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Author

Ng, C.Y.

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C. Y. Ng, D. J. Trevor, P. W. Tiedemann, S. T. Ceyer,
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PHOTOIONIZATION OF DIMERIC POLYATOMIC MOLECULES: PROTON AFFINITIES OF H_2O AND HF

C. Y. Ng,* D. J. Trevor, P. W. Tiedemann, S. T. Ceyer

P. L. Kronebusch, B. H. Mahan and Y. T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California 94720

JUNE 1977

ABSTRACT

Photoionization studies of $(H_2O)_2$ and $(HF)_2$ producing H_3O^+ and H_2F^+ yield 7.18 ± 0.08 eV (165.8 ± 1.8 kcal/mole) and 4.09 ± 0.06 eV (94.3 ± 1.4 kcal/mole) as the proton affinities of H_2O and HF, respectively. The measured ionization potential of $(H_2O)_2$, 11.21 ± 0.09 eV, along with the known ionization potential of H_2O, 12.615 ± 0.001 eV, allow the deduction of a lower bound for the dissociation energy of $(H_2O)_2^+$: 1.58 ± 0.13 eV (36 ± 3 kcal/mole). The experiments have demonstrated that photoionization of dimers is one of the most useful general methods for the determination of proton affinities.

*Present address: Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50011

INTRODUCTION

Proton transfer represents one of the fastest and most important classes of reactions in both the gas and condensed phases. When proton transfer between two molecules is exothermic, it is usually the dominant reaction. The equilibrium $M_1H^+ + M_2 \rightleftharpoons M_1 + M_2H^+$ will be displaced to the side of the molecule with the higher proton affinity. Relative values of proton affinities can easily be obtained by measurements of $[M_1H^+]/[M_2H^+]$, and $[M_1]/[M_2]$ when the system is at equilibrium in the ion source of a mass spectrometer. This will give the equilibrium constant and therefore $\Delta G°$ of the reaction. Since $\Delta S°$ for the proton transfer reaction is usually very small, the relative proton affinity or the enthalpy change for transfer of a proton from one entity to another can be derived.[1] However, in order to translate these measurements into absolute proton affinities, there is a need for accurate absolute proton affinities of a few reference compounds. Usually absolute values of proton affinities are obtainable by appearance potential measurements of MH^+ in a mass spectrometer, low energy ion-neutral scattering cross section measurements, collision induced dissociation, crystal lattice energy determinations, and NMR experiments.

The fine control of photon energy makes the photoionization mass spectrometric method one of the most accurate means for the determination of the proton affinity of M from the appearance potential measurement of MH^+ from a suitable parent molecule. Nevertheless, the major drawbacks of photoionization techniques in finding the proton affinity of a molecule is the low fluxes of monochromatic vacuum ultraviolet photons available from laboratory discharge light sources and the possible lack of suitable parent molecules to produce MH^+. Recent developments in molecular beam photoionization mass spectrometry,[2] involving careful optimization of relatively high intensity light sources, a sensitive mass spectrometer, and an intense molecular beam production system have allowed the photoionization study of dimers[3,4] synthesized in supersonic expansions. Polyatomic dimers are actually excellent parent molecules for the photoionization production of those MH^+ which cannot be obtained from other stable molecules.

In this report we present the photoionization studies of $(H_2O)_2$ and $(HF)_2$ as examples to illustrate a new general and sensitive method for the determination of proton affinities of many hydrogen containing molecules.

EXPERIMENTAL

The apparatus and procedures were essentially the same as previously described.[2-4] Depending on the spectral region either the helium Hopfield continuum or the hydrogen many-line pseudocontinuum was used. The spectrometer grating was MgF_2 or gold coated, ruled with 1200 lines/mm, having a reciprocal dispersion of 8.3 Å/mm. The H_2O molecular beam was produced by seeding water vapor at 89°C in 150 torr of Ar and then expanding through a 0.15 mm diameter Pyrex nozzle. The HF (99.9% minimum purity) was obtained from Matheson and used without further purification. A monel nozzle, 0.127 mm in diameter, was used. The nozzle stagnation pressure, ~400 torr as measured by an MKS Baratron capacitance pressure gauge, was maintained by immersing the HF cylinder in a water-ice bath.

