

Photoionization mass spectrometric study of CH₃OF

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The vacuum ultraviolet photoionization mass spectrum of CH₃OF displays a prominent parent ion peak, whose adiabatic onset is 11.340 ± 0.008 eV, although much lower energy fragmentation processes (CH₂O⁺ + HF, 8.0 eV; CH₂OH⁺ + F, 9.3 eV) are possible. These lower energy processes have very low intensity. Two higher energy processes, to CH₃⁺ + OF and CH₂O⁺ + H + F, are observed. Their thresholds are used to determine ΔH_{f0}^0 (CH₃OF) > -23.0 ± 0.7 kcal/mol, or D_0 (CH₃O-F) < 47.4 ± 1.2 kcal/mol. CH₂OF⁺ is a significant fragment, whose appearance energy leads to ΔH_{f0}^0 (CH₂OF⁺) $\approx 215.1 \pm 0.8$ kcal/mol.

I. INTRODUCTION

Methyl hypofluorite, CH₃OF, has recently been synthesized.¹ Its electron impact mass spectrum (70 eV) displays a prominent parent peak, as well as prominent fragments at M15 (CH₃⁺) and M29 (HCO⁺). From a correlation of ¹⁹F nuclear magnetic resonance (NMR) shifts in hypofluorites with O-F bond energies, it has been estimated¹ that the O-F bond energy in CH₃OF is 48–49 kcal/mol, only slightly smaller than that in HOF.² (The dissociation energy of diatomic OF is 51.4 kcal/mol.³) Upon reflection, the existence of a prominent parent ion is somewhat puzzling.

If we take⁴ ΔH_{f0}^0 (CH₃O) = 5.9 ± 1.0 kcal/mol and ΔH_{f0}^0 (F) = 18.47 ± 0.07 kcal/mol,⁵ and assume an O-F bond energy of 48.5 kcal/mol, then ΔH_{f0}^0 (CH₃OF) = -24.1 kcal/mol. Thus CH₃OF is stable with respect to decomposition into the elements in their standard states, but highly unstable⁶ (by ~ 66 kcal) with respect to decomposition into CH₂O + HF. The ionization potential of CH₃OF is not likely to be less than that of CH₃OH (~ 10.85 eV).⁵ However, the thermochemical threshold for formation of CH₂O⁺ + HF is only 8.01 eV, and that for formation of CH₂OH⁺ + F, 9.30 eV [based on ΔH_{f0}^0 (CH₃OF) ~ -24 kcal/mol]. Even the two-step process leading to HCO⁺ + H + HF should have an onset at 9.01 eV. Since the estimated appearance potentials of at least two primary fragment channels are significantly lower than the estimated ionization potential, it is surprising that one observes a prominent parent ion peak.

The photoionization mass spectrometric method offers a means of determining the ionization potential of CH₃OF, as well as setting limits on ΔH_{f0}^0 (CH₃OF). In addition, the various channels for fragmentation could be explored, in order to better understand the dynamics of the unimolecular decomposition of CH₃OF⁺.

II. EXPERIMENTAL ARRANGEMENT

The instrumental setup consisting of a 3 m vuv monochromator, an ionization region, a quadrupole mass filter, and ion and light detectors has been described previously.⁷

The wavelength resolution was kept at 0.84 FWHM throughout all experiments. In the wavelength region where the many-line H₂ lamp was employed (~ 950 Å and longer), measurements were confined to light peaks.

