.^oReference 32.^pThe reported value is determined as an enthalpy of reaction for $\text{CF}_4 \rightarrow \text{CF}_3^+ + \text{F} + e^-$ at some unknown temperature, tacitly assumed to be 298 K.^qThreshold value picked as "first onset;" it is not clear how to convert from 0 K to 298 K or vice versa.^rReference 35.^sReference 36.

photoelectron spectroscopy.²² With the 0.06 ± 0.01 eV gap of Walter *et al.*,¹⁸ one derives $\text{IP}(\text{CF}_3) = 9.05 \pm 0.02$ eV, which is, in our opinion, the best currently available experimental value for this quantity, in reasonably good agreement with the latest calculated²¹ IP of 8.98 ± 0.05 eV.

Besides $\text{IP}(\text{CF}_3)$, the key to determining $D_0(\text{CF}_3\text{--X})$ by photoionization methods are accurate values for $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{X})$. 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_3X species was performed by Noutary.²⁴ *Inter alia*, he reports $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{X}) = 15.52$ eV, 12.57 eV, 11.84 eV, 10.89 eV, and 14.14 eV for $\text{X} = \text{F}$, 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 $\text{IP}(\text{CF}_3) \leq 8.62$ eV and consequently $\Delta H_{f,0}^\circ(\text{CF}_3^+) \leq 87.3$ 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 $\text{CF}_3^+ + \text{F}$ 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 $\text{IP}(\text{CF}_4)$ and $\text{AP}_0(\text{CF}_3^+/\text{CF}_4)$ is semantic, since both correspond to the same transition, from the ground state of CF_4 directly to the $\text{CF}_3^+ + \text{F}$ 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 $\text{AP}(\text{CF}_3^+/\text{CF}_4) \leq 15.35$ eV. More recently, Powis²⁹ derived an improved limit of $\leq 14.7 \pm 0.3$ eV from energy release coincidence measurements. Using ion/molecule reaction techniques, Tichy *et al.*³² obtained $\text{AP}(\text{CF}_3^+/\text{CF}_4) = 14.2 \pm 0.1$ eV, later refined by Fisher and Armentrout³³ to 14.24 ± 0.07 eV. (Here, “AP” is actually the room-temperature enthalpy of the reaction $\text{CF}_4 \rightarrow \text{CF}_3^+ + \text{F}$, which differs from the related room-temperature photoionization appearance potential.) The value of Fisher and Armentrout³³ yields $\Delta H_{f,298}^\circ(\text{CF}_3^+) = 86.4 \pm 1.6$ kcal/mol, while the upper limit of Powis²⁹ implies $\leq 99 \pm 7$ kcal/mol. Coupling these values to $\Delta H_f^\circ(\text{CF}_3)$ from JANAF,⁶ one obtains $\text{IP}(\text{CF}_3) \leq 9.2 \pm 0.3$ 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_3Cl , CF_3Br , and CF_3I have been revisited several times by photoionization mass spectrometry. Ajello *et al.*³⁴ reported $\text{AP}_{300}(\text{CF}_3^+/\text{CF}_3\text{Cl}) = 12.65 \pm 0.04$ 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 $\Delta H_{f,300}^\circ(\text{CF}_3^+) = 93.5$ kcal/mol in a table, while in the text they use AP_0 to obtain $\Delta H_{f,0}^\circ(\text{CF}_3^+) = 98.8$ kcal/mol. The two values are inconsistent by ~ 4.6 kcal/mol. Remark- ing that the value is probably too low and thus refraining from using it to infer $\Delta H_f^\circ(\text{CF}_3^+)$, Jochims *et al.*³⁵ report an appearance potential of CF_3^+ from CF_3Cl of 12.55 eV, “in agreement with Noutary’s value.” Very recently, Creasey *et al.*³⁶ examined CF_3Cl 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_3Br , 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 $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Br}) = 11.56 \pm 0.02$ eV and derive $\Delta H_{f,0}^\circ(\text{CF}_3^+) = 86.6 \pm 1.1$ kcal/mol, implying $\text{IP}(\text{CF}_3) = 8.60$ 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_3I has been studied by Berman and Beauchamp.³⁸ From the photoion fragment yield curve they obtain $\text{AP}_{298}(\text{CF}_3^+/\text{CF}_3\text{I}) = 11.27$ eV, and after correcting for the available internal energy, they derive $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{I}) = 11.36 \pm 0.02$ eV, and hence $\Delta H_{f,0}^\circ(\text{CF}_3^+) = 98.3$ kcal/mol. A subsequent paper from the same group³⁹ reexamines this threshold by coincidence techniques and selects a somewhat lower $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{I}) = 11.26 \pm 0.05$ eV, yielding $\Delta H_{f,0}^\circ(\text{CF}_3^+) = 96.1 \pm 1.2$ kcal/mol. These two values of $\Delta H_f^\circ(\text{CF}_3^+)$ imply $\text{IP}(\text{CF}_3) \approx 9.1\text{--}9.0$ eV.

