IONIZATION OF AIR BY H^+ *AND* H_2^+ *IONS*

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An investigation has been made of the secondary ions that are produced in single collisions between air molecules and H^+ and H_2^+ ions with energies between 5 and 180 kev. The following secondary ions were found: N_2^+, O_2^+, N^+, O^+, N^{2+}, O^{2+}, and Ar^+.

The cross sections for secondary ion formation have been measured. The cross sections for electron capture by H^+ and H_2^+ and the total cross section for ionization of the air molecules have also been investigated.

INTRODUCTION

THE ionization of air by protons has been studied chiefly in connection with investigations of the dependence of proton range on energy.[1] The magnitude and position of the maximum of the ionization cross section have been determined by various indirect methods, all of which are characterized by poor accuracy.[2] To the best of our knowledge, no direct measurements of the ionization cross section for air by protons or the dependence of cross section on energy have been carried out.

The present work was undertaken to investigate ionization in single collisions of H^+ and H_2^+ ions with air molecules. Collisions between fast positive ions and gas atoms are characterized by the detachment of electrons from the shells of both colliding particles and by electron exchange. These and other processes lead to the formation of singly-charged and multiply-charged secondary ions.[3] Because of electron capture by the fast primary ions the total charge of the secondary ions is usually greater than the total charge of the secondary electrons. Furthermore, since it is not a fixed quantity, the total charge of the secondary ions does not give a direct indication of the number of secondary ions. For this reason the "number of ion pairs," which is generally used to characterize ionization, is not a reliable parameter. The total ionization cross section is more properly denoted by the cross section for the formation of the free electrons, which are detached from the shells of the colliding particles. Hence, in the present work the total ionization cross section was determined directly by recording the electrons produced when an ion beam was passed through a chamber containing air. The total electron capture cross sections for H^+ and H_2^+ were also determined; this quantity was also reported in reference 4. In addition, mass-spectrometer measurements were carried out to determine the identity of the secondary ions. The cross sections for the formation of these ions were also measured.

MEASUREMENT PROCEDURE

The method of measurement has been described in detail in earlier papers[3,5] and will be discussed only briefly here.

A beam of primary H^+ or H_2^+ ions, which first passes through a monochrometer, enters a system of collimating slits and the collision chamber, which contains air at 1.5×10^{-4} mm Hg. It has been found that this pressure is low enough to satisfy the requirements for single collisions. A pressure less than 5×10^{-6} mm Hg is maintained in the rest of the system by means of differential pumping.

The collision chamber contains a measuring condenser; this condenser is used to collect the secondary ions and electrons which are formed when the primary ion beam passes through the chamber. The measuring condenser is used to determine the total cross section for the formation of positive ions [reduced to unit charge (σ_+)] and the total ionization cross section (σ_-) by the formulas

$$\sigma_+ = i_+ / i_1 nl; \qquad (1)$$

$$\sigma_- = i_- / i_1 nl. \qquad (2)$$

In Eqs. (1) and (2), i_1 is the current of primary ions, i_+ and i_- are the saturation currents for positive and negative particles respectively when the collision chamber is filled with air (taking

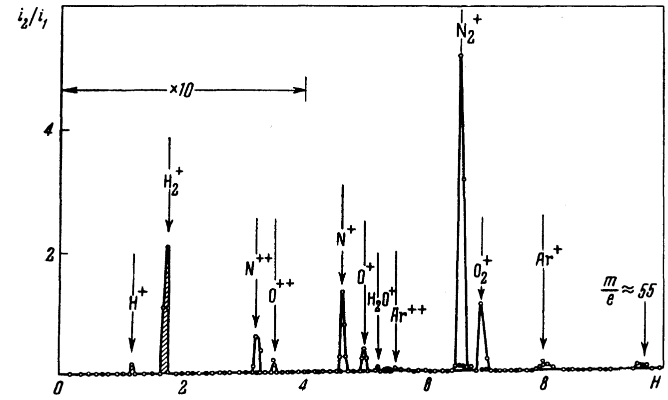

FIG. 1. Secondary-ion spectrogram. o) spectrum at an air pressure of 1.5×10^{-4} mm Hg in the collision chamber, ●) spectrum with a residual pressure of 5×10^{-6} mm Hg. The lines due to the residual gases are shown cross-hatched.