Methyl hypofluorite was prepared by the reaction of elemental fluorine (10% in Ar + N₂) with a 50% solution of methanol in propionitrile at -78 °C.¹ The reaction mixture was warmed to -45 °C, and the methyl hypofluorite was transferred in a stream of N₂ to a Kel-F U tube cooled with liquid N₂. The N₂ was subsequently removed in high vacuum. The sample was admitted into the ionization cell from the Kel-F U tube, which was immersed in a constant temperature slush bath (methylcyclohexane, -127 °C). In order to keep the decomposition into HF and CH₂O to a minimum, all connections were made using stainless steel, Teflon, and Kel-F. *One ~ 200 mg sample of CH₃OF exploded violently in the slush bath, destroying both the U tube and the Dewar containing the bath, and underscoring the inherent instability of the compound. Adequate safety precautions must be employed when working with methyl hypofluorite, including the use of face shield and gloves, and quantities should be limited to the smallest amounts needed for the particular experiment.*

III. EXPERIMENTAL RESULTS

Figure 1 displays the photoion yield curve of CH₃OF⁺, and on the same scale, the various fragment ion yield curves. The parent ion is indeed prominent. Onset of CH₃OF⁺ is rather abrupt; the adiabatic ionization potential is determined to be 1093.3 ± 0.7 Å $\equiv 11.340 \pm 0.008$ eV, the vertical ionization potential (mid-rise) about 1076 Å $\equiv 11.52$ eV. There is a hint of step structure, with a step width of $\sim 950 \pm 100$ cm⁻¹. The ion yield remains roughly constant between ~ 1050 and 850 Å, gradually declining toward higher energy.

The postulated low energy fragment ions CH₂O⁺ (M30) and CH₂OH⁺ (M31) are very weak. CH₂OH⁺ is estimated to be ≤ 0.03 of CH₃OF⁺ at all wavelengths. The measured ion intensities at M31 are mostly attributable to an impurity of methanol (used in preparing the sample). Below

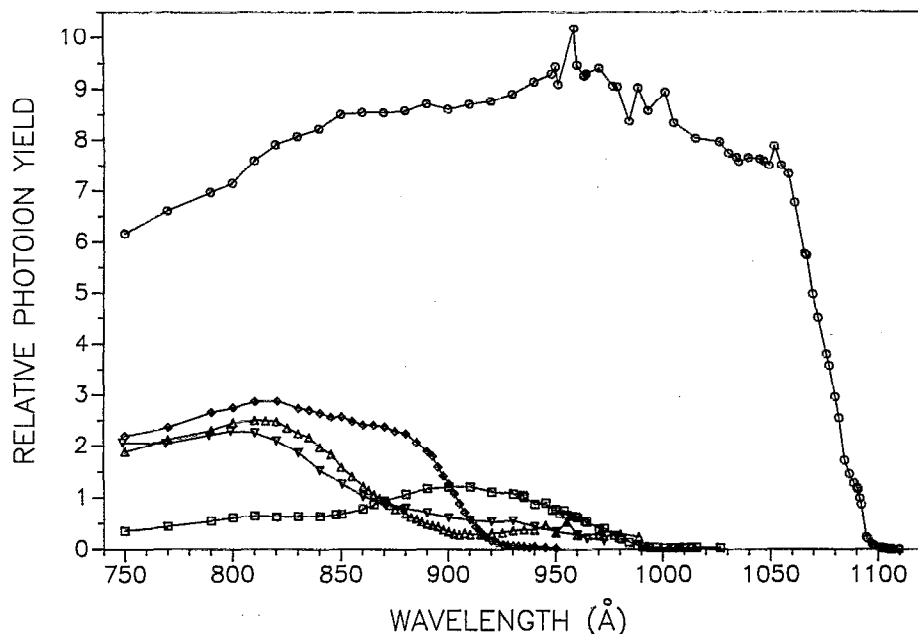


FIG. 1. Photoion yield curves of species observed in the photoionization of CH_3OF . The relative intensities are faithfully reproduced in the figure. \circ M50, CH_3OF^+ ; \square M49, CH_2OF^+ ; \triangle M30, CH_2O^+ ; ∇ M29, HCO^+ ; \diamond M15, CH_3^+ .

13.75 eV ($> 902 \text{ \AA}$), M30 (CH_2O^+) is mostly from formaldehyde, a decomposition product of CH_3OF . At about 10.2 eV ($\sim 1220 \text{ \AA}$), there may be very small tails of CH_2O^+ and CH_2OH^+ , perhaps due to CH_3OF , but both are ~ 0.001 of the parent ion at $\sim 11.5 \text{ eV}$.

