JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 70A, No. 6, November–December 1966

Mass Spectrometric Study of Photoionization V. Water and Ammonia

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(August 11, 1966)

Photoionization efficiency curves are obtained for the molecule and fragment ions of H_2O and NH_3 in the wavelength region extending from onset of ionization to 600 Å. Threshold values of 12.593 eV and 10.162 eV are observed for the H_2O^+ and NH_3^+ ions, respectively. Vibrationally excited states of the molecule ions and autoionization of Rydberg levels are observed. A determination of the bond angle of the H_2O^+ ion from the Franck-Condon factors of the bending overtones results in a value of 112 degrees. Threshold values of the fragment ions permit calculations of heats of formation of the OH^+ and NH_2^+ ions and result in the ionization energies,

$$I(OH) = 12.94 \text{ eV and } I(NH_2) = 11.22 \text{ eV}.$$

Key Words: Autoionization, electronic, excited states, H_2O^+, NH_3^+, NH_2^+, OH^+ ions, heats of formation, ionization thresholds, mass spectrometer, photoionization, radicals, Rydberg levels, vacuum monochromators.

1. Introduction

Photon absorption in the wavelength region 600 to 1100 Å, and photoionization cross sections for H_2O have recently been remeasured [1–3][1] using photoelectric techniques. In general, the results are in good agreement with previous photographic [4–6] and photoelectric [7–8] studies, although only one [2] has suggested the possibility of autoionization in the wavelength region 850 to 950 Å.

The threshold for photoionization of H_2O, 12.59 ± 0.01 eV [9,10] seems to be well established although possibly not within the stated limits as recently published studies by Watanabe [2] would seem to indicate. However, it is in good agreement with recent electron impact measurements (12.60 ± 0.01 eV) [11] and with the value (12.61 eV) obtained from retarding potential measurements of photoejected electrons [12]. The latter two studies also report thresholds for two higher electronic states of the H_2O^+ ion. Only the electron impact study [11] employed mass analysis to identify the ionic species. Furthermore, no recent measurements of thresholds for dissociative ionization of water have been reported although these have long been known to exist in this energy region [13].

The photon absorption and photoionization of NH_3 have also been remeasured recently by photoelectric [1,3,14] and by photographic [15–17] means. These are generally in agreement with earlier measurements by both techniques [18–20]. However, some inconsistencies are observed among the photoelectric measurements [1] particularly in regions in which dissociative ionization is known to occur [13].

The threshold for photoionization of NH_3 is reported to be 10.15 eV [9] probably with an uncertainty of ±0.01 eV. This is in fair agreement with the value of 10.18 eV obtained by extrapolation of Rydberg levels [15]. Recent electron impact measurements have been consistently higher than this value, usually by an amount which is nearly an order of magnitude greater than the claimed uncertainties. For examples, compare the electron impact values: 10.40 ± 0.02 eV [11], 10.52 ± 0.04 [22], and 10.34 ± 0.07 eV [23]. However, measurements of the kinetic energy of photoejected electrons [12] result in the threshold value of 10.16 eV, in excellent agreement with other photoionization data.

In the present study, mass analysis is combined with nearly monoenergetic photon beams to examine the ionization efficiency curves for the molecule and fragment ions of water and ammonia and to remeasure the threshold energies of the specific ionization and dissociative ionization processes.

2. Experimental Procedure

The windowless vacuum ultraviolet monochromator and mass spectrometer, described in detail in the first paper of this series [24], were used in the present work with only minor modifications. Both Hinteregger-type and microwave discharge lamps were used as photon sources. To obtain suitable overlapping of the spectral regions, the argon continuum was used in the wavelength region from threshold to about 1060 Å. The hydrogen many-line spectrum was used from about 1060 to 950 Å and the Hopfield continuum of helium employed from 950 to 600 Å.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Data were obtained principally by the use of 100-micron optical slits and a 600 grooves/mm, MgF_2-coated aluminum grating blazed at 1500 Å. In the 1-meter monochromator, this provided an optical resolving power of about 2 Å. Some threshold measurements were made using a 1200 grooves/mm, gold-coated grating blazed at 800 Å, providing a resolution of about 1 Å. The photon intensity for a 2 Å band width at the maximum of the argon continuum (about 1080 Å) was estimated from photoelectric yield curves for a tungsten detector [25] to be of the order of 2×10^8 photons/sec.

