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A discharge flow–photoionization mass spectrometric study of the FO(X $^2\Pi_i$) radical. Photoionization efficiency spectrum and ionization energy

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Abstract

Photoionization efficiency spectra of FO were measured over the wavelength range 80.0–100.0 nm and in the ionization threshold region, 94.0–100.0 nm, using a discharge flow–photoionization mass spectrometer apparatus coupled to a synchrotron radiation source. FO was generated by the reaction of F(^{2}P) atoms with NO_3 and via a F_2/O_2 discharge. A value of 12.78±0.03 eV was obtained for the adiabatic ionization energy of FO from photoion thresholds which corresponds to $FO^+(X\,^3\Sigma^-)\leftarrow FO(X\,^2\Pi_i)$. These results, which are the first to be obtained by direct PIMS measurements, corroborate those of a photoelectron spectroscopy study; however, the ionization energy determined here is free from interferences due to other species which complicated the PES measurement. A value of 109.5±8.0 kJ mol^{-1} for $\Delta_f H^0_{298}$(FO) is computed from the present value of IE(FO) and a previous appearance energy measurement, and a value for the proton affinity of FO is calculated to be 511.5±10.0 kJ mol^{-1}.

1. Introduction

In contrast to the extensively studied ClO and BrO, fluorine monoxide (FO) has received much less attention in regard to both kinetics and thermochemistry. The lowest energy ionization of FO, using vacuum ultraviolet (VUV) light of $\lambda > 40$ nm, is expected to originate from the 2π orbital, corresponding to $FO^+(X\,^3\Sigma^-)\leftarrow FO(X\,^2\Pi_i)$. Clyne and Watson [1] were the first, in 1971, to report detection of FO in the gas phase although it had been isolated in solid matrix earlier [2]. FO was generated in discharge flow studies [1,3,4] by the reaction of F with O_3, sampled via a molecular beam and detected by electron impact mass spectrometry. Along with kinetic data, Clyne and Watson reported the relative energies for ionization of FO and the appearance of FO^+ from F_2O but not an absolute value for the ionization energy (IE) of FO. Estimates for IE(FO) have been reported in indirect electron impact studies [5,6], an evaluation/calculation [7] and a photoionization study of dissociative ionization of F_2O [8]. In the only direct determination of IE(FO) [9], photoelectron spectroscopy (PES) was employed to obtain a value of 12.77±0.01 eV. The PES spectrum of FO, however, was somewhat obscured by overlapping bands of molecular oxygen, formed along with FO in the reaction of F with ozone. As a continuation of our

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photoionization studies of halogen monoxides and related species [10,11], we present in this work the first determination of the ionization energy for FO($X\,^2\Pi_i$) to be obtained via direct photoionization threshold measurement.

2. Experimental

Experiments were performed by employing a discharge flow–photoionization mass spectrometer (DF-PIMS) apparatus coupled to beam line U-11 at the National Synchrotron Light Source (NSLS) [10-15] at Brookhaven National Laboratory. FO radicals were produced in a teflon lined flow reactor by the reaction sequence

$$F(^2P)+HNO_3 \rightarrow NO_3+HF\,,$$

$$k_1(298\ \mathrm{K})=2.3\times10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ [16], \qquad (1)$$

$$F(^2P)+NO_3 \rightarrow FO+NO_2\,,$$

$$k_2(298\ \mathrm{K})=3\times10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ [17]\,, \qquad (2)$$

with $[F]>[HNO_3]$. Fluorine atoms were produced by passing F_2 through a microwave discharge (<70 W, 2450 MHz) at the upstream end of the flow tube (about 100 cm from the nozzle). The HNO_3 vapor was introduced through the tip of the sliding injector at a distance of 15 cm from the sampling nozzle. The experiments were conducted at ambient temperature ($T=298\pm2$ K) and at a flow reactor pressure of about 4 Torr with helium carrier gas. With the tip of the injector at 15 cm from the nozzle and a flow velocity of 1400 cm s^{-1}, the reaction time was 10.7 ms. FO radicals were also generated (but less efficiently than by reactions (1) and (2)) by microwave discharge of a gas mixture of F_2 and O_2 in He.