Peaks characteristic of CH_2O^+ (CH_2O)⁸ can be discerned at ~ 945 and 955 \AA . However, at $\sim 820 \text{ \AA} \equiv 15.1 \text{ eV}$, the CH_2O^+ intensity has grown beyond that attributable to formaldehyde, and attains an intensity about 1/3 that of the parent ion. The onset of this marked growth occurs at $902 \pm 2 \text{ \AA} \equiv 13.75 \pm 0.03 \text{ eV}$ (see Fig. 2). Similarly, about half of the M29 intensity at $\sim 930 \text{ \AA}$ can be attributed to

HCO^+ from the formaldehyde impurity,⁸ but at shorter wavelength the curve does not track HCO^+ (CH_2O). Between 970 and 930 \AA , there is an almost linear increase in the ion yield, followed by a plateau (930–910 \AA) and then a more rapid and markedly curved ascent without a distinct onset to a maximum at ~ 810 – 800 \AA . No thermochemically significant threshold can be gleaned from this photoion yield curve, at least partly because it is a superposition of HCO^+ (CH_2O) and HCO^+ (CH_3OF), and perhaps also HCO^+ (CH_3OH).

Besides CH_3OF^+ , the major ions devoid of significant impurity contributions are M15 (CH_3^+) and M49

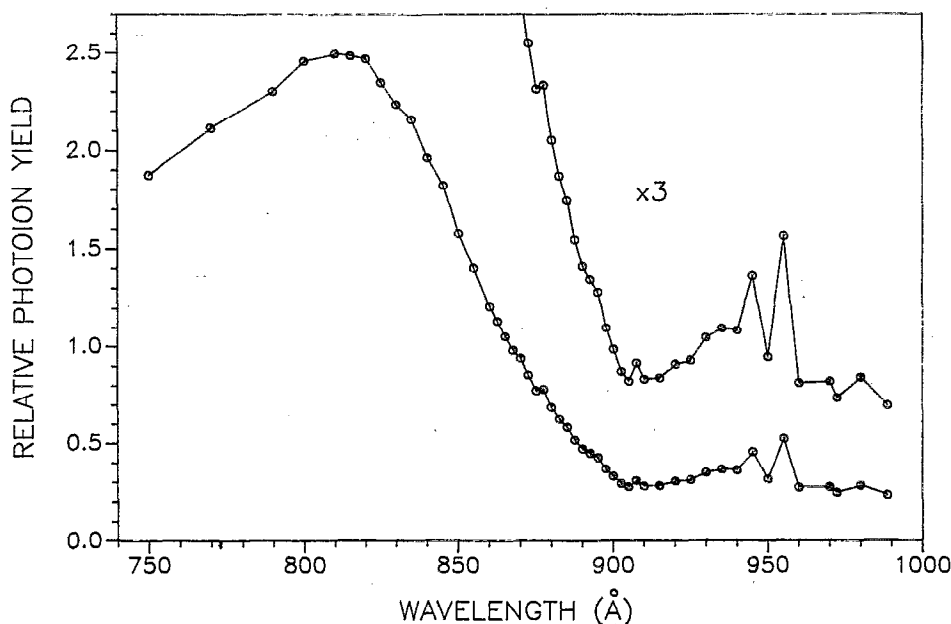


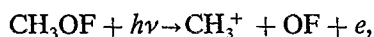
FIG. 2. Photoion yield curve of CH_2O^+ (CH_3OF). The region above $\sim 910 \text{ \AA}$ is attributable to CH_2O^+ (CH_2O).

(CH₂OF⁺). The methyl cation attains an intensity about 1/3 that of the parent ion at $\sim 820 \text{ \AA} \equiv 15.1 \text{ eV}$. The extrapolated onset for this ion (see Fig. 3) is $920.5 \pm 1 \text{ \AA} \equiv 13.469 \pm 0.015 \text{ eV}$. The CH₂OF⁺ fragment ion increases to ~ 0.15 of the parent-ion intensity at $\sim 910 \text{ \AA} \equiv 13.6 \text{ eV}$. Its extrapolated threshold (see Fig. 4) is $992.5 \pm 1.0 \text{ \AA} \equiv 12.492 \pm 0.013 \text{ eV}$.

