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Ionization Energies, Appearance Energies, and Thermochemistry of CF₂O and FCO

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With the discharge flow–photoionization mass spectrometer (DF-PIMS) coupled to the U-11 beamline at the National Synchrotron Light Source, we have measured the ionization energies of C_2F_4, CF_2, and CF_2O and appearance energy of FCO^+ from CF_2O. The PIMS results corroborate those determined by other techniques. With high-level *ab initio* calculations that utilize a large basis set and isogyric corrections, we have determined an ionization energy of 9.3 ± 0.1 eV for FCO. At 298 K, the heats of formation of FCO (-152 ± 12 kJ/mol) and FCO^+ (745.3 ± 9.6 kJ/mol) [relative to $\Delta_f H°_{298}(CF_2O) = -607.9 \pm 7.1$ kJ/mol] were determined and agree to within the uncertainties of other measurements but with much higher precision. We have evaluated the bond strengths $D°_{298}(F–CFO)$ and $D°_{298}(F–CO)$ to be 535 ± 12 and 121 ± 12 kJ/mol, respectively.

Introduction

Carbonic difluoride (CF_2O) and fluorooxomethyl radical (FCO) are important intermediates in the oxidative degradation of many fluorinated compounds. These species are involved in the mechanism of flame suppression by fluorinated compounds.[1] The breakdown of CF_2O to FCO may serve as an unreactive bottleneck in the flame reaction scheme, and so the thermochemistry of these species is particularly important. These species are also formed in the fluorocarbon/oxygen plasmas currently used in many etching processes. Reactions of O atoms with CF_2[2] and of O_2^+ and O^+ with fluorocarbons[3] in plasmas involve FCO, FCO^+, and CF_2O^+ as intermediates that sustain the production of F which is presumed to be the primary etchant. In the troposphere, a number of hydrofluorocarbons (HFCs) react with OH[4,5] to produce CF_3 which subsequently reacts with oxygen, ultimately to produce HF and CF_2O. In the stratosphere, photolysis of CF_2Cl_2 produces CF_2Cl, which also yields CF_2O, after reaction with O_2. Indeed, increasing amounts of CF_2O have been measured in the upper stratosphere.[6]

The thermochemistry of CF_2O and of FCO has received renewed attention recently amid controversies surrounding the heat of formation of CF_2O and the ionization energy (IE) of FCO. For example, $\Delta_f H°_{298}(CF_2O)$ has been calculated in three independent studies[1,7,8] to be about 30 kJ mol^{-1} larger (i.e., less stable) than the recommended value[9,10] of -638.9 ± 1.7 kJ mol^{-1}. Also, values calculated for IE(FCO), although within a larger uncertainty, are consistently larger (at 9.0 eV)[11,12] than that derived from a photoelectron spectroscopy study (at 8.76 $\pm$ 0.32 eV).[13]

An accurate assessment of the kinetic processes which involve fluorine-containing species requires knowledge of their ther-

mochemical properties. In this study, we have measured photoionization efficiency (PIE) spectra for C_2F_4, CF_2O, CF_2, and FCO to determine IE's. In addition, we have measured the appearance energy (AE) of FCO^+ from CF_2O, and we have calculated IE(FCO) at a high level of theory. The results of these determinations have been utilized in an evaluation of the enthalpies of formation of CF_2O, FCO, and FCO^+.

Experimental Section

Experiments were performed by employing a discharge flow–photoionization mass spectrometer (DF-PIMS) apparatus coupled to the U-11 beamline at the National Synchrotron Light Source (NSLS).[14–19] The flow tube was similar in design and operation to one used for kinetic measurements in previous work.[20] The gaseous mixture in the flow tube was sampled as a molecular beam that was formed in a free-jet expansion (1 mm nozzle, 1.5 mm skimmer/collimator). The source chamber and detection chamber were maintained at about 1×10^{-2} and 7×10^{-4} Pa (1×10^{-4} and 5×10^{-6} Torr), respectively. Since the molecular beam source was in the transition region, it was necessary to determine the molecular beam density at the ionizer (3.0 cm from the nozzle) experimentally.[21] By comparing the NO ion signal from a beam of NO/He with the NO ion signal from NO as background gas in the detection chamber, it was calculated that the gas density at the ionizer was 180–200 times smaller than that in the flow tube.[16]

A modified Wadsworth monochromator[22] with a normal incidence grating (1200 lines/mm) was used to disperse the VUV light, and a LiF filter ($\lambda \geq 103$ nm) was used to eliminate second- and higher-order radiation. The IE(CF_2O) and AE(FCO^+,CF_2O) measurements were performed under windowless conditions because the thresholds are below the wavelength cutoff of LiF. Corrections of the photoion efficiency (PIE) spectra for second-order light were made by scanning the

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spectral range at one-half the wavelength and one-half the step size. These "second-order wavelength" PIE scans were normalized (to reflect the intensity of second-order light for the normal scan) and subtracted from the raw PIE data. The nominal monochromator slit width was 750 μm, and the resulting spectral bandwidth (fwhm) was 0.2 nm. At a nominal ring current at 500 mA, the light intensity in the ionizing region of the mass spectrometer was typically 10^{13} photons s^{-1} at the 0.2 nm bandwidth as measured by using a calibrated photodiode.[19] The zero-order setting for calibration of the monochromator was adjusted to ± 0.01 nm at the beginning and checked at the end of each filling of the VUV synchrotron ring. Typically, variations between the beginning and ending settings of zero-order corresponded to variations in the wavelength calibration of about ± 0.05 nm (i.e., ± 0.007 eV at 100 nm).