The gaseous mixture in the flow reactor was sampled as a molecular beam into the sample chamber and subsequently into the photoionization source of the mass spectrometer. Ions were mass selected with an axially aligned quadrupole mass filter, detected with a channeltron/pulse pre-amp and thence counted for preset integration times. Measurements of photoionization efficiency (PIE) spectra, the ratio of ion counts/light intensity versus wavelength, were made using tunable vacuum-ultraviolet (VUV) radiation at the NSLS [15]. A monochromator with a normal incidence grating (1200 line/mm) was used to disperse the VUV light. Since all measurements in this work were carried out under windowless conditions, correction of the PIE spectra for second-order radiation was made by scanning the spectral range at one half the wavelength and one half the wavelength step-size. These short wavelength scans were normalized to reflect the intensity of second-order radiation on the regular scan and subtracted from the raw data. The intensity of the VUV light was monitored via a sodium salicylate coated window with attached photomultiplier tube. The monochromator slit width was varied between 380 and 750 μm to give a spectral bandwidth (fwhm) of 0.12 to 0.23 nm.

The helium (MG Industries, 99.9999%) and fluorine in helium mixture (Cryogenic Rare Gas, 5% v/v F_2 in He, F_2 is 99.9%) were used directly from cylinders. The oxygen (MG Industries, 99.999%) in helium mixture ($\approx5\%$ v/v) was made up in the gas handling system. Mixtures of sulfuric acid and nitric acid (2:1, Mallinckrodt, Analytical Reagent grade, $\geqslant90\%$) were thoroughly outgassed at ice-water temperature (≈0°C). Samples of HNO_3 vapor were taken from above the outgassed acid solutions at $T=15$–20°C (vapor pressure ≈16 Torr) and thence diluted (to about 2% v/v) with helium. The HNO_3 samples typically showed low levels of NO_2 ($\approx5\times10^{-3}\%$).

3. Results and discussion

As an example of the PIMS experiment, the PIE spectrum of O_2 was measured over the wavelength range of 90.0 to 106.0 nm, as shown in Fig. 1. The onset at 102.6_5 nm corresponds to $IE(O_2)=12.07_8$ eV, in good agreement with the recommended value of 12.071 ± 0.001 eV [18]. This level of agreement indicates that: (1) the wavelength calibration, established by the location of zeroth-order, is reliable, and (2) considerable rotational cooling is achieved in the nozzle expansion [15] and therefore the threshold is not perturbed by thermal effects within the experimental uncertainty (±0.02 eV).

PIE spectra for FO at $m/z=35$ are shown in Fig. 2 in the wavelength region of 80.0–100.0 nm at 0.1 nm

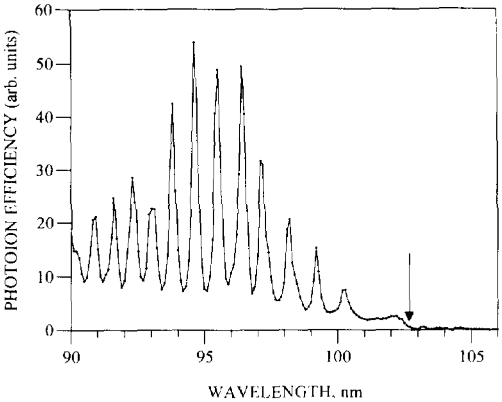

Fig. 1. Photoionization efficiency spectrum of O_2 between $\lambda=90.0$ and 106.0 nm at a nominal resolution of 0.14 and 0.1 nm steps. The photoion efficiency is ion counts at $m/z=32$ divided by the light intensity in arbitrary units. The onset of ionization is at $\lambda=102.6_5$ nm (IE $=12.07_8\pm0.01_6$ eV). $[O_2]=1.46\times10^{15}$ molecule cm^{-3}.