Each of the fragment-ion thresholds should be increased by the internal energy of CH₃OF at 298 K to convert them to an equivalent 0 K threshold.⁹ The internal energy of CH₃OF at 298 K is calculated to be 0.070 eV, using *ab initio* calculated¹⁰ vibrational frequencies, reduced by 10%.

IV. INTERPRETATION OF RESULTS

From 0 K appearance potential ($\leq 13.539 \pm 0.015 \text{ eV}$) for the reaction



$\Delta H_{f0}^0(\text{CH}_3) = 35.78 \pm 0.12 \text{ kcal/mol}$,⁵ I.P.(CH₃) = $9.843_4 \pm 0.000_6 \text{ eV}$ ¹¹ and $\Delta H_{f0}^0(\text{OF}) = 26.1 \pm 2.3 \text{ kcal/mol}$,¹² we can deduce that $\Delta H_{f0}^0(\text{CH}_3\text{OF}) > -23.3 \pm 2.3 \text{ kcal/mol}$. Hence it is slightly less stable than our initial estimate. With this support, we can examine the significance of the marked growth in CH₂O⁺, commencing at $902 \text{ \AA} (13.82 \pm 0.03 \text{ eV at 0 K})$. If the products were CH₂O⁺ + HF, the predicted onset would be about 5.8 eV lower. The dissociation would presumably proceed through a tight, four-center transition state. Under those circumstances, it is very unlikely that the dissociation probability would suddenly start increasing 5.8 eV above threshold, which would imply that some excited state is being formed with much greater probability than the ground state. A more plausible explanation is that the products are CH₂O⁺ + H + F, which would not involve a

tight transition state and would correspond to about the predicted threshold for this process. These products could be formed sequentially, i.e., $\text{CH}_3\text{OF}^+ \rightarrow \text{CH}_2\text{OF}^+ + \text{H} \rightarrow \text{CH}_2\text{O}^+ + \text{F} + \text{H}$ (see below). By combining the 0 K threshold for CH₂O⁺ with $\Delta H_{f0}^0(\text{CH}_2\text{O}^+) = 225.58 \pm 0.13 \text{ kcal/mol}$,^{5,8} $\Delta H_{f0}^0(\text{H}) = 51.634 \text{ kcal/mol}$ ⁵ and $\Delta H_{f0}^0(\text{F}) = 18.47 \pm 0.07 \text{ kcal/mol}$,⁵ we obtain

$$\Delta H_{f0}^0(\text{CH}_3\text{OF}) > -23.0 \pm 0.7 \text{ kcal/mol}.$$

Hence this interpretation for the threshold of CH₂O⁺ is almost certainly the correct one, and reduces the stability of CH₃OF slightly. From the threshold for M49 (CH₂OF⁺), we can now estimate

$$\Delta H_{f0}^0(\text{CH}_2\text{OF}^+) \approx 215.1 \pm 0.8 \text{ kcal/mol}.$$

We are unaware of any previous value for this quantity.

V. DISCUSSION

A. Energetics

From the limiting values for $\Delta H_{f0}^0(\text{CH}_3\text{OF})$ deduced in Sec. IV, we can infer limiting values for the O-F bond energy in this molecule. Thus, from the CH₃⁺ threshold, we obtain $D_0(\text{CH}_3\text{O-F}) \leq 47.7 \pm 2.5 \text{ kcal/mol}$; from the CH₂O⁺ threshold, $D_0(\text{CH}_3\text{O-F}) \leq 47.4 \pm 1.2 \text{ kcal/mol}$. The latter is the more defining value, since its upper limit is lower, and it has a smaller uncertainty, although the two results agree within experimental errors.