account of the background due to the residual gas), n is the number of air molecules per cm^3, and l is the length of the electrodes. The total cross section for electron capture by primary ions (σ_{10}) is defined as

$$\sigma_{10} = \sigma_{+} - \sigma_{-}. \quad (3)$$

A magnetic mass analyzer is used with the collision chamber; this analyzer is used to analyze the e/m ratios of the secondary ions. Using the mass analyzer the cross section for the formation of secondary ions A^{n+} ($\sigma_{A^{n+}}$) is determined from the expression

$$\sigma_{A^{n+}} = \frac{1}{n}\sigma_{+}\alpha_{A^{n+}}, \quad (4)$$

where $\sigma_{A^{n+}}$ is the relative intensity of the line for the A^{n+} ion in the secondary-ion spectrum.

The primary-ion current and the saturation currents at the plates of the condenser are 5×10^{-6} to

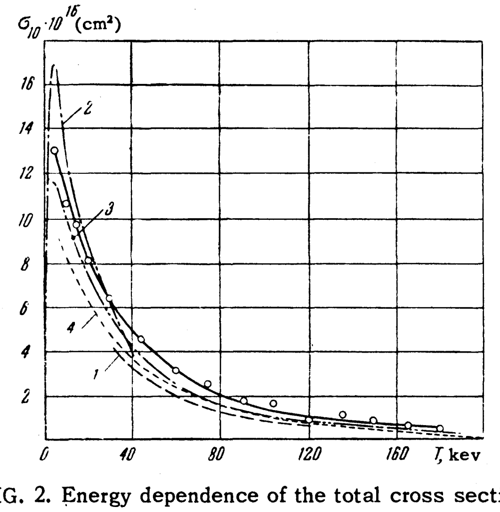

FIG. 2. Energy dependence of the total cross section for electron capture by protons. The solid curve represents the air data of the present work. The dotted curves are as follows: 1) data of reference 4 for air, 2) data of reference 7 for nitrogen, 3) and 4) data of reference 6 for N_2 and O_2 respectively.

5×10^{-8} amp and 4×10^{-7} to 8×10^{-10} amp respectively and are measured with a mirror galvanometer. The current at the collector of the mass analyzer is 8×10^{-10} to 4×10^{-14} amp and is measured with a vacuum-tube voltmeter with a sensitivity of 1×10^{-14} amp/division.

The air pressure in the collision chamber is measured with a radiometer gauge and is monitored with a manometer.

The errors in the cross section measurements are estimated at ±12% of the measured quantities and consist of the errors in the pressure measurements (±6%) and the errors in the current measurements (±6%).

RESULTS OF THE MEASUREMENTS AND DISCUSSION

1. Mass Spectrometric Analysis of the Secondary Ions

A spectrogram of the secondary ions formed in the passage of 75-kev protons through air is shown in Fig. 1. The spectrogram was taken at a pressure of 1.5×10^{-4} mm Hg; the residual pressure in the chamber was 5×10^{-6} mm Hg after evacuation. The intensity of the lines is plotted along the vertical axis while the strength of the magnetic field is plotted along the horizontal axis (both quantities are plotted in arbitrary units).

The strongest lines in the spectrum were assigned to the following ions: N_2^+, O_2^+, N^+, O^+, N^{2+}, O^{2+}, and Ar^+. Lines due to H^+, H_2^+, and H_2O^+ were observed; these were attributed to the residual gases. The H^+ and H_2^+ lines are due to the presence of a small amount of water (from the ion source) in the collision chamber while the line characterized by m/e ≈ 55 is apparently due to vapors of organic compounds. The total contamination of the air was less than 2%.