At this point one should mention several pertinent spectroscopic details which may influence the shape of the CF_3^+ fragmentation threshold. In CF_3X^+ , there are two low-lying dissociation asymptotes to $\text{CF}_3^+ + \text{X}$, reflecting the $^2P_{3/2}\text{--}^2P_{1/2}$ 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_3X^+ 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, $\text{CF}_3^+ (^1\text{A}_1') + \text{X} (^2\text{P}_{3/2})$.

Recently it has been suggested³⁷ that $\text{CF}_3\text{Br}^+ (^2\text{E}_{3/2})$ fragments significantly more slowly than $\text{CF}_3\text{Br}^+ (^2\text{E}_{1/2})$, and hence the thermodynamic threshold for CF_3^+ is expected to be very weak, presumably gaining significantly in intensity after the onset of $\text{CF}_3\text{Br}^+ (^2\text{E}_{1/2})$. Clay *et al.*³⁷ report $\text{IP}(\text{CF}_3\text{Br}) = 11.404$ eV; using the Landé interval rule, one estimates the location of $\text{CF}_3\text{Br}^+ (^2\text{E}_{1/2})$ as 11.709 eV. Accepting the very low $\text{IP}(\text{CF}_3) = 8.6$ eV, which corresponds to $\Delta H_f^\circ(\text{CF}_3^+) = 86.6$ kcal/mol, locates³⁷ the $\text{CF}_3^+ + \text{Br} (^2\text{P}_{3/2})$ asymptote at 11.56 eV, ~ 0.15 eV below the $^2\text{E}_{1/2}$ state. However, the more plausible $\text{IP}(\text{CF}_3) = 9.05$ eV, together with the existing range of literature values for $\Delta H_f^\circ(\text{CF}_3)$, leads to an estimated threshold of ~ 12.01 – 12.13 eV, significantly above the onset of $\text{CF}_3\text{Br}^+ (^2\text{E}_{1/2})$. In CF_3I , the possibly slow dissociation of the $^2\text{E}_{3/2}$ state is even less of a concern. With $\text{IP}(\text{CF}_3\text{I}) = 10.32 \pm 0.03$ eV from Berman *et al.*³⁸ and Landé interval rule, the estimated onset of $\text{CF}_3\text{X}^+ (^2\text{E}_{1/2})$ is 10.95 eV, while $\text{IP}(\text{CF}_3\text{I}) = 10.23$ eV from Lias *et al.*¹⁰ places the $^2\text{E}_{1/2}$ state even lower, at 10.86 eV. Even with the low $\Delta H_f^\circ(\text{CF}_3^+) = 86.6$ kcal/mol, the CF_3^+ fragmentation asymptote is located at 10.91 eV, approximately at, or only slightly below the onset of $\text{CF}_3\text{X}^+ (^2\text{E}_{1/2})$. With $\text{IP}(\text{CF}_3) = 9.05$ 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 $\text{IP}(\text{CF}_3\text{X})$ and $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{X})$, corresponding to the $\text{CF}_3^+ - \text{X}$ 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 $\text{IP}(\text{CF}_3\text{X})$ and $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{X})$ 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 $\Delta H_f^\circ(\text{CF}_3)$ and ~ 10 – 15 kcal/mol in $\Delta H_f^\circ(\text{CF}_3^+)$. The former reflects discrepancies in determinations of $D_0(\text{CF}_3 - \text{X})$ 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 method⁴² 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 onset⁴² may suffer from a certain degree of subjectivity in selecting the threshold value.

Recently, we have developed a procedure⁴³ 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 $\Delta H_f^\circ(\text{CF}_3^+)$. 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 $\text{IP}(\text{CF}_3)$ is the crucial link between $\Delta H_f^\circ(\text{CF}_3^+)$ and $\Delta H_f^\circ(\text{CF}_3)$, 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 $\text{AP}(\text{CF}^+/\text{C}_2\text{F}_4) - \text{AP}(\text{CF}_3^+/\text{C}_2\text{F}_4)$ 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 lines⁴⁴ (Ne I, N II, and H I) in the He

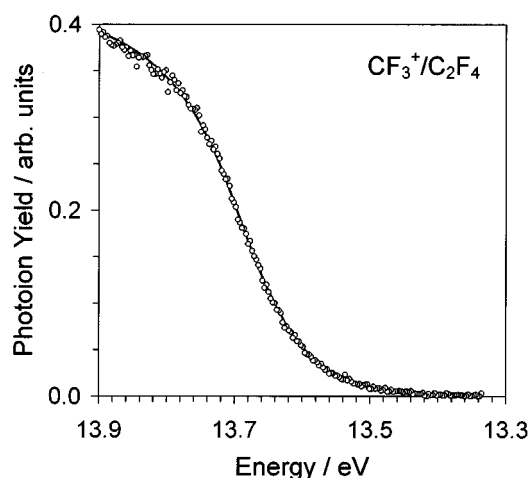


FIG. 1. The expanded threshold region of the CF_3^+ fragment ion yield curve from C_2F_4 . The solid line is a least-square fit with the appropriate model function, as described in the text, and yields $\text{AP}_0(\text{CF}_3^+/\text{C}_2\text{F}_4) = 13.721 \pm 0.005$ eV.