It will be recalled that the ¹⁹F NMR shifts, when correlated with bond energies of other hypofluorites, implied a bond energy for CH₃O-F about 1-3 kcal/mol less than $D_0(\text{HO-F})$. A reassessment of the latter quantity¹³ leads to D_0

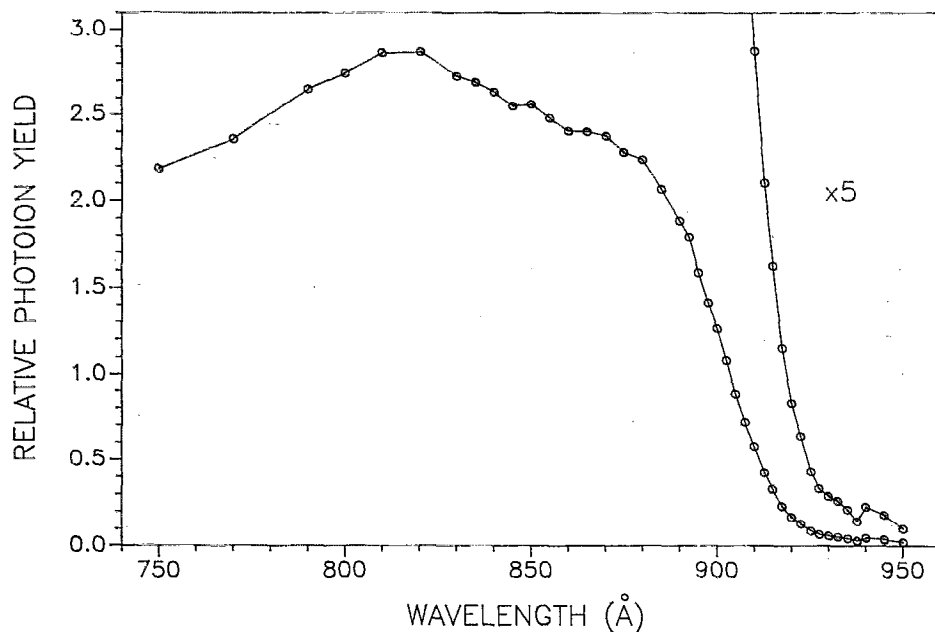


FIG. 3. Photoion yield curve of CH₃⁺ (CH₃OF).

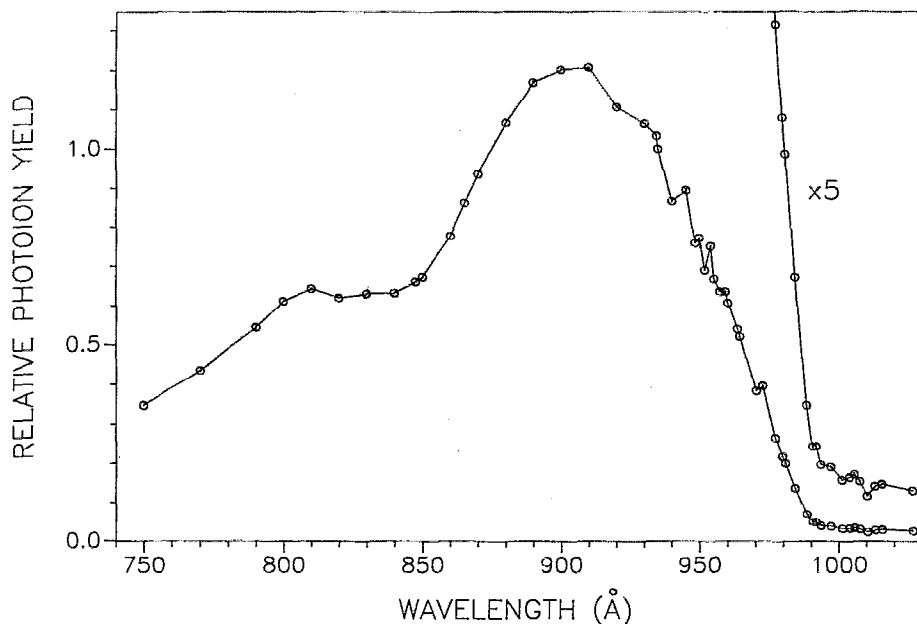


FIG. 4. Photoion yield curve of CH₂OF⁺ (CH₃OF).