At each selected wavelength above the first onset a sufficient number of ion counts were obtained to result in a probable error of less than one percent. No correction was made to the observed relative abundances of ions for differences in detector response resulting from ions of different mass or structure. The estimated uncertainty in the measured photon intensity was about 3 percent at most wavelengths.

The ammonia was obtained from the Matheson Corporation and was used without further purification. The purity, stated by the supplier, is better than 98 mole percent NH_3 and no impurities were detected in the mass spectrum obtained at 21.23 eV.

The water sample was obtained from the laboratory supply of distilled water. When introducing H_2O, the sample inlet line in the vicinity of the pinhole leak was warmed to about 30 °C to prevent condensation or freezing at the leak.

3. Results and Discussion

H_2O: The respective relative abundances of the H_2O^+, OH^+, and O^+ ions of water observed at 584Å (21.23 eV) were found to be identical with the values reported by Samson and Cook [26]; namely, 1.0, 0.4, and 0.05. The low abundance of the O^+ ion prevents the measurement of the ionization efficiency curve for that ion in the present study. Also, an unsuccessful search was made for the negative ions, OH^- and O^-.

Figure 1 shows a typical set of photoionization efficiency curves for the H_2O^+ and the OH^+ ions. The wavelength in angstroms is plotted as the abscissa and ion current per photon transmitted is plotted in arbitrary units as the ordinate. The ordinate scale for the OH^+ ion is four times that of the H_2O^+ ion. The energies in electron-volts equivalent to several wavelengths are also given. If the ionization efficiency curves for the two ions are summed with proper consideration for the relative sensitivities as indicated above, a total ionization curve is obtained which is quite similar to that reported by Metzger and Cook [1].

The first long-wavelength onset of the H_2O^+ ion curve is ascribed to the (000)–(000) transition to the ground ($^2B_1$) state of the ion. The point of steepest ascent is 984.5±1 Å (12.59_3 eV). This is in excellent agreement not only with previous photoionization values [9, 10], but also with electron impact data [11]. This agreement between adiabatic and vertical ionization energies in the case of H_2O would appear to support Mulliken's prediction [27] regarding the comparison of threshold measurements for electrons in nonbonding orbitals as obtained by spectroscopic and by electron impact methods.

Above the threshold there are two pronounced steps at 970 Å (12.78 eV) and 955 Å (12.98 eV), two small steps at about half these intervals and, at wavelengths shorter than 955 Å, considerable structure attributable to autoionization.

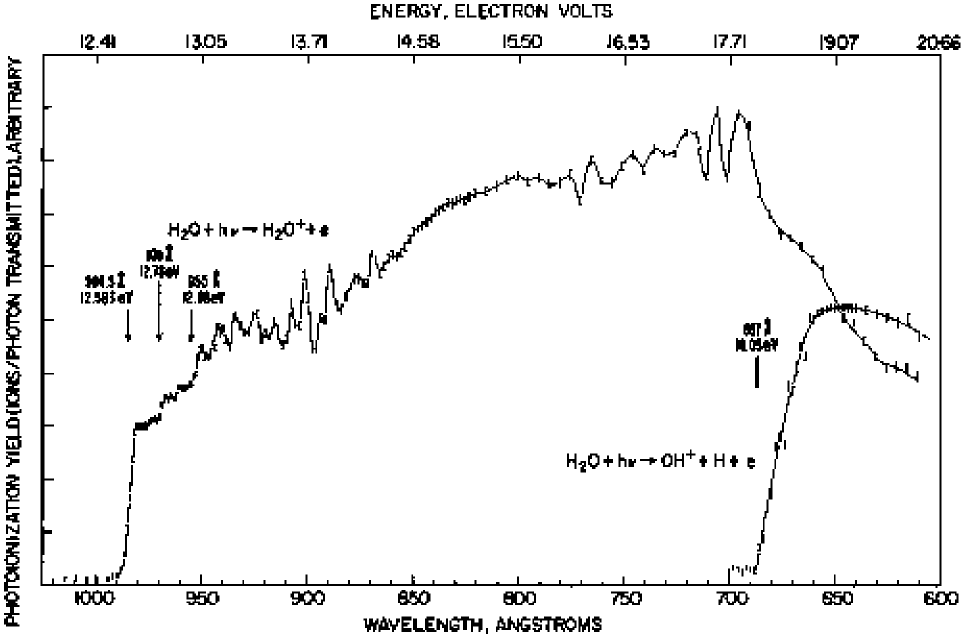

FIGURE 1. *Photoionization efficiency curves for the* H_2O^+ *and* OH^+ *ions of water.*

The $\Delta\nu$ between onset and 970 Å is about 1500 cm^{-1}, suggesting a bending overtone. The corresponding value for the 955 Å-step (ca 3100 cm^{-1}) could correspond to either the second bending overtone or the first stretching overtone of the ion.