Ions were mass selected and detected by using a quadrupole mass spectrometer (EXTREL Model C50) operated in the ion counting mode with 2.75 kV on the channeltron detector that was aligned axially with the molecular beam.[16] To obtain a photoion efficiency spectrum for either ionization energy or appearance energy measurements, ion intensity was measured relative to light intensity as a function of wavelength. The light intensity was monitored as a relative quantity by using a sodium salicylate scintillator and an attached photomultiplier (PM). This scintillator has an essentially constant quantum yield in the VUV region;[23] therefore, the PM output was directly proportional to the absolute light intensity. The PM signal was processed first with a picoammeter and thence with a voltage-to-frequency converter to ultimately obtain the light intensity in digital form. The ion counts and the light counts were accumulated simultaneously, at each wavelength step, in a digital data acquisition system for a prescribed integration time.
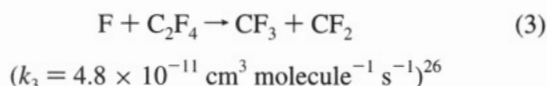
All experiments were conducted at ambient temperature (298 $\pm$ 2 K), at flow tube pressures of 500–700 Pa (4–5 Torr), and with flow velocities of about 800 or 1400 cm s^{-1}. Premixed CF$_2$O/He and C$_2$F$_4$/He samples were used for the measurements of IE(CF$_2$O), IE(C$_2$F$_4$), and AE(FCO$^+$,CF$_2$O). Additionally, carbonic difluoride (CF$_2$O) and difluoromethylene (CF$_2$) were generated *in situ* by the reaction of O atoms with tetrafluoroethylene, where O atoms were produced at the upstream end of the flow tube in a microwave discharge of O$_2$ in He carrier gas:

$$O + C_2F_4 \rightarrow CF_2O + CF_2 \qquad (1)$$

$$(k_1 = 9.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{24}$$
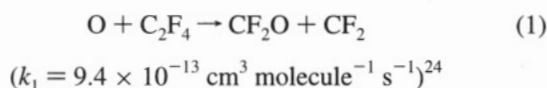
The C$_2$F$_4$/He mixture was introduced through a movable injector whose tip was located 15 cm from the nozzle. Under conditions of these experiments ([C$_2$F$_4$] $\approx$ 1 $\times$ 10^{14} molecules cm^{-3}, flow velocity $v \approx$ 1400 cm s^{-1}) reaction 1 was 60–70% complete. The loss of radicals on the wall was minimized by using a Teflon tube insert. Fluorooxomethyl radicals (FCO) were produced in the reaction sequence of (1) followed by (2):

$$O + CF_2 \rightarrow FCO + F \qquad (2)$$

$$(k_2 = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{25}$$
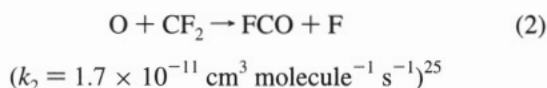
Under conditions in the flow tube where reaction 2 occurs, F atom react rapidly with C$_2$F$_4$ to form CF$_3$ and more CF$_2$:

$$F + C_2F_4 \rightarrow CF_3 + CF_2 \qquad (3)$$

$$(k_3 = 4.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{26}$$
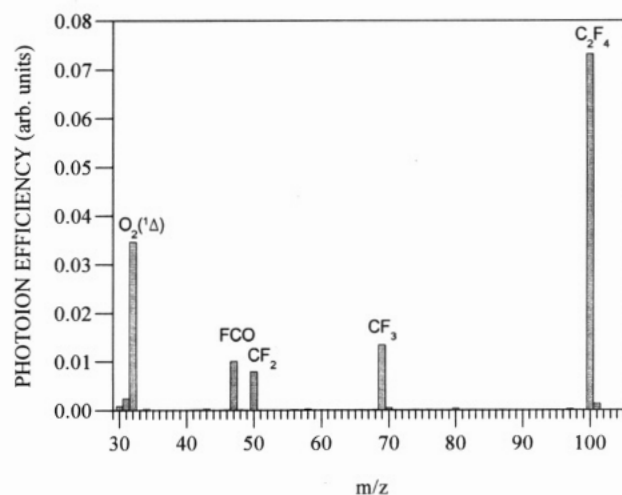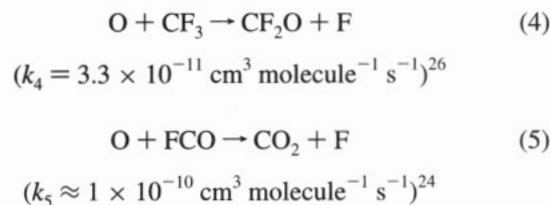
This system may be further influenced by reaction of O with

Figure 1. Mass spectrum of reaction products of C$_2$F$_4$ + O over the range of m/z = 30–105 at an excitation wavelength of 106 nm (11.7 eV) after a reaction time of 7 ms. [O$_2$] = 1 $\times$ 10^{15} molecules cm^{-3} and [C$_2$F$_4$] = 7 $\times$ 10^{13} molecules cm^{-3}.