2. Total Cross Section For Electron Capture by Primary Ions σ_{10}

The energy dependence of σ_{10}, the total electron capture cross section protons in air is shown in Fig. 2. This cross section falls off as the proton energy is increased (for the entire region which was investigated). The cross section for electron capture by protons has also been measured by Kanner.[4] The σ_{10}(T) curve obtained in the present work lies above the curve obtained in reference 4; however the difference lies within the experimental errors. The figure also shows the electron capture cross sections measured by Stier and Barnett[6] in oxygen and nitrogen and by Gilbody and Hasted[7]

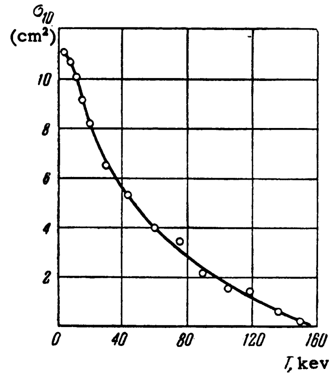

FIG. 3. Energy dependence of the total cross section for electron capture by H_2^+ ions in air (the quantity $\sigma_{10} \times 10^{16}$ is plotted along the ordinate axis).

in nitrogen. The capture cross sections in these gases are approximately the same as those in air.

Figure 3 shows the energy dependence of the total electron capture cross section (σ_{10}) for H_2^+ ions in air. This cross section is similar to the proton capture cross section in that both fall off with increasing energy over the entire range which was investigated.

3. Total Ionization Cross Section σ_-

In Fig. 4 is shown the total ionization cross section for air (σ_-) as a function of the energy of the primary ions, H^+ and H_2^+. The $\sigma_-(T)$ curve has a broad maximum for proton ionization at about 60 kev, at which $\sigma_- \approx 6.3 \times 10^{-16}$ cm^2. According to the data of reference 2 the maximum of the cross section for ionization of air by protons, as determined by indirect methods lies, in the 50 to 120 kev region; the maximum cross section is 8.6 to 12.5×10^{-16} cm^2, i.e., somewhat higher than the value obtained in the present work. The position of the ionization maximum found in the present work is in agreement with the position of the maximum of the stopping power of air for protons. According to the data of various authors, reported in the review paper by Allison and Warshaw,[8] this maximum lies in the 60 to 80 kev region.

Figure 5 shows the velocity dependence of the cross section for ionization of air by H^+ and H_2^+ ions and the cross section for ionization of nitrogen and oxygen by electrons as reported in reference 9. It is apparent from Fig. 5 that the ionization maximum for protons and H_2^+ ions lies in the

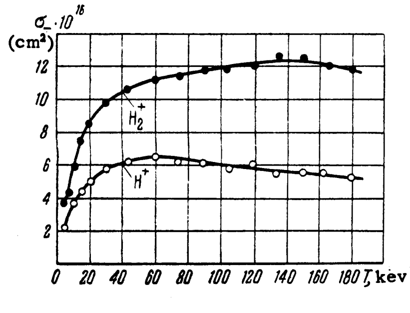

FIG. 4. The total cross section for ionization of air as a function of primary-ion energy (H^+ and H_2^+).

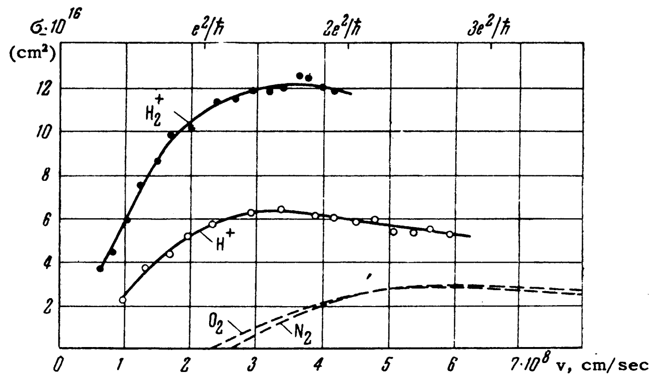

FIG. 5. Velocity dependence of the total ionization cross section. Solid curves are the data of the present work (the designations of the primary ions are given on the corresponding curves); the dotted curves are the data of reference 9 for ionization of nitrogen and oxygen by electrons.