Krauss [28] has calculated the geometries of the H_2O molecules and ion using SCF-Gaussian basis methods. His results indicate that the equilibrium bond angle in the ion is 119 deg or some 15 deg greater than in the neutral molecule. Johns [6] has carried out a rotational analysis of the first member of the $^1B_1$ Rydberg series in the 1220 to 1240 Å region leading to a bond angle of 106.9 deg for H_2O and 107.6 deg for D_2O with an increase in bond length of 0.06 Å. More recently, Bell [29] has measured the intensities of the vibrational structure of the $^1B_1$ and $^1A_1$ transitions for D_2O, determining the geometry by means of the Franck-Condon method of Coon and co-workers [30]. Bell obtained bond angles of 109.7 deg and 113.0 deg for the $^1B_1$ and $^1A_1$ states, respectively, with a probable error of ±1.8 deg. The increases in bond length were 0.065 and 0.067 Å, respectively.

Using the method of Sharp and Rosenstock [31], and the force constants for the $^1A_1$ state given by Bell [29], we have calculated the intensities of the bending and symmetric stretching overtones relative to the (000–000) transition for various bond lengths and angles of the ion. These are plotted in figure 2. From the photoionization curve (figure 1) the 010/000 intensity ratio is 0.18 ±0.03. This leads to a value for the angle quite close to Bell's estimate. Accepting the increase in bond length determined by Johns and by Bell we obtain a value of about 112 deg for the H_2O^+ ion, see figure 2c.

The intensity of the second prominent step identified with the (100)–(000) transition cannot be determined accurately because of the autoionization structure. We have no explanation for the steps of $\Delta\nu = 800$ cm^{-1}, although progressions of this interval have been observed in absorption spectra [32] but not assigned.

Beginning at about 950 Å, the H_2O^+ ion curve shows more or less regularly spaced peaks which merge to a continuum at about 860 Å. These peaks are attributed to autoionizing Rydberg levels converging to the 14.2 eV [11, 12] threshold of the $^2A_1$, state of H_2O^+. This observation confirms an earlier suggestion [2] that diffuse bands observed in this region of absorption spectra might result from autoionization.

Initial members of another group of autoionizing Rydberg levels appear at about 780 Å, apparently merging to a continuum at about 690 Å (18.0 eV). If so, this would be in excellent agreement with the reported threshold of 18.02 eV [12] for the second excited state ($^2B_2$) of the H_2O^+ ion. The value 16.34 eV for the second ionization potential obtained by RPD electron impact methods [11] is located near the onset of this autoionizing series. The break in the electron impact ionization efficiency curve may well be due to excitation of these levels.

Except for the sharp onset, the OH^+ ionization efficiency curve is apparently featureless. The threshold occurs at 687 Å (18.05 eV). It is interesting to note that this is very near the wavelength (690 Å) at which the ionization efficiency for the molecule ion shows a marked decrease. It is probably also just above the threshold for the $^2B_2$ state of the H_2O^+ ion. It is suggested, therefore that the OH^+ ion arises from that state of the molecule ion. No metastable transition was observed in a very detailed study of the electron impact mass spectrum.

The observed value for the onset of dissociative ionization is considerably below the previously accepted electron impact value of 18.8 eV [13] and the photoionization value of 18.3 ±0.2 eV [26]. Assuming no excess kinetic energy of the fragments at threshold, the heat of reaction of the process $H_2O + h\nu \rightarrow OH^+ + H + e$ is 18.05 eV or 416.2 kcal [33] with an estimated uncertainty of 0.5 kcal. From this value and the heats of formation [34] of water and of the hydrogen atom, we calculate the $\Delta Hf°(OH^+) = 307.5$ kcal-mol^{-1}