CF$_3$ (reaction 4) and the loss of FCO *via* reaction with O atoms (reaction 5):

$$O + CF_3 \rightarrow CF_2O + F \qquad (4)$$

$$(k_4 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{26}$$

$$O + FCO \rightarrow CO_2 + F \qquad (5)$$

$$(k_5 \approx 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{24}$$

The resulting mechanism, reactions 1–5, was modeled by using the ACUCHEM code.[27,28] Taking [C$_2$F$_4$] $\approx$ 1 $\times$ 10^{14} molecules cm^{-3} and [O] $\approx$ 1 $\times$ 10^{13} atoms cm^{-3}, a value for [FCO] of about 1 $\times$ 10^{12} radicals cm^{-3} was determined for a reaction time of 10–15 ms.

Difluoromethylene radicals, CF$_2$, were generated in separate experiments *via* reaction 3 where fluorine atoms were produced at the upstream end of the flow tube in a microwave discharge of F$_2$ in He carrier gas. Taking [C$_2$F$_4$] $\approx$ 4 $\times$ 10^{13} molecules cm^{-3}, the reaction was 98% complete within 3 cm of the tip of the movable injector.

Helium (MG Industries, 99.9999%), O$_2$ (MG Industries, 99.995%), and F$_2$ (MG Industries, 99.99% purity, diluted in helium at 2% v/v) were used as supplied. The CF$_2$O sample was from Specialty Chemicals Corp. The C$_2$F$_4$ sample was from PCR Inc. Analysis of C$_2$F$_4$ by GC-MS showed two minor impurities: a small amount of CF$_3$CH$_2$CF$_3$ and a larger unknown peak, possibly C$_2$F$_5$OH. The impurities present did not have any interference peaks at the masses we studied. The CF$_2$O and C$_2$F$_4$ samples were outgassed at 77 K prior to making mixtures in He.

Results

The products of the O + C$_2$F$_4$ reaction were examined over the range m/z = 30–105 at an excitation wavelength of 106 nm (11.7 eV) after a reaction time of 7 ms. The mass spectrum is shown in Figure 1. Major ion peaks were observed at m/z = 100, 69, 50, 47, and 32 corresponding to C$_2$F$_4^+$, CF$_3^+$, CF$_2^+$, and FCO$^+$ along with O$_2^+$ formed from O$_2$($^1\Delta$) that was generated in the microwave discharge. The product CF$_2$O (m/z = 66) was not observed at this wavelength since its ionization energy (13.03 eV) is well above the photon energy.

The PIE spectrum of C$_2$F$_4^+$ ion produced from C$_2$F$_4$ over the wavelength region 110–125 nm is shown in Figure 2. Two
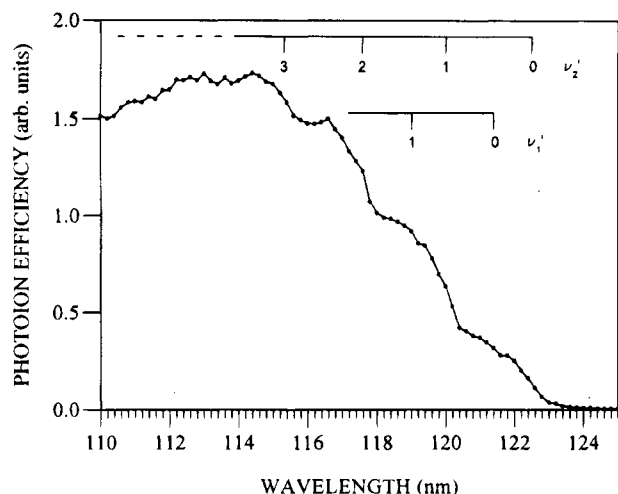
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Figure 2. PIE spectrum of C_2F_4 ($m/z = 100$) over the wavelength range 110–125 nm at a resolution of 0.23 nm and with 0.2 nm steps. Photoionization efficiency is ion counts divided by light intensity in arbitrary units. $[C_2F_4] = 8 \times 10^{13}$ molecules cm^{-3}. Vibrational progressions for ν_1' (119.0 and 121.4 nm) and ν_2' (115.3, 117.6, 120.0, and 122.5 nm) are from Brundle et al.[29]

vibrational progressions, ν_1', the C–C stretch progression of 1660 cm^{-1}, and ν_2', one quanta of C–F stretch of 790 cm^{-1} combined with the C–C progression, reported by Brundle et al.,[29] are observable in our PIMS spectrum. The threshold region marks the ionization energy of the C_2F_4 molecule by a sharp rise in the PIE curve. We obtain an IE of 10.114 ± 0.010 eV (122.59 ± 0.12 nm) from the average of five different spectra. Our measurement is in excellent agreement with photoelectron spectroscopy (PES) values of 10.10,[29] 10.12 ± 0.02,[30] and 10.14 eV.[31]

The ionization energy of CF₂O was determined using neat CF₂O taken directly from a cylinder and CF₂O produced *in situ* via the $C_2F_4 + O$ reaction. The CF₂O generated in the flow tube via reaction 1 displayed a factor of 10 weaker signal but was identical in shape to that from the neat molecular species. This demonstrates that the reaction products were thermalized on the time scale of the experiment and that hot bands did not complicate the analyses. Figure 3 compares the PIE signals in the threshold region for the two sources of the CF₂O. The two PIE spectra are nearly identical with the CF₂O from the cylinder taken at higher resolution and better signal to counting noise. The ionization energy of CF₂O from the cylinder is 13.033 ± 0.010 eV (95.13 ± 0.07 nm) while the reaction product CF₂O gives 13.037 ± 0.020 V (95.10 ± 0.15 nm), both determined at their half-rise points. These results are in excellent agreement with the accepted PES values of 13.02[29] and 13.03 eV,[30] where the former was complicated by a slight contamination with CO₂. Another PES measurement gave 13.04 eV for the adiabatic value.[32] The band reported may have had some interference from the presence of CO₂ in the prepared CF₂O. Evidently, the carbon dioxide impurities did not interfere with the PES measurements of IE(CF₂O).