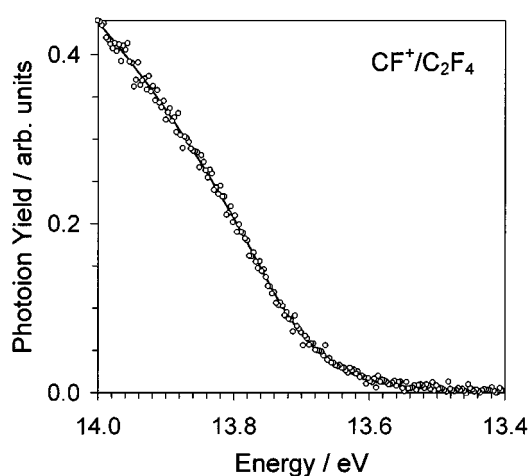


FIG. 2. The expanded threshold region of the CF^+ fragment ion yield curve from C_2F_4 . The solid line is a least-square fit with the appropriate model function, and yields $\text{AP}_0(\text{CF}^+/\text{C}_2\text{F}_4) = 13.777 \pm 0.005$ eV. Together with $\text{AP}_0(\text{CF}_3^+/\text{C}_2\text{F}_4)$, it leads to $\text{IP}(\text{CF}) - \text{IP}(\text{CF}_3) = 0.055 \pm 0.003$ 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_2F_4 and CF_3Br from AGA, CF_3Cl and CF_3I 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_2F_4

The photoionization of C_2F_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's⁴⁶ approximate expression for the density of states, calculated numerically in the range of interest by using known frequencies for C_2F_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 kJ 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 $\text{AP}_0(\text{CF}_3^+/\text{C}_2\text{F}_4) = 13.721 \pm 0.005$ eV and $\text{AP}_0(\text{CF}^+/\text{C}_2\text{F}_4) = 13.777 \pm 0.005$ 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_3Cl

Figure 3 provides an overview of the photoion yield curves of the parent CF_3Cl^+ 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_3Cl^+ 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.

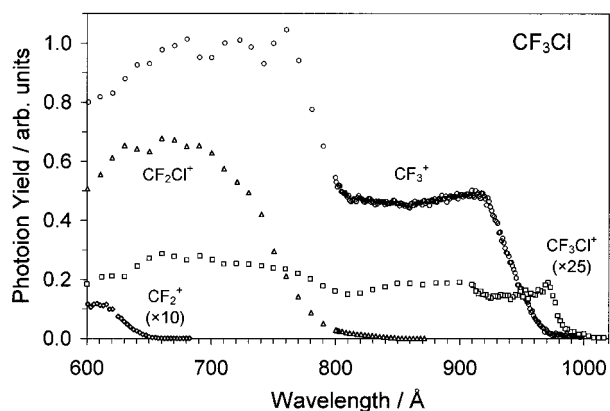


FIG. 3. An overview of the photoion yield curves of the parent CF_3Cl^+ and its principal fragments, with only sparse points at shorter wavelengths. The CF_3^+ fragment corresponds to the first fragmentation process and is the most abundant species in the spectrum. The gap between the onset of the parent and that of the fragment is relatively small, only ~ 0.3 eV.

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

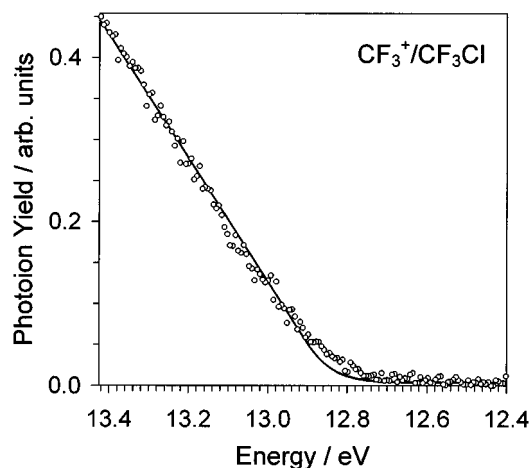


FIG. 4. The expanded threshold region of the CF_3^+ fragment from CF_3Cl . The solid line is the least-squares fit with a single-kernel model function, and it misses some of the roundness in the tail region. A fit with a model function that includes two kernels with a fixed gap of 0.1094 eV between their thresholds, which should reflect more appropriately the existence of two spin-orbit split asymptotes, $\text{CF}_3^+(^1A_1) + \text{Cl}(^2P_{3/2})$ and $\text{CF}_3^+(^1A_1) + \text{Cl}(^2P_{1/2})$ 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 $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Cl}) < 12.867 \pm 0.008$ eV, is only an upper limit to the true threshold.