velocity range $v \approx (1.5 \text{ to } 2) e^2/\hbar$ ($e^2/\hbar = 2.2 \times 10^8$ cm sec is the electron velocity in the Bohr hydrogen atom). The ionization maxima in oxygen and nitrogen for electrons corresponds to the higher velocity value $v \approx 3e^2/\hbar$. The maximum cross section for ionization of air by electron collision is approximately one half the value for proton ionization and four times smaller than that for ionization by H_2^+ ions. It is also apparent that ionization of air by protons and H_2^+ ions takes place in the velocity region $v \approx 3e^2/\hbar$, where ionization by electron impact does not occur.

4. Cross Section For the Formation of Secondary Ions

(a) Formation of Secondary ions in air. In Fig. 6 are shown the dependences of the cross sections for the formation of nitrogen and oxygen ions when air is ionized by protons. In Fig. 7 the same relations are shown for H_2^+ ions. Data on the ionization of argon atoms by H^+ and H_2^+ ions have been reported in reference 10 and have not been investigated in

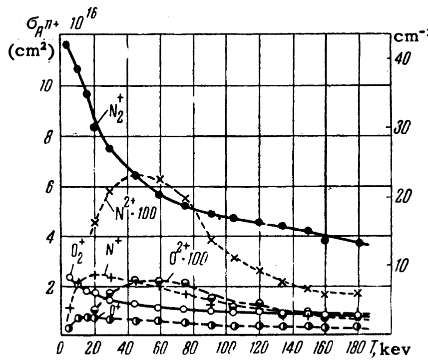

FIG. 6. Energy dependence of the cross sections for the formation of secondary ions in air for ionization by protons. The designations of the secondary ions are given on the corresponding curves.

the present work. The cross sections are expressed in cm^2 and in cm^{-1}, giving the number of secondary ions formed in one centimeter of primary-ion path at 1 mm Hg and 0°C. The cross sections are computed for one primary ion and one molecule. Examination of Figs. 6 and 7 shows that the number of secondary nitrogen ions is approximately four times greater than the number of oxygen ions.

Secondary ions can be produced in the readjustment of the electron shells of the colliding particles. When the energies of the primary ions (hydrogen) are of the order of several kev the collision time is less than 10^{-15} sec. Hence, in the ionization of air (which consists essentially of molecular gases) this readjustment process should be governed by the Franck-Condon principle. Under these conditions the collision of the primary ion with a molecule leads to the formation of a secondary molecular ion with charge equal to the number of electrons detached from the shell of the molecule. The molecular ions which are formed can be stable or unstable. In the latter case they dissociate into atomic particles.

In the interaction of protons with nitrogen molecules the most probable processes which lead to the formation of secondary ions are the following:

$$H^+ + N_2 \rightarrow H^0 + N_2^+, \tag{I}$$

$$H^+ + N_2 \rightarrow H^+ + N_2^+ + e, \tag{II}$$

$$H^+ + N_2 \rightarrow H^0 + N_2^{++} + e, \tag{III}$$

$$H^+ + N_2 \rightarrow H^+ + N_2^{++} + 2e. \tag{IV}$$

Here (I) is the reaction in which an electron is captured by a proton, (II) and (IV) are ionization reactions in which one and two electrons are detached respectively, and (III) is a capture reaction accompanied by ionization. It is obvious that there are also reactions in which three or more electrons are detached from the molecular shells and capture

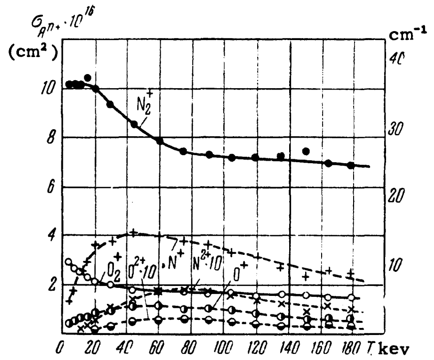

FIG. 7. Energy dependence of the cross sections for the formation of secondary ions in air for ionization by H_2^+ ions. The designations of the secondary ions are given on the corresponding curves.