The CF₂ radical was observed as a product in two different reaction systems: $C_2F_4 + F$ and $C_2F_4 + O$, where in the latter reaction CF₂ is produced in an electronically excited state.[33] We did not observe any difference between the PIE spectra for CF₂ obtained in the two different sources which demonstrates that the electronically excited CF₂ was collisionally quenched on the time scale of the experiment. Figure 4 shows the CF₂⁺ photoionization signal in the 106–111 nm range from CF₂ generated in the $C_2F_4 + F$ reaction. Clearly visible are the first three levels of the ν_2' vibrational manifold. The ionization
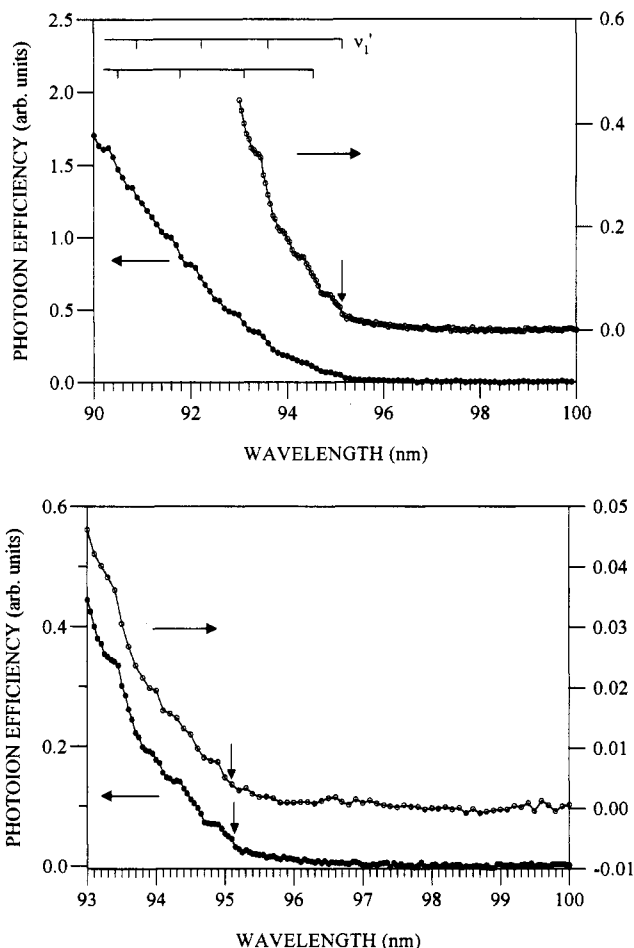

Figure 3. (a, top) PIE spectra of CF₂O over the wavelength range 90–100 nm. Both plots had a resolution of 0.07 nm, but the step sizes are 0.10 nm for the lower plot (●) and 0.05 nm for the upper plot (○). CF₂O was taken directly from cylinder. $[CF_2O] = 2 \times 10^{14}$ molecules cm^{-3}. Vertical arrow in threshold region (○) indicates threshold at 95.13 nm. Vibrational progression for ν_1': 90.90, 92.20, 93.60, and 95.13 nm. The second progression is for ν_1' + one quantum of ν_3': 90.50, 91.75, 93.10, and 94.55 nm. (b, bottom) PIE spectra of CF₂O over the wavelength range 93–100 nm. The lower plot (●) had a resolution of 0.07 and 0.05 nm steps, and the upper plot (○) had a resolution of 0.14 and 0.10 nm steps. CF₂O was taken directly from cylinder (●), $[CF_2O] = 2 \times 10^{14}$ molecules cm^{-3}, and generated *in situ* by O + C_2F_4 (○), $[O_2] = 1 \times 10^{14}$ molecules cm^{-3} and $[C_2F_4] = 1 \times 10^{14}$ molecules cm^{-3}. Vertical arrows indicate step thresholds at 95.13 and 95.10 nm, respectively.

threshold region was evaluated by determining the half-rise point. From an average of five measurements, the ionization energy is 11.445 ± 0.025 eV (108.33 ± 0.24 nm), which is in good agreement with the photoelectron result of 11.42 ± 0.01 eV[34] where the CF₂ radicals were made by microwave discharge of C_2F_4.