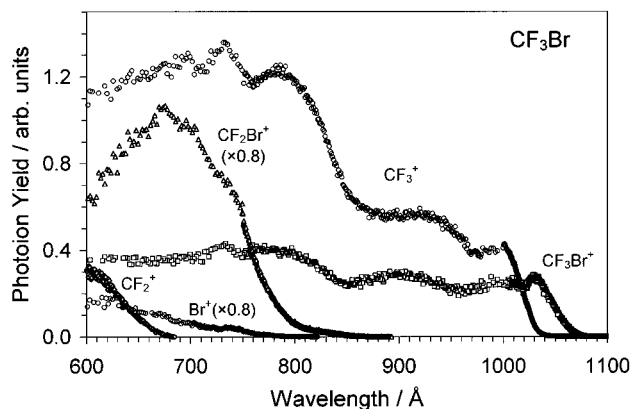


FIG. 5. An overview of the photoion yield curves of the parent CF_3Br^+ and its principal fragments. At shorter wavelength points have been recorded at larger intervals. The gap between the onset of the parent and that of the fragment is ~ 0.5 eV, which allows the parent CF_3Br^+ to attain a significantly higher abundance than in the chloro analog.

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 $\text{IP}(\text{CF}_3\text{Cl}) = 12.52 \pm 0.05$ 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 configuration⁴⁹). This, of course, does not rule out the possibility of additional effects resulting from a hypothetical slower fragmentation of CF_3Cl^+ ($^2E_{3/2}$).

Regardless of the reason for the imperfect fit, the derived threshold value is only an upper limit, $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Cl}) < 12.867 \pm 0.008$ 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_3Br

An overview of the photoion yield curves of the parent CF_3Br^+ and its principal fragments is shown in Fig. 5. The

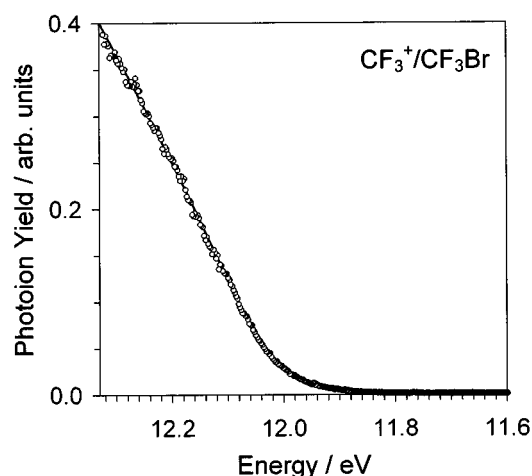


FIG. 6. The expanded threshold region of the CF_3^+ fragment ion yield curve from CF_3Br . The solid line is a least-square fit with the appropriate model function, as described in the text, and yields $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Br}) = 12.095 \pm 0.005$ eV. As opposed to the chloro analog, 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.

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_3Cl 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_3Br^+ 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, ~ 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_3Cl , the quality of the fit is excellent. The resulting threshold is $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Br}) = 12.095 \pm 0.005$ 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 $\text{IP}(\text{CF}_3\text{Br}) = 11.40 \pm 0.01$ eV, while Creasey *et al.*³⁶ give 11.63 ± 0.05 eV. These lead to estimated onsets for CF_3Br^+ ($^2E_{1/2}$) 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_3Br , 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 spectroscopy⁴⁹).

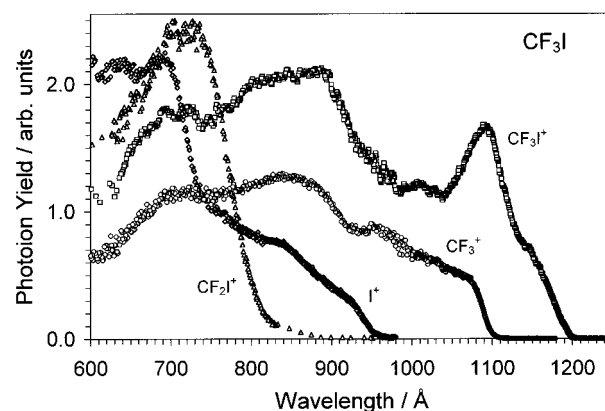


FIG. 7. An overview of the photoion yield curves of the parent CF_3I^+ and its principal fragments. As opposed to the chloro and bromo analogs, the CF_3I^+ parent is much more prominent and is the dominant species at least until 800 Å. The gap between the onset of the parent and that of the fragment is significantly larger (~ 1.0 – 1.1 eV) than in the case of lighter analogs.

D. CF_3^+ fragment from CF_3I

Figure 7 gives an overview of the parent and the most prominent fragment ion yield curves resulting from photoionization of CF_3I . As before, the relative intensities are meaningful, apart from the discrimination factors of the quadrupole filter. In contrast to the lighter analogs, the CF_3I^+ parent is very prominent and is the dominant species until ~ 800 Å. After the threshold, it exhibits strong growth which ends in a giant autoionization resonance centered at ~ 1100 Å. The initial rise of the parent displays an inflection at ~ 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_3Cl and CF_3Br . However, the gap between the ionization onset and the onset of CF_3^+ is significantly larger (~ 1.0 – 1.1 eV) than in the lighter analogs.

