

THE POSITIVE RAY ANALYSIS OF WATER VAPOR IONIZED
BY IMPACT OF SLOW ELECTRONS

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ABSTRACT

An electromagnetic method of separating gas ions of different mass, such as that used by Dempster, has been employed in a study of the ions produced by electron impact in water vapor. The principal ions appearing were $(\text{H}_2\text{O})^+$ and $(\text{OH})^+$. Of these the $(\text{H}_2\text{O})^+$ ions were more abundant. Unmistakable evidence was obtained that a third type of ion, probably $(\text{H}_3\text{O})^+$, was produced in very small quantities. H^+ and H_2^+ ions were always very few in number or unobservable. No $(\text{OH})^-$ or any other negative ions were observed.

Ionization potentials for $(\text{H}_2\text{O})^+$ and $(\text{OH})^+$.—The ionization potential corresponding to $(\text{H}_2\text{O})^+$ was 13 ± 1.5 volts, being probably in agreement with the ordinarily measured ionization potential. The $(\text{OH})^+$ ionization potential was not distinguishably different, but it was difficult to measure this quantity owing to some overlapping of the $(\text{H}_2\text{O})^+$ and $(\text{OH})^+$ peaks.

Relative abundance of the ions as a function of pressure.—A study was made of variation in the relative abundance of the ions as a function of pressure. The $(\text{H}_2\text{O})^+$ ion appears to be the primary ion, as it predominates at low pressures, but is of the same order of magnitude as the $(\text{OH})^+$ ion at high pressures (0.007 mm).

INTRODUCTION

WITHIN the past few years the method of positive ray analysis due to Dempster has been developed and applied to the study of ionization in monatomic and diatomic gases by several experimenters, including Smyth,¹ Hogness and Lunn,¹ Harnwell,² Brasefield,³ and one of the authors.^{4,5} The present research was undertaken as the first step of a similar investigation of several gases composed of molecules of more than two atoms.⁶

Smyth⁷ discovered, and one of the authors⁴ also later noted, that in a freshly evacuated tube electron impacts of sufficient energy produced water ions. These were doubtless due to water vapor present in the tube, the source of the vapor being layers adsorbed by the glass walls. On account of the polar nature of the water molecule, it would be expected that a large quantity of water could be so retained by a glass surface and then released gradually after evacuation. The experiments to be described confirm this point of view, since sufficient water vapor for detection by ionization was present, even

¹ For references see: H. D. Smyth, *Phys. Rev.* **25**, 452 (1925), note 1; T. R. Hogness and E. G. Lunn, *Phys. Rev.* **30**, 26 (1927), note 1.

² G. P. Harnwell, *Phys. Rev.* **29**, 683 and 830 (1927).

³ C. J. Brasefield, *Phys. Rev.* **31**, 52 (1928).

⁴ H. A. Barton, *Phys. Rev.* **25**, 469 (1925).

⁵ H. A. Barton, *Phys. Rev.* **30**, 614 (1927).

⁶ This field was opened with salt vapors by: V. Kondratjeff and N. Semenov, *Zeits. f. Physik* **22**, 1 (1924); V. Kondratjeff, *idem* **32**, 535 (1925) and **39**, 191 (1926), note 2.

⁷ H. D. Smyth, *Proc. Roy. Soc.* **A104**, 127 (1923).

after the system had been standing under a vacuum for two weeks. Conditions were thus favorable to study the nature of the ionization in water vapor as a representative polyatomic gas and to obtain useful information concerning tubes which cannot be baked out and so may contain water vapor as an impurity. In the early part of the present work, when only the nature of the ions was the subject of study, it was not found necessary to augment the water vapor present in the tube. Later, additional water vapor was supplied by evaporation of an adjusted mixture of water and concentrated sulphuric acid.

As in the experiments cited above, ^{1,2,3,4,5} gas pressures were of the order of 0.001 mm, and the electron impacts were of energies ranging from 0 to 100 volts.