Figure 5 shows the PIE spectrum of FCO, with the threshold region expanded. Our IE measurements of FCO do not give a distinct threshold and can only provide an upper limit value of about 9.7 eV (128.8 nm) for the ionization energy. A PES study of FCO by Dyke et al.[13] also did not find an adiabatic threshold while the lowest energy feature in their PES data is at about 10.5 eV. Their reported adiabatic IE value of 8.76 ± 0.32 eV was derived from a Franck–Condon calculation using the observed vibrational structure. Through differentiation of the smoothed FCO wide-scan wavelength spectrum, we obtain a vertical ionization energy of 11.16 ± 0.03 eV (111.1 ± 0.3 nm), which is close to the 11.26 ± 0.01 eV determined in the PES experiment of Dyke et al.[13]
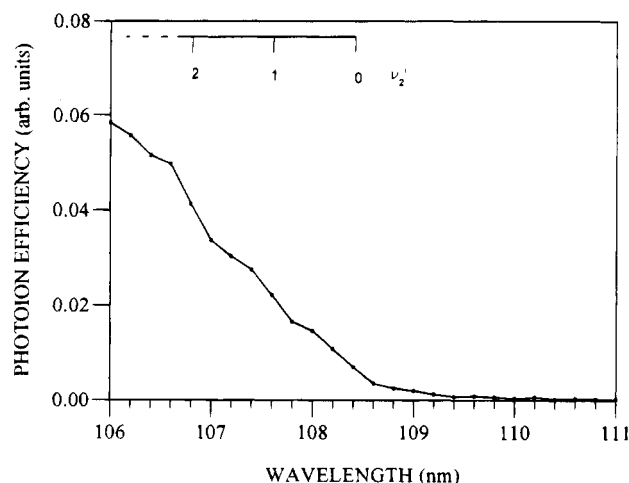
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Figure 4. PIE spectrum of CF_2 ($\leftarrow$ F + C_2F_4), m/z = 50, over the wavelength range 106−111 nm at a resolution of 0.23 nm and with 0.2 nm steps. $[F_2]$ = 2 × 10^{13} molecules cm^{-3} and $[C_2F_4]$ = 3 × 10^{13} molecules cm^{-3}. Threshold is at 108.4 nm (11.44 ± 0.02 eV). Vibrational progression for v_2' (106.8, 107.6, and 108.4 nm) yields vibrational spacing of 690 cm^{-1}.
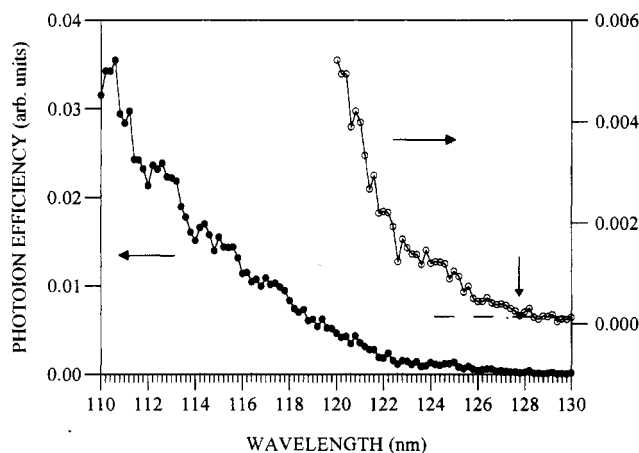

Figure 5. Wide scan (●) and onset region (○) of PIE spectra of FCO ($\leftarrow$ CF_2 + O). The wavelength range is 110−130 nm and resolution is 0.23 nm with 0.2 nm steps. $[O_2]$ = 6 × 10^{14} molecules cm^{-3} and $[C_2F_4]$ = 7 × 10^{13} molecules cm^{-3}. Vertical arrow indicates onset at 127.80 nm.

Since the IE of FCO cannot be directly measured, we turned to computational methods to obtain a reliable value. The ionization energy of FCO was determined by calculating the energies of the isogyric reactions 6 and 7,

$$FCO + HCO^+ \rightarrow FCO^+ + HCO \tag{6}$$

$$FCO + CF^+ \rightarrow FCO^+ + CF \tag{7}$$
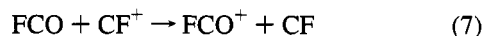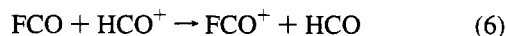
and using the known ionization energies of HCO (8.10 ± 0.05)[35] and CF (9.11 ± 0.01).[36] The geometries were optimized at MP2/6-311+G(d) using the GAUSSIAN 92 series of programs.[37] The energies were calculated at QCISD(T)/6-311+G(3df,2p) and are listed in Table 1. The vibrational zero-point energies (ZPE) were determined using HF/6-31G* geometries and frequencies. The zero-point energies were scaled by 0.89 (the accepted scaling factor for this level of theory) and are listed in Table 1. This method can predict ionization energies to within 0.1 eV.[38] The FCO ionization energies derived using reactions 6 and 7 are 9.261 and 9.333 eV, respectively. The average of these two values yields an ionization energy for FCO of 9.30 ± 0.10 eV. An approxima-

TABLE 1: Calculation of the Ionization Energy of FCO[a]

	FCO	HCO	CF
neutral (hartrees)	−212.830890	−113.685765	−137.604366
ion (hartrees)	−212.494287	−113.392448	−137.274424
difference (hartrees)	0.336603	0.293317	0.329942
ZPE neutral (cm^{-1})	1807	2810	627
ZPE ion (cm^{-1})	2392	3534	874
ΔZPE (cm^{-1})	585	725	247
calculated IE (eV)	9.232	8.071	9.009
literature IE (eV)		8.100	9.110
IE(FCO) corrected (eV)		9.261[b]	9.333[c]