Figure 8 provides a view of the threshold region of the

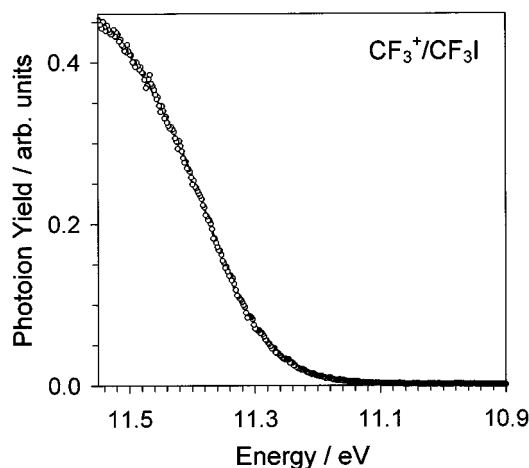


FIG. 8. The expanded threshold region of the CF_3^+ fragment ion yield curve from CF_3I . The solid line, barely discernible behind the data points, is a least-square fit with the appropriate model function, as described in the text. The resulting threshold value is $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{I}) = 11.384 \pm 0.005$ 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 $3.554 kT = 0.0913 \text{ eV}$ (298 K). As in the bromo analog, the quality of the fit is excellent. The resulting threshold $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{I}) = 11.384 \pm 0.005 \text{ eV}$ 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. $\text{IP}(\text{CF}_3)$

From our refined value for $\text{AP}(\text{CF}^+/\text{C}_2\text{F}_4) - \text{AP}(\text{CF}_3^+/\text{C}_2\text{F}_4) = 0.055 \pm 0.003 \text{ eV}$ and $\text{IP}(\text{CF}) = 9.11 \pm 0.01 \text{ eV}$ from Dyke *et al.*,²² we obtain $\text{IP}(\text{CF}_3) = 9.05_5 \pm 0.01_1 \text{ eV}$, in excellent agreement with the value inferred in the Introduction. One should note that the bulk of the error bar of $\text{IP}(\text{CF}_3)$ propagates from the uncertainty in $\text{IP}(\text{CF})$.

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 $\text{IP}(\text{CF}_3) \approx 8.6 \text{ eV}$ arising from the data of Noutary,²⁴ Fisher and Armentrout,³³ and Clay *et al.*,³⁷ as well as the estimated value of $\leq 8.9 \text{ eV}$ by Logunov *et al.*²⁰ (see Table II). The present determination of $9.05_5 \pm 0.01_1 \text{ eV}$ for the $\text{IP}(\text{CF}_3)$ is quite close to 9.11 eV inferred by Walter *et al.*¹⁸ from unpublished¹⁹ 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. $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{X})$ and $D_0(\text{CF}_3-\text{X})$

In Sec. III B we have shown that photoionization measurements provide only an upper limit to the AP of CF_3^+ from CF_3Cl , $< 12.867 \pm 0.008 \text{ eV}$ at 0 K (or $< 12.788 \pm 0.008 \text{ eV}$ at 298 K). This threshold is in good agreement with the “estimated” AP_0 of $12.81 \pm 0.04 \text{ eV}$ 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 $12.65 \pm 0.04 \text{ eV}$, selected as the “first onset,” is significantly lower, as are the analogous “first onset” of Noutary²⁴ (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 $12.75 \pm 0.05 \text{ eV}$ by Creasey *et al.*,³⁶ also defined as a “first departure,” is very close to our 298 K value.

$\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Cl}) < 12.867 \pm 0.008 \text{ eV}$, with $\text{IP}(\text{CF}_3) = 9.05_5 \pm 0.01_1 \text{ eV}$, yields the upper limit $D_0(\text{CF}_3-\text{Cl}) < 87.9 \pm 0.3 \text{ kcal/mol}$ (or $< 88.8 \pm 0.3 \text{ kcal/mol}$ at 298 K). JANAF^{6,50} gives $D_0(\text{CF}_3-\text{Cl}) = 84.9 \pm 1.3 \text{ kcal/mol}$ ($85.8 \pm 1.3 \text{ kcal/mol}$ at 298 K), well below our upper bound. The recent experimental inference of $D_0(\text{CF}_3-\text{Cl}) = 89.0 \pm 1.5 \text{ kcal/mol}$ 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 $D_0(\text{CF}_3-\text{Cl}) = 87.3 \pm 1.3 \text{ kcal/mol}$ ($88.2 \pm 1.3 \text{ kcal/mol}$ at 298 K), which can be obtained from Tsang’s¹¹ $\Delta H_f^\circ(\text{CF}_3) = -110.0 \pm 1.0 \text{ kcal/mol}$ (-109.3 ± 1.0 at 0 K) and auxiliary heats of formation.⁵⁰ If a value of $D_0(\text{CF}_3-\text{Cl}) \sim 87.5$ – 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’s⁶ value of 84.9 kcal/mol requires the true threshold to be $\sim 0.13 \text{ eV}$ 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., $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Cl}) > 12.74 \text{ eV}$.