TYPES OF ION

During preliminary runs, positive ions were noticed in the mass range 24 to 30, approximately, with a maximum near 28 probably due to CO. These

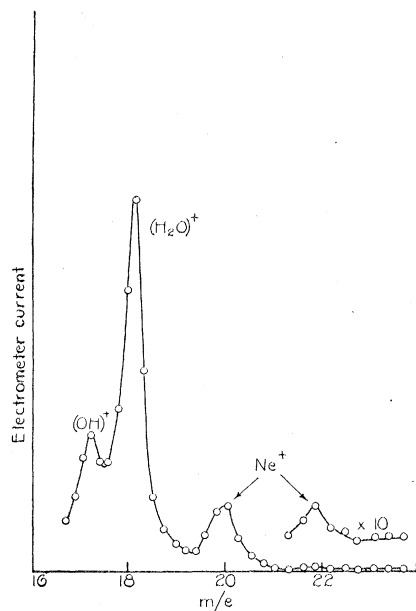


Fig. 1

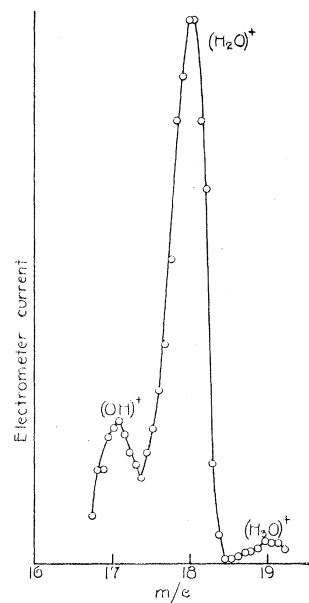


Fig. 2

ions correspond in general to those observed by Aston⁸ and attributed by him to the hydrocarbons arising from the waxes and greases present in the tube.

In the study of water vapor, two principal types of ion occurred near $m/e = 18$. To fix the mass scale accurately and thus determine the precise composition of these ions, neon, having known isotopes at 20 and 22, was mixed with the water vapor. The mass spectrum which was obtained is

⁸ F. W. Aston, *Isotopes* (1924), p. 66.

shown in Fig. 1. The neon isotopes appear with the expected abundance-ratio, here determined quantitatively and directly for the first time, of approximately 10:1, agreeing with that calculated from the atomic weight of neon on the basis of Aston's⁸ work. Since the abscissas of the plot are proportional to m/e , it is obvious, by extrapolating, that the water ion peaks correspond to $m/e=18$ and 17. Accordingly, these must be interpreted as having the compositions $(\text{H}_2\text{O})^+$ and $(\text{OH})^+$, respectively.

Later, with neon absent and the resolving power of the apparatus improved, a mass spectrum such as is shown in Fig. 2 was obtained. It is evident that a third type of ion, corresponding to $m/e=19$, occurs, although in small quantities. This third type of ion was present whenever the conditions were such that all the ions were abundant. According to J. J. Thomson,⁹ a corresponding line is very frequently found on positive ray photographs. It could be due to fluorine, but as this element could not have been present in more than negligible quantities in the present work, the peak is ascribed to the ion $(\text{H}_3\text{O})^+$. It is probable that these ions were formed either by the attachment of protons to neutral water molecules or by some reaction, e.g. $(\text{H}_2\text{O})^+ + \text{H}_2\text{O} \rightarrow (\text{H}_3\text{O})^+ + \text{OH}$.

Thus, as far as the positive ions are concerned, they agree exactly with the results of Aston,⁸ who found the $(\text{H}_3\text{O})^+$ ion "always very faint." On the other hand, no negative ions of any sort which might be due to water vapor were found, even though search was made repeatedly. This is in marked distinction from the result of J. J. Thomson¹⁰ who observed $(\text{OH})^-$ ions. Since the apparatus had easily detected Cl^- ions in HCl, there would seem to be no present experimental difficulty involved in the non-detection of such negative ions. In this connection it may be noted that Mohler¹¹ found that with small electron currents and low pressures, the negative ion current was small in comparison with that of the positive ions. With larger electron currents, the ratio of negative to positive ions increased. This is in good accord with the present results, but it leaves unexplained the large quantities of Cl^- ions observed by one of the writers in HCl.

$(\text{H})^+$ and $(\text{H}_2)^+$ ions were always few in number when it was possible to observe them.

