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Abstract

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MASS SPECTRA OF WATER UPON IONIZATION BY A STRONG ELECTRIC FIELD

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M. Inghram and R. Gomer (1) reported that the mass spectrum of water upon ionization of its molecules on the tungsten tip of an ion projector consists of associates of the type $(H_2O)_n^+$, where $n \leqslant 4$. Later H. Beqey (2) showed that in fact the associates of water correspond to the formula $(H_2O)_nH^+$, where likewise $n \leqslant 4$. Beqey proposed a mechanism for the formation of the oxonium ion and its hydrates in a strong electric field, which reduces to the reaction in the layer condensed on the tip:

$$H_2O^+ + H_2O = H_3O^+ + OH, \tag{1}$$

although the OH^+ line in these experiments was not detected at all, and the H_2O^+ line was very weak. Its intensity amounted to only 0.1% of the intensity of the oxonium-ion line. Beqey explained the absence of the OH^+ line by the low probability of ionization of the OH radical, and the absence of the H_2O^+ line by the specific conditions in the condensed layer.

We have investigated the ionization of water on tips made of tungsten, molybdenum, platinum, and gold, and also on a nichrome filament at a potential gradient of the order of $10^7 \div 10^8$ V/cm.

The investigations were carried out on a 90° mass spectrometer with circular magnetic-field boundaries, assembled in the laboratory, and with a radius of the central ion trajectory of 30 cm. The gas or vapor under investigation was introduced into a region bounded by the walls of a fluoroplastic cup and a copper diaphragm, which provided the necessary pressure difference between the ionization space and the chamber of the mass analyzer.

Near the diaphragm a tip or a thin filament was installed, the potential of which was maintained constant and was +3 kV relative to the analyzer chamber. The potential of the diaphragm was regulated within the limits from 0 to 20 kV. The ions formed on the needle or filament were accelerated by the field of the diaphragm and, after passing through it and the ion-optical system, entered the chamber of the mass analyzer. The ion current was measured by an ion-electron multiplier and, after amplification, was recorded by a self-recording automatic potentiometer. The mass numbers of the ions studied were established in each experiment by measuring the magnetic field according to the proton-resonance frequency.

When water vapor was admitted onto a tungsten tip, ions with mass numbers 19, 37, 55, and 73 a.m.u. were formed. This group of lines corresponds to the formula $(H_2O)_nH^+$ ($n = 1, 2, 3, 4$), in complete agreement with the experimental data of H. Beqey (^{2}) and the quantum-mechanical calculations of R. Grana (^{3}).

In addition, very weak lines at 17 and 18 a.m.u. were detected, which we assigned to the ions OH^+ and H_2O^+, as well as a series of lines with fractional mass numbers, which are explained by the decomposition of water associates according to the scheme

$$(H_2O)_nH^+ \to (H_2O)_mH^+ + (H_2O)_{n-m} \tag{2}$$

in accordance with the well-known formula

$$M = \frac{M_{\text{frag}}^2}{M_{\text{par}}}, \tag{3}$$

where M is the measured mass number, M_{frag} is the mass of the fragment ion, and M_{par} is the mass of the primary ion. Data on these lines are presented in Table 1.

Table 1

Metastable ions in the mass spectrum of water

Decaying ion	Fragment ion	Calculated mass	Experiment
$(H_2O)_2H^+$	H_2OH^+	9.76	9.7
$(H_2O)_3H^+$	H_2OH^+	6.56	6.4
$(H_2O)_4H^+$	H_2OH^+	4.94	4.9
$(H_2O)_3H^+$	$(H_2O)_2H^+$	24.89	24.9

Studies of pure D_2O confirm the proposed interpretation of the mass spectra, since in this case the mass numbers of the ions obtained correspond to the same formulas with the corresponding replacement of hydrogen by deuterium.

Mixtures of light and heavy water with a known deuterium concentration were also analyzed in order to study the possibility of isotopic analysis. In this case the mass spectrum of each type of stable ion should consist of $k+1$ lines, where k is the sum of the atoms of light and heavy hydrogen in this ion, and the distribution of their intensities is determined by the formula:

$$I_l = \frac{C_k^l}{(1+\Delta)^k}\Delta^l. \tag{4}$$

Fig. 1. Mass spectrum of a 50% mixture of H2O and of the oxonium ion (n = 1) (A) or hydrate of the oxonium ion (n = 2) (B)

Figure 1: Fig. 1. Mass spectrum of a 50% mixture of H2O and of the oxonium ion (n = 1) (A) or hydrate of the oxonium ion (n = 2) (B)

Fig. 2. Mass spectrogram of the oxonium ion formed as a result of dissociation of its deuterated hydrate ($\Delta = 1.1$)

Figure 2: Fig. 2. Mass spectrogram of the oxonium ion formed as a result of dissociation of its deuterated hydrate ($\Delta = 1.1$)

Here: Δ is the ratio of the number of deuterium atoms to the number of hydrogen atoms in the aqueous mixture, and l is the number of deuterium atoms.

Fig. 1. Mass spectrum of a 50% mixture of H_2O and D_2O of the oxonium ion ($n = 1$) (A) or the hydrate of the oxonium ion ($n = 2$) (B)

The mass spectrum of a 50% mixture of H_2O and D_2O ($\Delta = 1$) for $n = 1$ and $n = 2$, shown in Fig. 1, demonstrates that (4) is fulfilled both in the number of lines and in the ratio of their intensities.

As for the "metastable" ions observed as a result of decay according to scheme (2), it can be shown that deuteration leads to the appearance of $j(k - j + 2)$ lines instead of one corresponding to pure H_2O.

The distribution of the intensities of these lines should be described by the formula

$$I_{li} = \frac{C_k^l}{(1+\Delta)^k} \Delta^l \frac{C_{k-l}^{j-i} C_l^i}{C_k^j}, \tag{5}$$

where j is the sum of the hydrogen and deuterium atoms in the fragment ion, i is the number of deuterium atoms in the fragment ion, and l and k are the same as in formula (4) and refer to the primary "metastable" ion. Thus, for dissociation into an oxonium ion and one water molecule, the experiment should give 12 lines with an average spacing of 0.25 mass units between them. Since the lines of the fragment ions are substantially broader than the lines of ordinary ions, in our experiment one could expect to obtain a single broad line with an emerging fine structure. This is indeed what was obtained, as can be seen from Fig. 2, which shows the mass spectrogram corresponding to the indicated dissociation for $\Delta = 1.1$.

Fig. 2. Mass spectrogram of the oxonium ion formed as a result of dissociation of its deuterated hydrate ($\Delta = 1.1$).

The same spectrogram shows the calculated distribution of intensities in the form of vertical lines, according to formula (5).

Similar results were obtained upon ionization of water vapor on a molybdenum tip and a nichrome filament. In ionization on tips made of gold and platinum there is a substantial difference from ionization on tungsten. Thus, in the mass spectra corresponding to noble metals, there is an intense line of H_2O^+, and the ratio of the ion currents H_2O^+/H_3O^+ depends sharply on the potential gradient. For large potentials on the diaphragm this ratio is of the order of unity, whereas for tungsten it does not exceed 10^{-3}.

Ionization of water was also studied in the presence of mercury vapor, alcohols, ethers, benzene, and acetic acid. For all these compounds their associates with the oxonium ion were found.

An interpretation of the results obtained will be given in a more detailed article.

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CITED LITERATURE

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