RESULTS AND DISCUSSION

The photoion yield curves of $(H_2O)_2^+$, H_2O^+ and H_3O^+ in the spectral range from 950 Å to 1100 Å were measured with a photon bandwidth of 2.5 Å FWHM and are shown in Fig. 1. Due to the low signal of $(H_2O)_2^+$ no distinct threshold was observed. The ionization potential of 11.21 ± 0.09 eV corresponds to the point where the signal falls below 0.1 count/sec and thus is only an upper bound. The ionization potential of the dimer is shifted 1.40 ± 0.09 eV from that of the monomer,[5] yielding a binding energy of 1.58 ± 0.13 eV for the dimer ion relative to H_2O^+ and H_2O.[6] Carrying out SCF calculations on water monomer and dimer using experimentally determined structures, M. Newton determined the shift in the vertical ionization potentials to be 1.32 eV.[7]

The photoionization efficiency of the dimer increases gradually above the threshold indicative of a change in geometry. At 1055 Å a very sharp break in its general trend occurs which coincides with the onset of H_3O^+ formation. Accordingly, 0.52 ± 0.12 eV of internal excitation of the dimer ion is necessary for dissociation into H_3O^+. This suggests that H_3O^+ is formed by the following processes:

$$H_2O - H_2O + h\nu \longrightarrow H_2O - (H_2O^+)^{\ddagger} + e^- \longrightarrow H_3O^+ + OH + e^-$$

It is assumed that the second product is OH and not OH^- due to evidence[8] that H_2O does not dissociate via the ion-pair channel by photoexcitation in this energy range. It is expected that this process leaves no excess energy at the threshold since the monomer has been shown to dissociate in this manner.[9,10]

The threshold measurements for the dissociative ionization of $(H_2O)_2$ enable the determination of the proton affinity of H_2O via the set of reactions:

$$H_2O + H_2O \rightarrow (H_2O)_2 \tag{1}$$

$$(H_2O)_2 \rightarrow H_3O^+ + OH + e^- \tag{2}$$

$$H_2O \rightarrow H^+ + OH + e^- \tag{3}$$

$$H_2O + H^+ \rightarrow H_3O^+ \tag{4}$$

The exoergicity of (1) is taken as 4 ± 1 kcal mole.[6] The enthalpy of (2) is the observed appearance potential of H_3O^+: 11.73 ± 0.03 eV (270.5 ± 0.7 kcal/mole). The high degree of rotational and low frequency vibrational relaxation in the supersonic expansion makes a temperature correction to this threshold unnecessary. The fragmentation threshold of (3) is 15.75 ± 0.01 eV.[9,10] The appropriate sum of these enthalpies yields the proton affinity of H_2O (4) as 7.18 ± 0.08 eV (165.8 ± 1.8 kcal/mole) at 0°K. Other recent determinations of the proton affinity of water are listed in Table I for comparison.

The photoion yield spectra of H_2F^+ and HF^+ are depicted in Fig. 2 (the photon bandwidth is 2.5 Å FWHM). No $(HF)_2^+$ signal is observed in this spectral range. The ionization potential of HF is found to be 15.98 ± 0.04 eV, in agreement with previous measurements.[17] The photoion yield curve of H_2F^+ shows little structure and gradually and smoothly decreases toward threshold. The appearance potential of H_2F^+ is 15.65 ± 0.06 eV. Similar arguments as mentioned above lead us to assume that H_2F^+ is formed by the dissociative ionization of $(HF)_2$. Using the dissociation energy of $(HF)_2$ (6.8 kcal/mole)[18] and the endoergicity of the dissociative ionization of HF to form $H^+ + F$ (19.445 eV),[17] the proton affinity of HF is calculated as 4.09 ± 0.06 eV (94.3 ± 1.4 kcal/mole).

To our knowledge there is no direct proton affinity measurement for HF reported in the literature. Beauchamp[19] has estimated the proton affinity of HF as 131 kcal/mole based on the proton affinity of CH_3F and the methyl inductive effect. Proton affinities of many simple molecules have been calculated by quantum mechanical methods. It was found that CNDO/2[20] and ab initio[21] calculations tend to overestimate the stability of the protonated cations, whereas SCF calculations reproduce experimental proton affinities quite well. A SCF calculation by Hopkinson[21] gives a value of 108 kcal/mole for the proton affinity of HF, which is still larger than our experimental value.

Appearance potential measurements for the dissociative ionization processes of $(HF)_n$, $(H_2O)_n$, and $(NH_3)_n$ (where n > 2) to form $(HF)_{n-1}H^+$,

$(H_2O)_{n-1}H^+$ and $(NH_3)_{n-1}H^+$, respectively, are in progress. These measurements will yield information concerning solvation energies by one and more HF, H_2O, or NH_3 molecules. These results will be presented in detail in a separate report.