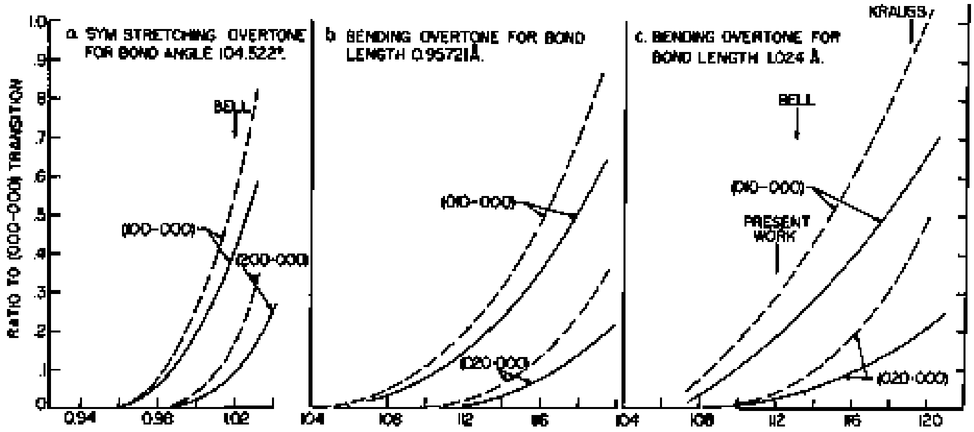

FIGURE 2. *Calculated intensities of the bending and symmetric stretching overtones relative to the (000–000) transition for various bond lengths and angles of the* H_2O^+ *ion* (——— H_2O^*, - - - D_2O^*).

at 0 °K. As the $\Delta Hf_0^\circ(\mathrm{OH}) = 9.25$ kcal [34] is well established, this results in I(OH) = 298.3 kcal (12.94 eV) with an estimated uncertainty of about 0.5 kcal. This is lower than the direct determination of I(OH) = 13.18 ± 0.1 eV (304 ± 2 kcal) reported by Foner and Hudson [35] but would be in agreement if the experimental error of the electron impact results were somewhat greater than quoted. The present results would appear to rule out the still higher value of I(OH) = 13.49 ± 0.08 eV reported by Lindeman and Guffy [36].

NH_3: The relative abundances of the NH_3^+, NH_2^+, and NH^+ ions observed with the 584 Å line of He were 1.0, 1.5, and 0.01, respectively. The N^+ ion was not observed at this energy and there was no indication of the negative ions NH_2^- or NH^- at any of a number of wavelengths longer than 584 Å. The low abundance of the NH^+ ion does not permit accurate threshold measurements in the present experiments.

Figure 3 shows typical photoionization efficiency curves for the NH_3^+ and NH_2^+ ions of ammonia plotted as in fig. 1. The scale for the NH_2^+ ion is reduced to one-half that of the NH_3^+ ion. Below the onset of fragmentation, the curve looks very similar to the total ionization curve recently obtained by Watanabe and Sood [14]. If the two curves are properly added, a total ionization curve is obtained that is also in good agreement with that reported by Metzger and Cook [1]. There is no clear evidence for autoionization within the energy region covered.

The initial portion of the curve for NH_3^+ is quite unlike that for H_2O^+. The first unequivocal step at 1220 ± 1 Å (10.162 ± 0.008 eV) is ascribed to the 0–0 transition of the ion. This value is in good agreement with 10.154 eV from recent photoionization data [9, 12] and with 10.166 eV from recent Rydberg band analysis [14]. It is considerably lower than recent electron impact results [11, 21, 22] although the latter are not entirely consistent among themselves. There is some spectroscopic [37] evidence for a difference of about 0.5 eV between the adiabatic and vertical ionization thresholds.

On a large scale, the NH_3^+ ion curve shows some indication of hot bands as suggested by Watanabe and Mottl [38]. However, the transition probability is only of the order of 0.1 of the 0–0 transition. The 0–0 transition is followed by about nine steps at wavelength intervals of about 13 Å (900 cm^{-1}). The first four of these give indications of splitting into two steps each with nearly equal intervals of 6 or 7 Å (450 cm^{-1}). Walsh and Warsop [39] have shown that the NH_3^+ ion is very nearly planar and have estimated that the v_2, out-of plane, vibrational frequency of the ground state of the ion is 920 ± 10 cm^{-1}. The intervals for the larger steps shown in figure 3 are in good agreement with that value. The increase in intensity of the progression and the general relation of the transition probabilities are in essential agreement with the conclusions reported by Walsh and Warsop.