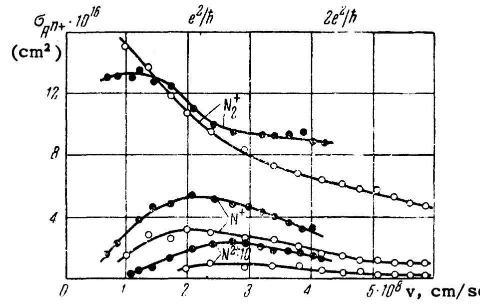

FIG. 8. The cross sections for the formation of secondary ions in nitrogen as a function of the velocity of the primary ion. The designations of the secondary ions are given on the corresponding curves. o) ionization by protons; •) ionization by H_2^+ ions.

reactions in which two electrons are captured by the proton. However, these reactions are much less probable than those given in (I) to (IV).

The N_2^+ ions which appear as a result of (I) and (II) and the N_2^{2+} ions which appear as a result of (III) and (IV) are predominantly stable.* The unstable secondary ions can dissociate by various modes, forming the atomic particles N, N^+ and N^{2+}. The O_2^+, O^+, and O^{2+} ions are formed as a result of similar processes.

(b) <u>Cross sections for the formation of singly charged molecular ions in nitrogen and oxygen ($\sigma_{N_2^+}$ and $\sigma_{O_2^+}$)</u>. Figures 8 and 9 show the velocity dependences of the cross sections for the formation of various secondary ions for the passage of protons and H_2^+ ions through pure gases (nitrogen and oxygen). In computing these cross sections from the data given in Figs. 6 and 7 it has been assumed that the air is 78% nitrogen and 21% oxygen. Inspection of the curves in Figs. 8 and 9

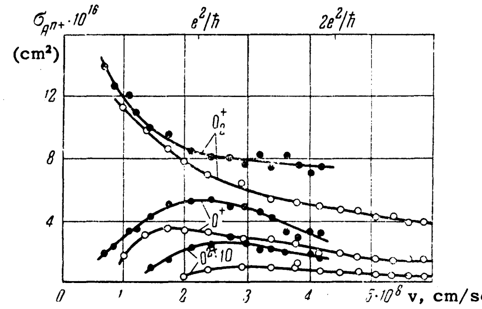

FIG. 9. The cross sections for the formation of secondary ions in oxygen as a function of the velocity of the primary ion. The designations of the secondary ions are given on the corresponding curves. o) ionization by protons; •) ionization by H_2^+ ions.

*It is apparent from Fig. 7 that the number of N^+ and N^{2+} atomic ions which arise as a result of dissociation is less than 50% of the number of molecular N_2^+ ions. It follows thus that the maximum number of unstable N_2^+ ions is less than one third of the total number.

shows that the formation cross sections for singly charged molecular ions fall off with increasing primary-ion velocity; the only exception is the cross section for the ionization of nitrogen by H_2^+, which has a maximum at $v \approx 1.2 \times 10^8$ cm/sec.

In the velocity region $v < e^2/\hbar$ the formation of secondary molecular ions is due chiefly to the capture of electrons by the primary ions. This follows from the fact that in this region the total capture cross section is greater than the cross sections $\sigma_{N_2^+}$ and $\sigma_{O_2^+}$ while the total ionization cross section is smaller than these cross sections. The shape of the $\sigma_{N_2^+}(v)$ and $\sigma_{O_2^+}(v)$ curves in this region is probably determined by the $\sigma_{10}(v)$ curve. On the other hand, in the velocity region $v > e^2/\hbar$ the molecular ions arise predominantly as a result of ionization. This result follows from the fact that the total electron capture cross section (σ_{10}) for $v > e^2/\hbar$ is considerably smaller than the cross sections $\sigma_{N_2^+}$ and $\sigma_{O_2^+}$.