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Table I. Proton Affinity of Water

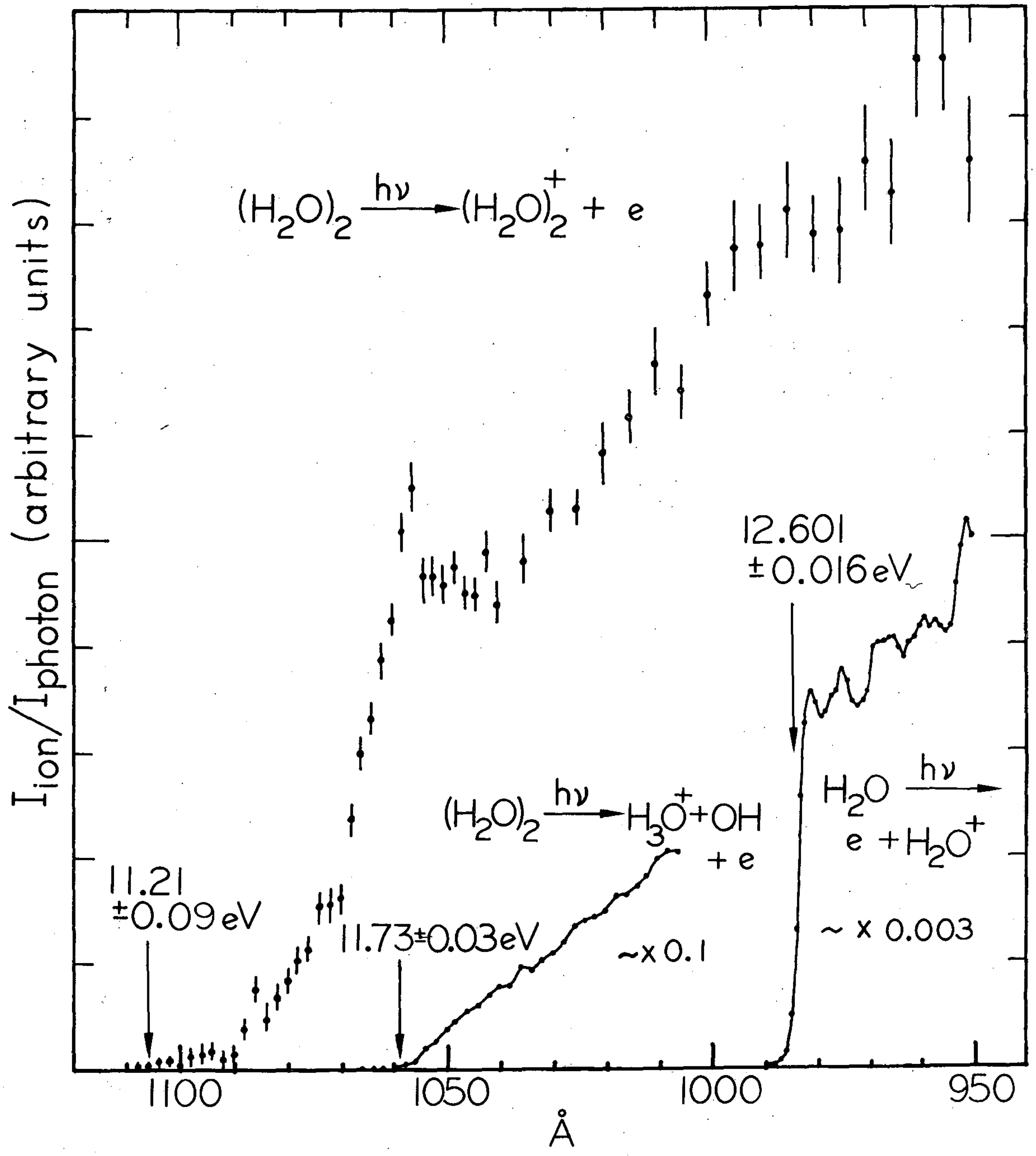
Value (kcal/mole)	Temp. (°K)	Ref.
165.8 ± 1.8	0	This Work
169 ± (1 or 2)	600	1
166.4 ± (1 or 2)	0	a
166 ± 2	-	12
165 ± 3	323-373	13
168.2 ± 3.4	340	14
164 ± 4	-	15
167.5		16

[a] Value of ref. 1 corrected to 0 K using ref. 11.