[a] The energies are computed at QCISD(T)/6-311+G(3df,2p)//MP2/6-311+G(d). The harmonic vibrational frequencies were calculated at HF/6-31G(d) and scaled by 0.89 to obtain the zero-point energy. [b] The calculated value for IE(FCO), 9.232 eV, with the isogyric correction obtained for HCO: +0.029 eV. [c] The calculated value for IE(FCO), 9.232 eV, with the isogyric correction obtained for CF: +0.101 eV.
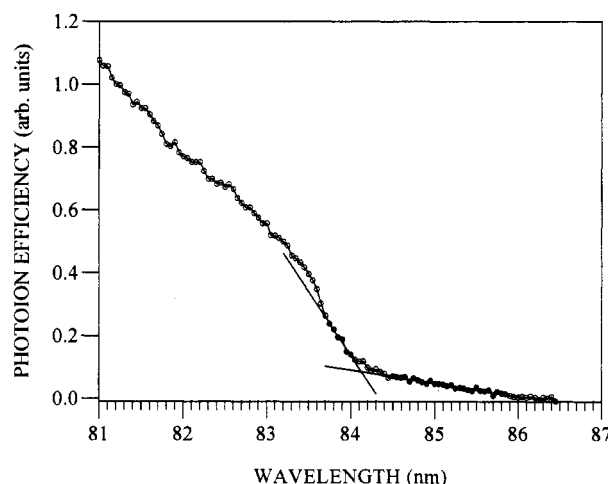

Figure 6. Threshold region of dissociative ionization of CF_2O (sample taken from cylinder) over the wavelength range 81−86.5 nm at a resolution of 0.07 nm and with 0.05 nm steps. $[CF_2O]$ = 2 × 10^{14} molecules cm^{-3}. Threshold at 84.14 nm indicates $AE_{298}(FCO^+, CF_2O)$ = 14.736 ± 0.012 eV.

tion of the vertical IE was determined by calculating the energy of the ion at the geometry of the neutral. The difference between the calculated adiabatic and vertical IE's is 1.847 eV. This approximation is expected to be good to within one vibrational interval, or 650 cm^{-1} (0.08 eV). We calculate a vertical ionization energy of 11.15 eV (9.30 + 1.85 eV) for FCO, which is close to the Dyke *et al.*[13] value of 11.26 ± 0.01 eV and in good agreement with our PIMS vertical ionization energy of 11.16 ± 0.03 eV.

The ionization energy of FCO was calculated by Krossner *et al.*[12] as part of a study on the excited states of FCO and the ground state of FCO^+. Krossner *et al.*[12] also calculated the Franck−Condon factors from the neutral ground state to the cation ground state (v_2' $\leftarrow$ v_2'') and derived a vertical ionization energy of 10.93 eV corresponding to v_2' = 20. This value is 0.2 eV lower than our calculated vertical ionization energy of 11.15 eV, which was determined using a larger basis set and isogyric corrections.

Fluorooxomethyl cations, FCO^+, were also produced by dissociative ionization of molecular CF_2O

$$CF_2O + h\nu \rightarrow FCO^+ + F + e^- \tag{8}$$
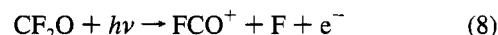
to give an appearance energy of 14.736 ± 0.012 eV (84.14 ± 0.07 nm). Figure 6 shows the threshold region of the PIMS data for this process. The present result is in reasonably good

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agreement with the photoelectron—photoion coincidence measurement of 14.85 ± 0.20 eV[39] and slightly higher than the electron impact measurement of 14.6 eV by ion cyclotron resonance mass spectrometry.[40] The base line for our AE measurement is not flat after second-order light correction. The residual signal could be from the process

$$CF_2O + h\nu \rightarrow FCO^+ + F^- \quad (9)$$
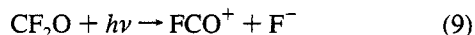
which would have a threshold 3.4 eV lower than that of reaction 8 (due to the electron affinity of F). However, we did not attempt to find the threshold for this process. Another possibility for the sloping base line might be the formation of metastable CF$_2$O$^+$ ions, which may decompose to form FCO$^+$, as suggested from PEPICO experiments.[39]

Discussion

The new data presented in this study, combined with results of others, provide an opportunity to reevaluate some thermochemical properties of CF$_2$O, FCO, and FCO$^+$. In addition, a sufficient number of independent and varied chemical processes that involve these species have been measured or calculated to evaluate the reliability of the data. The internal consistency between results of three scrutinized processes is demonstrated in the following discussion.