From about 1100 to 925 Å, the ionization efficiency for NH_3^+ is essentially constant. Above 925 Å, the curve rises to a maximum at about 785 Å and then drops rapidly to the end of the wavelength region. The threshold of an electronically excited state of the NH_3^+ ion has been reported to be about 15.0 eV [11, 12]. There is no indication of a threshold in this region of figure 3 although it may be completely masked by unresolved autoionizing levels.

The NH_2^+ ion shows a sharp onset at 788 ± 2 Å (15.73 ± 0.02 eV) at almost exactly the wavelength at which the intensity of the molecule ionization de-

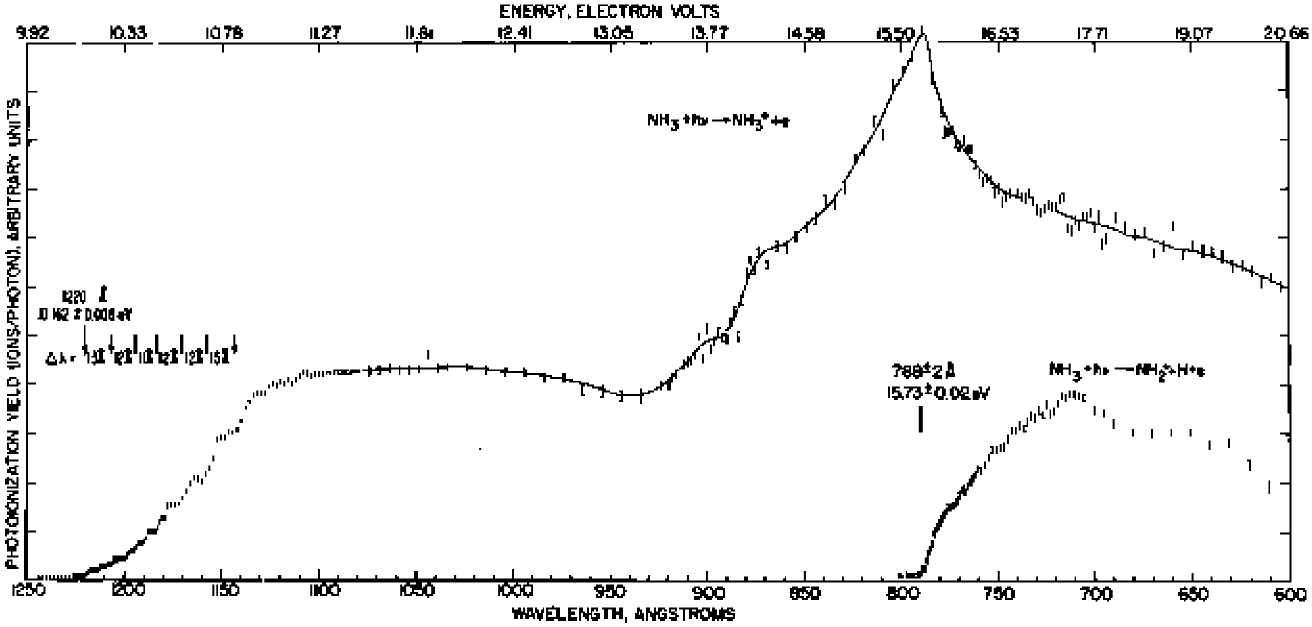

FIGURE 3. *Photoionization efficiency curves for the NH_3^+ and NH_2^+ ions of ammonia.*

creases sharply. The threshold of fragmentation is also above the reported onset of the first excited state of NH_3^+; i.e. 15.02 eV [12] and probably arises from that state. The value is again about 0.3 eV below the electron impact threshold as reported by Foner and Hudson [40] but is possibly in agreement with an earlier value (15.8 eV) [41] within the limits of combined estimated errors. Thus, from the heat of reaction of the process, $NH_3 + h\nu \rightarrow NH_2^+ + H + e$ of 15.73 eV or 362.6 kcal-mol^{-1} we calculate the $\Delta Hf^\circ(NH_2^+) = 301.6$ kcal-mol^{-1} at 0 °K. Also, using $D(NH_2-H) = 104 \pm 2$ kcal-mol^{-1} given by Altshuller [42] we calculate the ionization energy, $I(NH_2) = 258.6$ kcal-mol^{-1} (11.22 eV) or about 0.2 eV below that obtained by direct electron impact measurement.

We wish to acknowledge the assistance of Itiro Omura in obtaining some of the photoionization data.

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(Paper 70A6-417)