intervals. The spectra should be free of perturbations caused by vibrational hot bands because collisional deactivation is expected to occur rapidly [13]. The background signals in Fig. 2 were vanishingly small since there was no other FO^+ precursor than the FO radical at $m/z=35$. Spectrum (a) was obtained by producing FO via reactions (1) and (2). As with the PIMS spectrum of BrO [11], there is much structure in the PIE curve for FO. Structure in photoionization efficiency curves can arise both from direct transition to the ion and from autoionization of Rydberg states of the neutral with ion excited states as their limit. The ionic states contributing to the structure are X $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$, which have 2π character, and $^1\Sigma^-$, $^3\Sigma^-$, $^3\Delta$, $^3\Sigma^+$, $^1\Delta$ and $^1\Sigma^+$, which have 1π character and were calculated to be of similar energy [9]. There is also the possibility, at higher energies, of having a contribution from high-lying 5σ states such as $^3\Pi$ and $^1\Pi$ [9]. For comparison, spectrum (b) shows the PIE for FO that was generated by discharging an F_2/O_2 mixture. The poor signal in (b), relative to (a), may be due to recombination of FO+FO [19] since the FO radicals produced this way must traverse a distance of ≈ 100 cm.

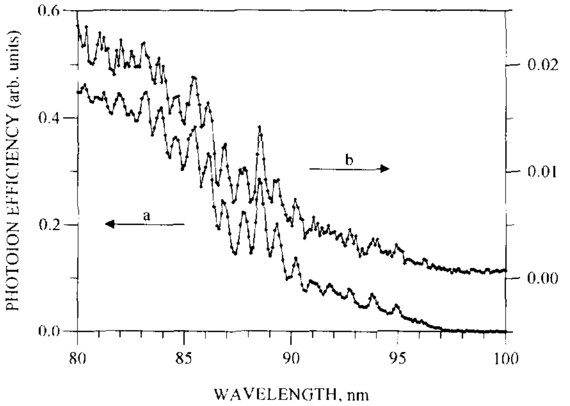

Fig. 2. Photoionization efficiency spectra of FO at a nominal resolution of 0.23 and 0.1 nm steps between $\lambda=80.0$ and 100.0 nm. The photoion efficiency is the ion counts at $m/z=35$ divided by the light intensity in arbitrary units. The FO radical was produced in panel (a) by the sequence of reactions (1) and (2) with $[F_2]_0=1.85\times10^{13}$ molecule cm^{-3} and $[HNO_3]_0=3.48\times10^{12}$ molecule cm^{-3}; and in panel (b) by discharging an $F_2/O_2/He$ mixture with $[F_2]_0=1.13\times10^{13}$ molecule cm^{-3} and $[O_2]_0\approx 3\times10^{10}$ molecule cm^{-3}.

The extensive structure in the PIE spectrum near threshold, $90\leqslant\lambda\leqslant96$ nm (Fig. 2), is due to the vibrational progression in the cation with superimposed autoionization. Such vibrational autoionization is known, for example, in the case of NO [20], to be caused by high Rydberg states that converge to an excited state of the cation. However, the intensity of the peaks seen here, for FO, is much larger than that reported for NO; and with such strong autoionization features, it is not possible to determine the vibrational spacing from the present PIE spectrum. The PES spectrum of FO, reported by Dyke et al. [9], however, was apparently not perturbed by autoionization (nor would it have been expected to be [21]), and so their determination of the vibrational spacing (1300 cm^{-1}) remains the only measured value.