Our PIMS measurements provided the appearance energy of the FCO$^+$ ion from carbonic difluoride *via* the dissociative photoionization process, reaction 8, giving a value of 14.736 ± 0.012 eV. The ionization energy of the FCO radical has an upper limit of about 9.7 eV for the process

$$FCO + h\nu \rightarrow FCO^+ + e^- \quad (10)$$
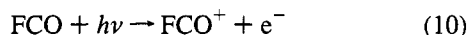
and a calculated value of 9.3 ± 0.1 eV from our work. Also, an experimental value for the process of dissociative electron capture of carbonic difluoride was reported, with the lowest energy process observed,

$$CF_2O + e^- \rightarrow F^- + FCO \quad (11)$$
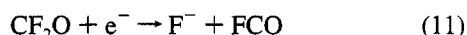
giving a sharp threshold at 2.1 ± 0.1 eV.[41]

Combining three of the preceding mentioned reactions gives the well-characterized process, the electron affinity of fluorine,

$$F + e^- \rightarrow F^- \quad (12)$$

on completion of the thermodynamic cycle: reaction 10 + reaction 11 − reaction 8. The derived electron affinity value from our thermodynamic cycle (calculated ionization energy, measured appearance energy, and dissociative electron capture energy)[42,43] is 3.39 ± 0.14 eV and is in excellent agreement with the accepted electron affinity of the fluorine atom, 3.399 ± 0.003 eV.[30] To obtain this result, the three individual values must be reasonably accurate or their respective errors must fortuitously cancel.

Accepting the heats of formation of F and F$^-$ while using the ion convention (i.e., the heat of formation of the electron is zero),[30] then the heat of formation of the three remaining species (CF$_2$O, FCO, and FCO$^+$) can be determined if one of them is known. The heat of formation of the stable molecular species CF$_2$O has been the focus of recent controversy. The often cited JANAF[9] value $\Delta_f H°_{298}(CF_2O) = -638.9 \pm 1.7$ kJ/mol was calculated, in part, using the enthalpy of hydrolysis measurements of CF$_2$O by Wartenberg and Riteris.[44] The hydrolysis measurements, however, were considered to be unreliable by Gurvich *et al.*[10] in a review which included the thermodynamic

TABLE 2: Thermochemical Values Used and Derived in This Work

species	$\Delta_f H°_0$ (kJ mol^{-1})	$\Delta_f H°_{298}$ (kJ mol^{-1})	reference
F	77.28 ± 0.30	79.39 ± 0.30	9
F$^-$	−250.67 ± 0.6	−248.88 ± 0.6[a]	9
CO	−113.81 ± 0.17	−110.53 ± 0.17	9, 10
CF$_2$O	−604.8 ± 7.1	−607.9 ± 7.1	8
FCO	−152.7 ± 12	−152.1 ± 12	this work
FCO$^+$	744.7 ± 8.6[b]	745.3 ± 9.6[c]	this work

[a] Corrected in accordance with the ion convention.[30] [b] Derived using reaction 8, the 0 K value of the appearance energy (see ref 42) and values listed in Table 2. Thus, $\Delta_f H°_0(FCO^+) = AE_0(FCO^+, CF_2O) - \Delta_f H°_0(F) + \Delta_f H°_0(CF_2O)$. [c] Derived by employing the ion convention[30] with integrated heat capacities from ref 9 and assuming the integrated heat capacity of FCO$^+$ is equal to that of FCO: 10.393 kJ/mol.[9] Thus, $\Delta_f H°_{298}(FCO^+) = \Delta_f H°_0(FCO^+) + (H°_{298} - H°_0)_{FCO^-} - \Sigma(H°_{298} - H°_0)_{elements}$.

properties of CF$_2$O. Nevertheless, Gurvich *et al.* incorporated these hydrolysis measurements, along with four other questionable values, in their evaluation to deduce a value, $\Delta_f H°_{298}(CF_2O) = -640 \pm 5$ kJ/mol, which is essentially identical to the JANAF[9] recommendation. However, recent theoretical studies suggest this value is about 30 kJ/mol too low. BAC-MP4 and G2 level *ab initio* calculations by Nyden *et al.*[1] gave values of $\Delta_f H°_{298}(CF_2O) = -598.3$ and -620.1 kJ/mol, respectively. The high-level *ab initio* calculations of Montgomery *et al.*[7] gave a result of -609.2 ± 4 kJ/mol. Fairly close to this value, Schneider and Wallington[8] obtained -600.6 kJ/mol; however, they recommended $\Delta_f H°_{298}(CF_2O) = -607.9 \pm 7.1$ kJ/mol, reflecting a compromise among results from different high-level calculations of theirs[8] and of Montgomery *et al.*[7] While none of the groups attempted to explain the discrepancy between their theoretical studies and the much earlier experimental measurements, Schneider and Wallington[8] were able to reconcile the differences among a number of debated thermodynamic values with their recommendation for $\Delta_f H°_{298}(CF_2O)$. We accept the value recommended by Schneider and Wallington as the basis of our thermochemical evaluations.

Reaction 8 may be combined with the reverse of reaction 10 to obtain the bond strength,

$$CF_2O \rightarrow FCO + F \quad (13)$$

$D°_0(F-CFO) = 529.4 \pm 9.7$ kJ/mol. A value of $\Delta_f H°_0(FCO) = -152.7$ kJ/mol may be computed[45] from this value of $D°_0(F-CFO)$ (see Table 2). The 298 K heat of formation of FCO, $\Delta_f H°_{298}(FCO)$, is similarly evaluated[46] to be -152.1 kJ/mol. In each case, the uncertainties are estimated to be about ±12 kJ/mol, primarily due to the uncertainty in $D°_{298}$ and $D°_0$. The value of $\Delta_f H°_{298}(FCO)$ can also be determined directly from reaction 11 using $\Delta_f H°_{298}(CF_2O)$ and $\Delta_f H°_{298}(F^-)$ (see Table 2) to give -156 kJ/mol. This result corroborates the value derived above (-152.1 ± 12 kJ/mol from reaction 13), which is higher than the JANAF value of -171.5 ± 63 kJ/mol but has much smaller uncertainty. The present value also agrees reasonably well with the heat of formation of FCO derived from a shock tube study, $\Delta_f H°_{298}(FCO) = -142 \pm 21$ kJ/mol.[47]