(HO-F) \leq 47.7 kcal/mol. Hence the more limiting photoionization values agrees in direction, though not in magnitude, with the inference from the NMR shifts.

B. Structure

Curtiss and Pople¹⁰ have calculated the geometric structures of CH₃OF and CH₃OF⁺. Both have C_s symmetry, with similar C-H and C-O distances. The major difference is a diminution in O-F distance from 1.451 Å in the neutral species to 1.313 Å in the cation. There is also a slight increase in the C-O-F angle, from 103° to 110°. Hence one can anticipate a Franck-Condon progression in the O-F stretching frequency upon photoionization. The calculated¹⁰ frequency is 1092.9 cm⁻¹, ~984 cm⁻¹ upon reduction by 10%. This agrees very well with the weak step structure observed (Sec. III), having an average spacing of 950 ± 100 cm⁻¹.

C. Dynamics

In Sec. I, it was anticipated that the appearance potentials for CH₂O⁺ (+ HF) and CH₂OH⁺ (+ F) would be much smaller than the ionization potential of CH₃OF. Our experiments have verified these views, and even increased the gaps. Thus I.P. (CH₃OF) = 11.340 ± 0.008 eV, and the appearance potentials calculated [based on our limiting value for ΔH_f^0 (CH₃OF)] are: CH₂O⁺, \leq 7.95 eV; CH₂OH⁺, \leq 9.25 eV. There are a number of cases known (CF₄ is perhaps the simplest¹⁴) in which no parent ion is observed, and the first fragment ion occurs at the ionization potential. The present case is unusual¹⁵ because the predicted onset of fragment ions occurs well below the ionization potential, but the metastable parent ion is, nevertheless, very prominent in the mass spectrum. Clearly, there must be a substantial activation barrier to this highly exoergic decomposition.

The photoion yield curve of CH₃OF⁺ (CH₃OF) indicates that CH₃OF⁺ is formed primarily near the local mini-

mum of the cation's potential energy surface. Once the cation is formed, its decomposition is inhibited, presumably by the aforementioned activation barrier. At energies below the ionization potential, Rydberg states may be formed with approximately the same molecular structure as CH₃OF⁺. In principle, these states could autoionize onto a portion of the CH₃OF⁺ surface closer to the region where decomposition occurs. If the process is electronic autoionization, Franck-Condon factors also enter here and substantially reduce the transition probability. Hence these Rydberg states would likely be predissociated, or reradiate, more rapidly than they could autoionize. The formation of CH₂OH⁺ + F can be described in similar terms.

The formation of CH₃⁺ (+ OF) may be a direct dissociation (as inferred⁶ in the corresponding CH₃⁺ formation from CH₃OH), or it may be rationalized by quasiequilibrium theory. Further work is required here. The formation of CH₂O⁺ (+ H + F) is very likely a stepwise process, rather than a three-body decomposition. The CH₂OF⁺ ion is initially observed at 12.49 eV; this ion probably decomposes further to CH₂O⁺ + F at 13.73 eV. Observation of a metastable ion at *M* = 18.37 amu would be revealing in this case.

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¹M. Kol. S. Rozen, and E. Appelman, *J. Am. Chem. Soc.* **113**, 2648 (1991).

²J. Berkowitz, E. H. Appelman, and W. A. Chupka, *J. Chem. Phys.* **58**, 1950 (1973).