In order to determine IE(FO), a detailed examination near the threshold was carried out. The PIE spectrum is plotted in Fig. 3 over the range 94.0–100.0 nm at 0.1 nm intervals with a nominal resolution of 0.14 nm. The statistics were enhanced by accumulating multiple wavelength scans to improve the signal-to-background ratio. The IE values for FO were determined from the half-rise point at the threshold, as indicated in Fig. 3. Results from repeated measurements, listed in Table 1, are in excellent agreement and lead to an average value of 12.78 ± 0.03 eV for the adiabatic ionization energy of FO. The quoted uncertainty is taken as the lowest experimental resolution (0.23 nm) which is more than twice the stan-

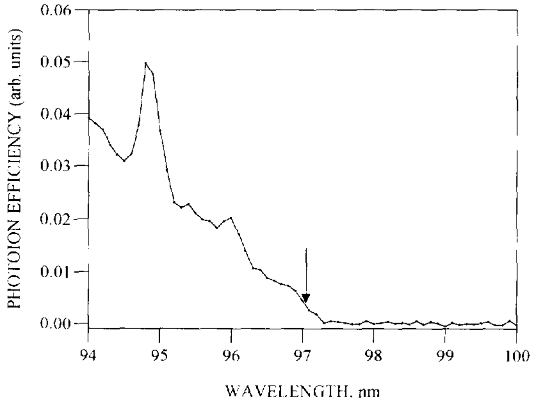

Fig. 3. Photoionization threshold region of FO at a nominal resolution of 0.14 and 0.1 nm steps between $\lambda=94.0$ and 100.0 nm. The photoion efficiency is ion counts at $m/z=35$ divided by the light intensity in arbitrary units. The onset of ionization is at $\lambda=97.05$ nm (12.78 ± 0.02 eV). $[F_2]_0=2.54\times10^{13}$ molecule cm^{-3} and $[HNO_3]_0=8.54\times10^{12}$ molecule cm^{-3}.

Table 1
Wavelength thresholds and ionization energies for FO

Nominal λ resolution [a] (nm)	Threshold [b] (nm)	IE [c] (eV)
0.14	97.05	12.78 ± 0.02
0.12	96.95	12.79 ± 0.02
0.14	96.95	12.79 ± 0.02
0.14	96.90	12.80 ± 0.02
0.14	97.00	12.78 ± 0.02
0.23	97.10	12.77 ± 0.03
0.23	97.05	12.78 ± 0.03
0.23	97.20	12.76 ± 0.03
0.23	96.95	12.79 ± 0.03
0.23	97.15	12.76 ± 0.03

[a] fwhm, see Section 2.

[b] Determined from half-rise point at the threshold for ionization, see text.

[c] Ionization energy; uncertainties are equal to the (±) resolution; average value is 12.78_0 eV with a standard deviation of $\pm0.01_3$ eV.

dard deviation ($\pm0.01_3$ eV) of the 10 independent determinations.

The present result for IE(FO) is compared to those of previous studies in Table 2. The appearance energy measurements of Dibeler et al. [4] and Malone and McGee [6] were reevaluated by O'Hare and Wahl [7] who also estimated a value for IE(FO) from self-consistent field calculations. The measurement of Dibeler et al. [4] was rejected by O'Hare and Wahl [7] and later also by Berkowitz et al. [8] but neither provided an explanation for the discrepancy. However, if the F_2O sample of Dibeler et al. had partially decomposed to F_2 and O_2 [22], an appearance energy for FO^+ near their value of 15.8 eV might be rationalized by ion pair formation ($F^+ + F^-$) from F_2 followed by the exothermic reaction of F^+ with O_2 ($\rightarrow FO^+ + O$). The appearance energy measurement of Berkowitz et al. [8] was combined, by those authors, with the energy difference between IE(FO) and AE(FO^+, F_2O) reported by Clyne and Watson [1] to derive the value IE(FO) = 12.79 ± 0.10 eV. The appearance energy measurement of Alekseev et al. [5], via electron impact-mass spectrometry, essentially corroborated the PIMS result of Berkowitz et al. [8]. In the PES study of Dyke et al. [9], which is the only direct measurement of IE(FO) in the literature to date, FO radicals were produced by the reaction $F+O_3\rightarrow FO+O_2$. The adiabatic ionization threshold in the PE spectrum was obscured by the presence of O_2^+ bands although the next two vibrational members were more clearly seen. After subtraction of the interfering bands, about 80% in the case of the ionization threshold, Dyke et al. were able to derive from the FO vibrational series, ascribed to the electronic transition $FO^+(X\,^3\Sigma^-)\leftarrow FO(X\,^2\Pi_i)$, an adiabatic ionization threshold value of 12.77 ± 0.01 eV. The IE(FO) value obtained in this work, 12.78 ± 0.03 eV, is therefore in good agreement with the results of two previous investigations, and the measurement has the advantage of being both direct and free from interferences (as a result of separation of FO^+ by mass selection) from precursors and other products.