From our $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Br}) = 12.095 \pm 0.005 \text{ eV}$ and $\text{IP}(\text{CF}_3) = 9.05_5 \pm 0.01_1 \text{ eV}$, we obtain $D_0(\text{CF}_3-\text{Br}) = 70.1 \pm 0.3 \text{ kcal/mol}$ (or $70.8 \pm 0.3 \text{ kcal/mol}$ at 298 K). This is in excellent agreement with the experimental determination of $D_{300}(\text{CF}_3-\text{Br}) = 70.5 \pm 1.0 \text{ kcal/mol}$ by Tsang,¹¹ and in reasonably good agreement with the bond energy of $71.1 \pm 1.2 \text{ kcal/mol}$ ($71.8 \pm 1.2 \text{ kcal/mol}$ at 298 K), which can be obtained from Tsang’s recommended¹¹ value for $\Delta H_f^\circ(\text{CF}_3)$ and auxiliary data.⁵⁰ JANAF’s⁶ $\Delta H_f^\circ(\text{CF}_3)$ leads to $D_0(\text{CF}_3-\text{Br}) = 68.7 \pm 1.2 \text{ kcal/mol}$ ($69.4 \pm 1.2 \text{ kcal/mol}$ at 298 K), $\sim 1.4 \text{ kcal/mol}$ lower than our value, but still overlapping within the combined error bars. In contrast to this, the “first onset” values for $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{Br})$ of 11.84 eV by Noutary²⁴ and $11.92 \pm 0.02 \text{ eV}$ by Creasey *et al.*,³⁶ when combined with $\text{IP}(\text{CF}_3) = 9.05_5 \pm 0.01_1 \text{ eV}$, yield low bond energies of 64.2 kcal/mol and $66.1 \pm 0.5 \text{ kcal/mol}$, respectively, while the AP of $11.56 \pm 0.02 \text{ eV}$ from Clay *et al.*³⁷ leads to the extremely low value of $57.7 \pm 0.5 \text{ kcal/mol}$.

Combining our $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{I}) = 11.384 \pm 0.005 \text{ eV}$ with $\text{IP}(\text{CF}_3)$ gives $D_0(\text{CF}_3-\text{I}) = 53.7 \pm 0.3 \text{ kcal/mol}$ (or $54.3 \pm 0.3 \text{ kcal/mol}$ at 298 K). This is in excellent agreement with JANAF’s⁶ value of $53.3 \pm 1.3 \text{ kcal/mol}$ ($53.9 \pm 1.3 \text{ kcal/mol}$ 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 $55.7 \pm 1.3 \text{ kcal/mol}$ ($56.3 \pm 1.3 \text{ kcal/mol}$ at 298 K) derived⁵⁰ from Tsang’s¹¹ $\Delta H_f^\circ(\text{CF}_3)$. The $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{I})$ by Berman and Beauchamp,³⁸ $11.36 \pm 0.02 \text{ eV}$, which is in very good agreement with our AP_0 , leads to $D_0(\text{CF}_3-\text{I}) = 53.2 \pm 0.5 \text{ kcal/mol}$, while the revised appear-

ance potential of 11.26 ± 0.05 eV by Bombach *et al.*³⁹ leads to the considerably lower $D_0(\text{CF}_3-\text{I}) = 50.8 \pm 1.2$ kcal/mol.

To reiterate, our $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{Br})$, $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{I})$, and $\text{IP}(\text{CF}_3)$ lead to $D_0(\text{CF}_3-\text{Br}) = 70.1 \pm 0.3$ kcal/mol and $D_0(\text{CF}_3-\text{I}) = 53.7 \pm 0.3$ 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 Tsang¹¹ 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 $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{X})$, chiefly obtained by the “first onset” approach, are too low.