The heat of formation of the FCO$^+$ cation, $\Delta_f H°_{298}(FCO^+)$, using reaction 8 is 745.3 ± 9.6 kJ/mol (see Table 2). This value is in good agreement with (but is of higher precision than) the ion heat of formation value of 748 ± 42 kJ/mol estimated from core electron binding energies.[48] On the other hand, the present result is significantly larger than that reported by Dyke *et al.*,[13] 669 ± 46 kJ/mol, which was derived from their determination of IE(FCO) and the JANAF value for the heat of formation of FCO. Both of those values, as noted above, are lower than the

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respective ones used here in the derivation of $\Delta_f H°_{298}(FCO^+)$. The derived heats of formation of FCO and FCO$^+$ are summarized in Table 2.

Finally, the C—F bond strength in FCO can be determined by evaluating the minimum energy required for reaction 14,

$$FCO \rightarrow CO + F \tag{14}$$

Using our $\Delta_f H°_{298}(FCO)$, along with the heats of formation of CO and F,[9,10] we derive $D°_{298}(F-CO) = 121 \pm 12$ kJ/mol. Bowers and Chau[49] derived a lower limit, $D°_{298}(F-CO) \geq 121$ kJ/mol, from ion—molecule reaction studies that is consistent with our result; however, they recommended a larger value of 142 ± 17 kJ/mol. The lower limit, $D°_{298}(F-CO) \geq 135$ kJ/mol, derived from the negative ion data of MacNeil and Thynne,[41] is clearly inconsistent with the present result.

Conclusion

In this work, we initiated our photoionization studies on fluorinated organic species employing the PIMS technique. The values obtained in the present investigation for IE's for C$_2$F$_4$, CF$_2$O, and CF$_2$ corroborate those determined previously by other techniques. Thus, in providing confirmation, the present results also serve to validate the PIMS apparatus and the analyses used in this work. Experimentally obtained AE(FCO$^+$,CF$_2$O) = 14.736 $\pm$ 0.012 eV and theoretically derived IE(FCO) = 9.3 $\pm$ 0.1 eV are shown to be consistent with each other and with literature values. Based upon these mutually consistent data, the relative heats of formation of CF$_2$O, FCO, and FCO$^+$ are now firmly established. In the present work, the calculated value[8] for $\Delta_f H°_{298}(CF_2O)$ was used because of deficiencies in reported experimental values;[10] however, the "high", calculated result clearly needs to be verified by experimental measurement. In addition, the computed bond strengths, $D°_{298}(F-CO)$ and $D°_{298}(F-CFO)$, should clarify the thermochemistry of these important species and may lend insight into their kinetic behavior.

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(42) The value for AE$_{298}$(FCO$^+$,CF$_2$O) was corrected for the internal energy of CF$_2$O, according to methods in Traeger and McLoughlin;[43] AE$_0$(FCO$^+$,CF$_2$O) = AE$_{298}$(FCO$^+$,CF$_2$O) + E_i, where E_i = $(H_{298} - H_0)_{CF_2O}$ − 5RT/2. Thus, AE$_0$(FCO$^+$,CF$_2$O) = 14.787 eV. The value for the ionization energy is assumed to be for the 0 K process. The value for the dissociative electron capture process should probably be corrected for internal energy, as was done for the AE measurement; however, the stated uncertainty of $\pm$0.1 eV is larger than the correction ($\approx$0.05 eV), and thus no correction was applied. The value for reaction 12, and overall uncertainty, was thus derived: (−14.787 $\pm$ 0.012 eV) + (9.3 $\pm$ 0.1 eV) + (2.1 $\pm$ 0.1 eV) = −3.39 $\pm$ 0.14 eV.

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(45) Taking $\Delta_f H^\circ_{298}(CF_2O) = -607.9 \pm 7.1$ kJ/mol, as recommended by Schneider and Wallington,[8] we compute $\Delta_f H^\circ_0(CF_2O) = -604.8$ kJ/mol using the integrated heat capacities of CF$_2$O and the elements given in ref 9. Then, $\Delta_f H^\circ_0(FCO) = D^\circ_0(CF_2O) - \Delta_f H^\circ_0(F) + \Delta_f H^\circ_0(CF_2O)$, where $D^\circ_0(CF_2O) = 529.4$ kJ/mol (from the present result), $\Delta_f H^\circ_0(F) = 77.3$ kJ/mol (from ref 9), and $\Delta_f H^\circ_0(CF_2O)$ was evaluated above. Thus, we compute $\Delta_f H^\circ_0(FCO) = -152.7$ kJ/mol.

(46) The 298 K bond strength, $D^\circ_{298}(F-CFO)$, is derived by correcting $D^\circ_0(F-CFO)$ for the integrated heat capacities of CF$_2$O, FCO, and F (11.2,

10.393, and 6.52 kJ/mol, respectively, from ref 9) to obtain $D^\circ_{298}(F-CFO)$ = 535.2 kJ/mol.

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