Finally, we compute the heat of formation and the proton affinity of FO at 298 K. First, $\Delta_f H^0_{298}(FO^+)$ is determined according to Traeger and McLaughlin [23] [1],

$$\begin{aligned} AE(FO^+, F_2O) = {} & \Delta_f H^0_{298}(FO^+) \\ & + \Delta_f H^0_{298}(F) - \Delta_f H^0_{298}(F_2O) \\ & - (H^0_{298}-H^0_0)_{FO^+} - (H^0_{298}-H^0_0)_F + \Delta H^* \,, \end{aligned} \quad (3)$$

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[1] Thermodynamic values were taken from Ref. [18], unless otherwise specified.

Table 2
Comparison of values for IE(FO)

IE(FO) (eV)	Method	Ref.
13.0	AE (FO^+, F_2O) [a], electron impact-MS [b]	[4,5]
14.1	re-evaluated from Ref. [4,5]	[7]
13.1 ± 0.3	re-calculated from Ref. [6]	[7]
13.1 ± 0.5	calculation	[7]
12.79 ± 0.10	AE (FO^+, F_2O) [a], PIMS	[8]
12.77 ± 0.01	PES	[9]
12.78 ± 0.03	PIMS	this work

[a] Appearance energy measurement, FO^+ from dissociative ionization of F_2O.
[b] Mass spectrometry.

where $\mathrm{AE}(FO^+, F_2O) = 14.389$ eV [6], $(H^0_{298} - H^0_0)$ are the integrated heat capacities [24] [2] and ΔH^* is taken as $\frac{5}{2}RT$. Thus, $\Delta_f H^0_{298}(FO^+) = 1343.1$ kJ mol^{-1}, with an estimated uncertainty of ± 5.5 kJ mol^{-1}. Next, from Eqs. (4) and (5),

$$\Delta H_{\mathrm{I}}(\mathrm{FO}) = \mathrm{IE}(\mathrm{FO}) + (H^0_{298} - H^0_0)_{\mathrm{FO}^+} - (H^0_{298} - H^0_0)_{\mathrm{FO}}\,, \quad (4)$$

$$\Delta_f H^0_{298}(\mathrm{FO}) = \Delta_f H^0_{298}(\mathrm{FO}^+) - \Delta H_{\mathrm{I}}(\mathrm{FO})\,, \quad (5)$$

we compute $\Delta_f H^0_{298}(FO) = 109.5$ kJ mol^{-1} with an estimated uncertainty of ± 8.0 kJ mol^{-1}, in good agreement with the value of 108.8 kJ mol^{-1} given in Refs. [18,24]. Last, the $\Delta_f H^0_{298}$ values given here and in Ref. [18] may be employed in

$$\mathrm{PA}(\mathrm{FO}) = \Delta_f H^0_{298}(\mathrm{FO}) + \Delta_f H^0_{298}(\mathrm{H}^+) - \Delta_f H^0_{298}(\mathrm{HOF}^+)\,, \quad (6)$$

to obtain a value for PA(FO) of 511.5 kJ mol^{-1} with an estimated uncertainty of ± 10.0 kJ mol^{-1}. There is no literature value with which to compare this result.

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[2] The value for $(H^0_{298} - H^0_0)_{FO^+}$ was estimated to be 9.3 kJ mol^{-1} by assuming the same difference between the integrated heat capacities for FO^+ and FO as that between FP^+ and FP.

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