C. $\Delta H_f^\circ(\text{CF}_3)$ and $\Delta H_f^\circ(\text{CF}_3^+)$

Our $D_0(\text{CF}_3-\text{Br}) = 70.1 \pm 0.3$ kcal/mol and JANAF's^{6,50} $\Delta H_f^\circ(\text{CF}_3\text{Br}) = -152.2 \pm 0.7$ kcal/mol gives $\Delta H_f^\circ(\text{CF}_3) = -110.3 \pm 0.8$ kcal/mol, close to one of the values of Tsang.¹¹ However, our $D_0(\text{CF}_3-\text{I}) = 53.7 \pm 0.3$ kcal/mol and JANAF's^{6,50} $\Delta H_f^\circ(\text{CF}_3\text{I}) = -139.4 \pm 0.8$ kcal/mol, yields $\Delta H_f^\circ(\text{CF}_3) = -111.3 \pm 0.9$ kcal/mol, exactly 1.0 kcal/mol lower, and closer to JANAF's⁶ value for $\Delta H_f^\circ(\text{CF}_3)$. Since our two derived values of $\Delta H_f^\circ(\text{CF}_3)$ overlap within their error bars, selecting a weighted average of $\Delta H_f^\circ(\text{CF}_3) = -110.7 \pm 0.9$ kcal/mol or $\Delta H_f^\circ(\text{CF}_3) = -111.4 \pm 0.9$ 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 $\Delta H_f^\circ(\text{CF}_3)$. 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 $\text{AP}(\text{CF}_3^+/\text{CF}_4)$ is the farthest from the thermodynamical threshold, while $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{I})$ is the closest. This interleaves well with the known aberration in CF_4 and perhaps also with our findings on $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{Cl})$, but it would imply that $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{Br})$ 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 $\Delta H_f^\circ(\text{CF}_3\text{Br})$ and $\Delta H_f^\circ(\text{CF}_3\text{I})$. 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_3X has been brought up also by Berman and Beauchamp,³⁸ who pointed out that $\Delta H_f^\circ(\text{CF}_3\text{Cl})$ and $\Delta H_f^\circ(\text{CF}_3\text{Br})$ were determined relative to $\Delta H_f^\circ(\text{CF}_3\text{I})$, while the latter has been determined relative to $\Delta H_f^\circ(\text{CF}_3\text{H})$. This would make it appear that $\Delta H_f^\circ(\text{CF}_3\text{I})$ is more fundamental than $\Delta H_f^\circ(\text{CF}_3\text{Br})$, and that therefore $\Delta H_f^\circ(\text{CF}_3)$ derived from $D_0(\text{CF}_3\text{I})$ is to be preferred. However, the least-squares adjustments of Syverud⁷ and Gurvich *et al.*⁸ introduce a more complex interdependence of the tabulated^{6,8} values for $\Delta H_f^\circ(\text{CF}_3\text{X})$, so that, in fact, $\Delta H_f^\circ(\text{CF}_3\text{Br})$ winds up with a slightly lower error bar than $\Delta H_f^\circ(\text{CF}_3\text{I})$.

The difference $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Br}) - \text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{I}) = 0.711 \pm 0.007$ eV $\equiv 16.4 \pm 0.2$ kcal/mol is a direct measure

of $D_0(\text{CF}_3\text{Br}) - D_0(\text{CF}_3\text{I})$. This may be equivalently expressed as $\Delta H_f^\circ(\text{CF}_3\text{Br}) - \Delta H_f^\circ(\text{CF}_3\text{I}) = 13.8 \pm 0.2$ kcal/mol, using⁵⁰ only $\Delta H_f^\circ(\text{Br})$ and $\Delta H_f^\circ(\text{I})$ in addition. The tabulated^{6,8} heats for formation of CF_3Br and CF_3I 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_3Br and CF_3I , which seem to be in need of a careful redetermination.

Taking tentatively the tabulated^{6,8,50} value for $\Delta H_f^\circ(\text{CF}_3\text{Cl})$ as correct, our $\Delta H_f^\circ(\text{CF}_3)$ leads to $D_0(\text{CF}_3-\text{Cl}) = 85.9 \pm 1.2$ kcal/mol, and with $\text{IP}(\text{CF}_3)$ yields $\text{AP}_0(\text{CF}_3^+/\text{CF}_3\text{Cl}) = 12.78 \pm 0.05$ 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 $\Delta H_f^\circ(\text{CF}_3\text{Cl})$ by 0.5–1 kcal/mol, would bring both the derived $D_0(\text{CF}_3-\text{Cl})$ closer to that of Kumaran *et al.*,¹⁵ and the derived $\text{AP}(\text{CF}_3^+/\text{CF}_3\text{Cl})$ closer to our limit.

Using our $\Delta H_f^\circ(\text{CF}_3)$ recommended above and $\text{IP}(\text{CF}_3) = 9.055 \pm 0.011$ eV, we obtain $\Delta H_f^\circ(\text{CF}_3^+) = 98.1 \pm 0.9$ kcal/mol and $\Delta H_f^\circ(\text{CF}_3^+) = 97.4 \pm 0.9$ kcal/mol. This is in good agreement with one of the values of Ajello *et al.*,³⁴ $\Delta H_f^\circ(\text{CF}_3^+) = 98.8$ kcal/mol, and with $\Delta H_f^\circ(\text{CF}_3^+) = 98.3$ kcal/mol by Berman and Beauchamp.³⁸ It also agrees well with the limit of $\leq 99 \pm 7$ kcal/mol implied by the results of Powis,²⁹ and is not too far from $\Delta H_f^\circ(\text{CF}_3^+) = 96.1 \pm 1.2$ kcal/mol by Bombach *et al.*³⁹ However, it is significantly higher than $\Delta H_f^\circ(\text{CF}_3^+) \leq 87.3$ kcal/mol of Noutary,²⁴ $\Delta H_f^\circ(\text{CF}_3^+) = 86.4 \pm 1.6$ kcal/mol implied by Fisher and Armentrout,³³ and $\Delta H_f^\circ(\text{CF}_3^+) = 86.6 \pm 1.1$ kcal/mol reported by Clay *et al.*³⁷