CRITICAL POTENTIALS

The lowest potential at which the $(\text{H}_2\text{O})^+$ ions appeared was 13 ± 1.5 volts, the weighted mean of ten determinations, as shown in Table I. This agrees well with the lowest ionizing potential of water vapor observed as 13.2 by Mackay and 13.0 by Foote and Mohler.¹² Attempts to determine the critical potential for the appearance of the $(\text{OH})^+$ ion gave roughly the same value. It is impossible to be sure that this properly applies to the $(\text{OH})^+$ ion,

⁹ J. J. Thomson, *Rays of Positive Electricity* (1921) p. 230.

¹⁰ J. J. Thompson, *Rays of Positive Electricity* (1921) p. 70 and 227.

¹¹ F. L. Mohler, *Phys. Rev.* **26**, 614 (1925).

¹² C. A. MacKay, *Phys. Rev.* **24**, 319 (1924); P. D. Foote and F. L. Mohler, *Phys. Rev.* **17**, 394 (1921).

since it was difficult to resolve this completely from the (H₂O)⁺ type. However, if, as appears from the pressure analysis, the (H₂O)⁺ ion is the primary

 TABLE I. Ionization potential for (H₂O)⁺.

Run	I. P.	Wt.	Run	I. P.	Wt.
145	13	21	5-26-1	13	11
146-1	15	8	5-26-2	12	10
146-2	12	11	5-26-3	14	10
146-3	13	12	5-26-4	11	8
147	15	7	5-26-5	14	5
			Weighted mean		13

ion, and the (OH)⁺ a secondary type in the sense to be discussed, it would be expected that the critical potentials of the two ions would be the same.

PRESSURE EFFECTS

In most other gases where more than one type of ion was produced, and in hydrogen especially, changes in the gas pressure caused marked changes in the relative intensity of the several types of ion. Such changes are in part interpreted as distinguishing between two classes of ion, called primary and secondary. By primary ions are meant those produced by the electron impact; by secondary ions are meant those produced from the primary ions when they undergo subsequent encounters with other molecules. Obviously, increasing the pressure increases the number of possible encounters and, therefore, the ratio of secondary to primary ions.

It was difficult to test for this phenomenon in water vapor because when the water vapor pressure was increased, the filaments were burned out or deactivated. However, it was possible to increase the number of encounters suffered by the primary ions by adding another gas not destructive to filaments, the total pressure being thereby raised. This was done with nitrogen at various total pressures and results obtained, of which those shown in Fig. 3 are an example. It must be acknowledged that the shape of the curves is somewhat doubtful, but it is fairly definite that the (H₂O)⁺ type of ion predominates at low pressures and so may be regarded as the primary type of ion produced by electron impact in water vapor.

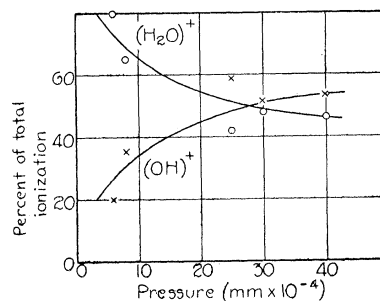


Fig. 3

DISCUSSION

Like most, if not all, non-polar gases and all polar gases which have so far been studied,¹³ the water molecule is primarily ionized by the removal of

¹³ See summary of results given in reference 5.

an electron without dissociation of the molecule. As in HCl there is no sign of a type of ionization consisting of the separation of the molecule into its polar ions, in this case H^+ and $(OH)^-$ or O^{--} . In both H_2O and HCl a second type of positive ion is observed whose composition is that of the primary ion with one hydrogen atom removed, i.e. Cl^+ and $(OH)^+$ respectively. The possibility in the case of H_2O that still another positive ion could be formed having two hydrogen atoms removed, i.e. O^+ , is not realized. In this connection it may be mentioned that the gas logically next in order after H_2O , namely ammonia (H_3N), is now being investigated by one of the writers.

The existence of the positive ion $(OH)^+$ may be regarded as a limiting case of the existence in excited states of the neutral OH molecule, which is generally held to be the emitter of a certain band spectrum associated with water vapor.¹⁴

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¹⁴ W. Watson, *Astrophys. J.* **60**, 145 (1924).