FIGURE CAPTIONS

Fig. 1. Photoion yield curves of $(H_2O)_2^+$, H_3O^+ and H_2O^+ in the spectral range from 950 Å to 1120 Å, scaled for relative signals at 950 Å.

Fig. 2. Photoion yield curve of H_2F^+ in the spectral range from 600 to 900 Å as compared to the photoion spectrum of HF^+ near the threshold.



XBL 776-9086

Fig. 1

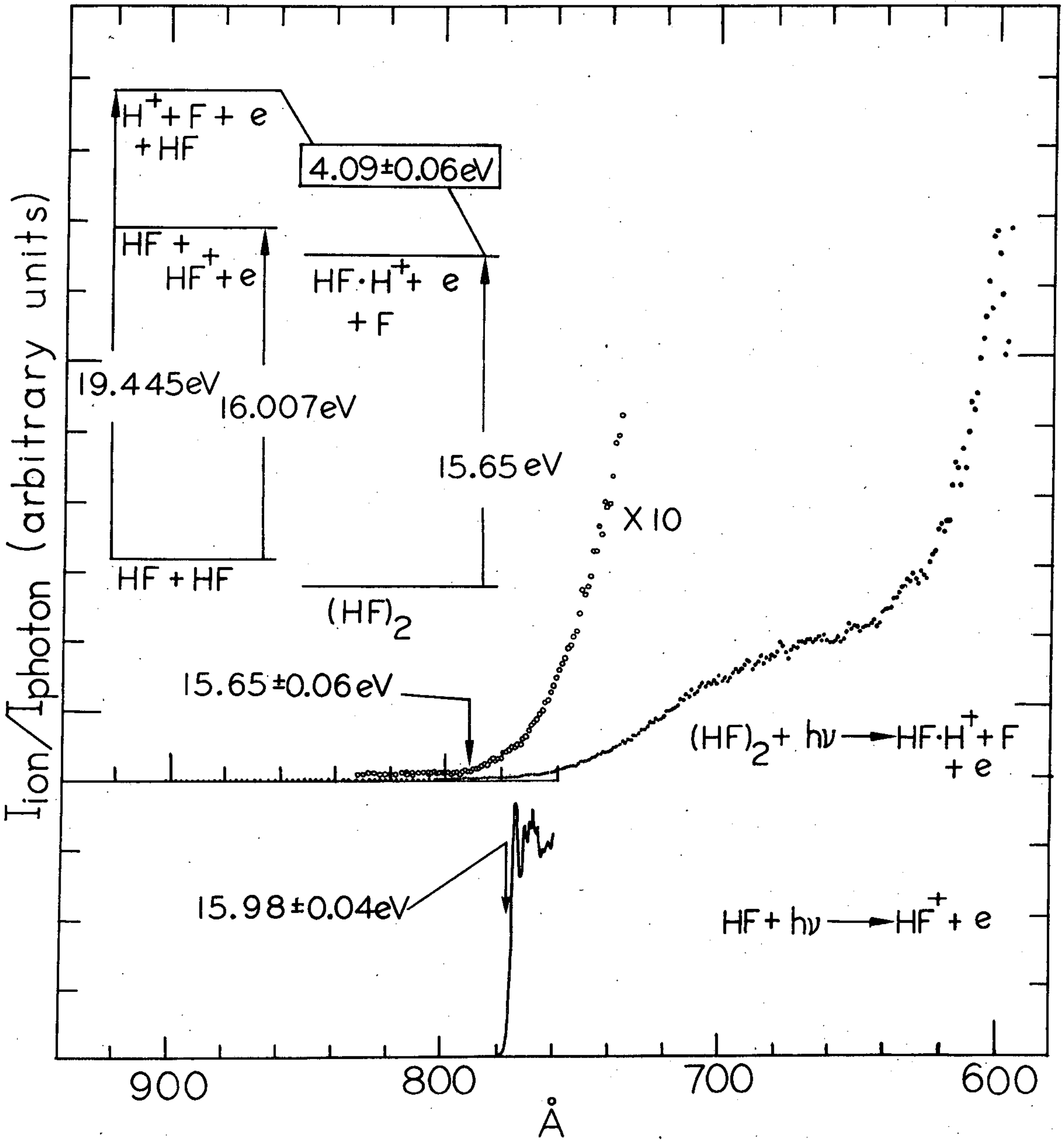


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Fig. 2

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LAWRENCE BERKELEY LABORATORY
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BERKELEY, CALIFORNIA 94720