³K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

⁴The value of ΔH_f^0 (CH₃O) currently favored is based on pyrolysis studies by Batt and co-workers. From the temperature dependence of the reaction CH₃ONO → CH₃O + NO, L. Batt and R. T. Milne [*Int. J. Chem. Kinet.*

6, 945 (1974)] obtained $\Delta H_{298} = 41.8 \pm 0.9$ kcal/mol, from which we compute $\Delta H_{f298}^{\circ}(\text{CH}_3\text{O}) = 4.0 \pm 1.0$ kcal/mol. Similarly, L. Batt and R. D. McCulloch [Int. J. Chem. Kinet. 8, 491 (1976)] obtained 37.6 ± 0.2 kcal/mol at 298 K for the enthalpy of decomposition of CH_3OOCH_3 into 2 CH_3O , from which we compute $\Delta H_{f298}^{\circ}(\text{CH}_3\text{O}) = 3.8 \pm 0.2$ kcal/mol. Taking the average of these values, and retaining the larger error limit, we arrive at $\Delta H_{f0}^{\circ}(\text{CH}_3\text{O}) = 5.9 \pm 1.0$ kcal/mol.

⁵V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veitz, V. A. Medvedev, G. A. Khachkuruzov, and V. S. Yungman, *Termodinamicheskie Svoistva Individual'nykh Veshchestv*, (Nauka, Moscow, 1978).

⁶J. Berkowitz, J. Chem. Phys. 69, 3044 (1978).

⁷S. T. Gibson, J. P. Greene, and J. Berkowitz, J. Chem. Phys. 83, 4319 (1985).

⁸P. M. Guyon, W. A. Chupka, and J. Berkowitz, J. Chem. Phys. 64, 1419 (1976).

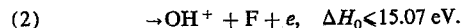
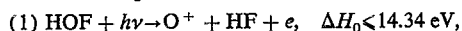
⁹P. M. Guyon and J. Berkowitz, J. Chem. Phys. 54, 1814 (1971).

¹⁰L. A. Curtiss and J. A. Pople, J. Chem. Phys. (submitted).

¹¹G. Herzberg, Proc. R. Soc. London, Ser. A 292, 291 (1961).

¹²J. Berkowitz, P. M. Dehmer, and W. A. Chupka, J. Chem. Phys. 59, 925 (1973).

¹³Berkowitz, Appelman, and Chupka (Ref. 2) measured two appearance potentials in the photoionization of HOF. These were



Both of these thresholds are upper limits. At the time these results were published, the I. P. of OH was not well established, and hence the first process (which was also the lowest energy process) had more credence. However, the photoion yield curve approached the threshold gradually, a behavior which could be attributed to the rearrangement required to produce $\text{O}^+ + \text{HF}$, and perhaps also to a Franck-Condon gap in this region of ionization of HOF. By contrast, the OH^+ fragment increased quasilinearly from threshold. With current values for $\Delta H_{f0}^{\circ}(\text{O}^+)$ and $\Delta H_{f0}^{\circ}(\text{HF})$, the onset for the first process yields $\Delta H_{f0}^{\circ}(\text{HOF}) > -23.0$ kcal/mol; since $\Delta H_{f0}^{\circ}(\text{OH}^+)$ is now well established, as well as $\Delta H_{f0}^{\circ}(\text{F})$, the threshold for process (2) yields $\Delta H_{f0}^{\circ}(\text{HOF}) > -20.0$ kcal/mol. Clearly, the limit from this second process is more stringent and significant than the first. Also, the threshold for process (2), together with the ionization potential of OH, yields directly an upper limit to the O-F bond energy in HOF of < 47.7 kcal/mol. This value is in good agreement with a recent *ab initio* calculation by Pople and Curtiss (Ref. 10) at the G1 level, which gives $D_0(\text{HO-F}) = 48.4$ kcal/mol.

¹⁴T. A. Walter, C. Lifshitz, W. A. Chupka, and J. Berkowitz, J. Chem. Phys. 51, 3531 (1969).

¹⁵We have encountered one additional case recently. The ionization potential of CH_3O is 10.72 eV, but $\text{HCO}^+ + \text{H}_2$ should occur at 8.3 eV, and is weak. B. Ruscic and J. Berkowitz, J. Chem. Phys. (accepted).