Our value for $\Delta H_f^\circ(\text{CF}_3^+)$, together with the well established^{6,8,50} $\Delta H_f^\circ(\text{CF}_4)$, yields $\text{AP}_0(\text{CF}_3^+/\text{CF}_4) = 14.67 \pm 0.04$ eV (14.73 ± 0.04 eV for AP_{298} or 339.4 ± 1.0 kcal/mol for ΔH_r° for the reaction $\text{CF}_4 \rightarrow \text{CF}_3^+ + \text{F}$) and also $\text{IP}(\text{CF}_4) = 14.67 \pm 0.04$ 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 Powis²⁹ 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_2F_4 present the opportunity to estimate the otherwise poorly established $\Delta H_f^\circ(\text{CF})$. From $\text{AP}_0(\text{CF}_3^+/\text{C}_2\text{F}_4) = 13.721 \pm 0.005$ eV and $\Delta H_f^\circ(\text{CF}_3^+) = 98.1 \pm 0.9$ kcal/mol, and assuming that JANAF's⁶ $\Delta H_f^\circ(\text{C}_2\text{F}_4) = -156.6 \pm 0.6$ kcal/mol is correct, we obtain $\Delta H_f^\circ(\text{CF}) = 61.7 \pm 1.1$ kcal/mol or $\Delta H_f^\circ(\text{CF}) = 62.5 \pm 1.1$ kcal/mol, implying $D_0(\text{CF}) = 5.50 \pm 0.05$ eV. This is in reasonable agreement with JANAF's⁶ inference of $\Delta H_f^\circ(\text{CF}) = 60 \pm 2$ 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 $\text{IP}(\text{CF})-\text{IP}(\text{CF}_3)=0.055\pm0.003$ eV, and, consequently, $\text{IP}(\text{CF}_3)=9.05_5\pm0.01_1$ 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 $D_0(\text{CF}_3-\text{Br})=70.1\pm0.3$ kcal/mol (70.8 ± 0.3 kcal/mol at 298 K) and $D_0(\text{CF}_3-\text{I})=53.7\pm0.3$ kcal/mol (54.3 ± 0.3 kcal/mol at 298 K). The tabulated^{6,8} heats of formation of halo-methanes are suspected to be inconsistent by ~ 1 kcal/mol and probably in need of redetermination. A compromise value of $\Delta H_f^\circ{}_{298}(\text{CF}_3)=-111.4\pm0.9$ kcal/mol (-110.7 ± 0.9 kcal/mol at 0 K) is selected, based on tabulated values of $\Delta H_f^\circ(\text{CF}_3\text{Br})$ and $\Delta H_f^\circ(\text{CF}_3\text{I})$. This leads to $\Delta H_f^\circ{}_{298}(\text{CF}_3^+)=97.4\pm0.9$ kcal/mol (98.1 ± 0.9 kcal/mol at 0 K). An $\text{IP}(\text{CF}_4)=\text{AP}_0(\text{CF}_3^+/\text{CF}_4)=14.67\pm0.04$ eV is also inferred. Together with data on C_2F_4 , the selected $\Delta H_f^\circ(\text{CF}_3)$ leads to $\Delta H_f^\circ{}_{298}(\text{CF})=62.5\pm1.1$ kcal/mol (61.7 ± 1.1 kcal/mol at 0 K) or $D_0(\text{CF})=5.50\pm0.05$ eV. Many earlier literature values for appearance potentials of CF_3^+ from CF_3X , which lead to very low $\Delta H_f^\circ(\text{CF}_3^+)$ and/or $\text{IP}(\text{CF}_3)$, are demonstrated to be wrong.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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⁵⁰From JANAF (Ref. 6), which is almost identical to Gurvich *et al.* (Ref. 8):
 $\Delta H_{f, 298}^\circ(\text{CF}_4) = -223.0 \pm 0.3$ kcal/mol (-221.6 ± 0.3 kcal/mol at 0 K),
 $\Delta H_{f, 298}^\circ(\text{CF}_3\text{Cl}) = -169.2 \pm 0.8$ kcal/mol (-168.0 ± 0.8 kcal/mol at 0 K),
 $\Delta H_{f, 298}^\circ(\text{CF}_3\text{Br}) = -155.1 \pm 0.7$ kcal/mol (-152.2 ± 0.7 kcal/mol at 0 K),
 $\Delta H_{f, 298}^\circ(\text{CF}_3\text{I}) = -140.8 \pm 0.8$ kcal/mol (-139.4 ± 0.8 kcal/mol at 0 K),
and $\Delta H_{f, 298}^\circ(\text{F}) = 18.97 \pm 0.07$ kcal/mol (18.47 ± 0.07 kcal/mol at 0 K),
 $\Delta H_{f, 298}^\circ(\text{Cl}) = 28.992 \pm 0.002$ kcal/mol (28.590 ± 0.002 kcal/mol at 0 K),
 $\Delta H_{f, 298}^\circ(\text{Br}) = 26.74 \pm 0.01$ kcal/mol (28.18 ± 0.01 kcal/mol at 0 K),
 $\Delta H_{f, 298}^\circ(\text{I}) = 25.52 \pm 0.01$ kcal/mol (25.61 ± 0.01 kcal/mol at 0 K).