(c) Cross sections for the formation of singly charged atomic ions in nitrogen and oxygen σ_{O^+} and σ_{N^+}. It is apparent from Figs 8 and 9 that the cross sections for the formation of singly charged atomic ions reach a maximum of about 50% of the cross sections for the formation of singly-charged molecular ions. The cross sections for the formation of the singly charged atomic ions (N^+ and O^+) reach a maximum in the region $v \approx (0.5 \text{ to } 1) \times e^2/\hbar$. It is interesting to note that the velocities corresponding to the appearance potentials of these ions in electron collision (according to the data of reference 11) are larger, being 2.6 to 2.9×10^8 cm/sec.

It is important to note that the maxima for the formation of secondary atomic ions occur at lower velocities than the maxima for total ionization by H^+ and H_2^+ ions. This experimental fact may be explained qualitatively as follows. The $\sigma_{N^+}(v)$ curve (and the $\sigma_{O^+}(v)$ curve) must be a superposition of the curves for capture with dissociation and ionization with dissociation. According to the data reported by Lindholm,[12] processes involving capture with subsequent dissociation can have cross sections which are comparable with the cross sections for ordinary charge exchange (at primary ion energies of the order of 1 kev). Hence it is reasonable to assume that the basic contribution in σ_{N^+} and σ_{O^+} in the velocity region $v \lesssim e^2/\hbar$ is due to processes involving capture with subsequent dissociation rather than ionization with dissociation, for which a relatively high energy is required.

The oxygen atom has a positive electron affinity; hence in the interaction of H^+ and H_2^+ ions with oxygen molecules the latter may dissociate with the formation of the negative atomic ions, O^-. In the present work we have estimated the cross section for the formation of negative oxygen ions for primary-ion energies between 11 and 29 kev. The results are shown in the table; the cross sections are given in units of 10^{-19} cm^2. It is apparent from the table that this cross section is much smaller than σ_{O^+} and falls off as the energy of the primary ions is increased.

Energy, kev	Primary ion	
	H^+	H_2^+
11	2.6	—
19	2 .	6
29	1.2	4

(d) Cross section for the formation of double charged atomic ions $\sigma_{O^{++}}$ and $\sigma_{N^{++}}$. The cross sections for the formation of doubly charged atomic ions have maxima which lie in the velocity region $v \approx (1 \text{ to } 1.5)e^2/\hbar$. The maximum values for ionization by protons are $\sigma_{O^{++}} \approx 1 \times 10^{-17}$ cm^2 and $\sigma_{N^{++}} \approx 8.3 \times 10^{-18}$ cm^2; for ionization by H_2^+ ions these cross sections are larger: $\sigma_{O^{++}} \approx 2.9 \times 10^{-17}$ cm^2 and $\sigma_{N^{++}} \approx 2.4 \times 10^{-17}$ cm^2. An estimate of the analogous cross sections for electron impact, made with the data of references 9 and 11, yields the values $\sigma_{O^{++}} < 3 \times 10^{-20}$ cm^2 and $\sigma_{N^{++}} \approx 8 \times 10^{-20}$ cm^2.

It is apparent from Figs. 8 and 9 that $\sigma_{O^{++}}$ and $\sigma_{N^{++}}$ and σ_{O^+} and σ_{N^+} for ionization by H_2^+ ions are 1.5 to 3 times greater than for ionization by protons. This would seem to indicate that the cross sections for processes which involve a sizeable consumption of energy increase with increasing atomic number of the primary ion. A similar conclusion was reached in earlier work, in which we investigated the ionization of argon by hydrogen ions.[10]

The experimental data of the present work lead to the following conclusions.

(1) Ionization of air by protons occurs at velocities smaller than $e^2/\hbar$, i.e., below the threshold for ionization by electron impact. The total cross section for ionization by H^+ and H_2^+ ions, at velocities corresponding to the threshold for electron ionization, are 6×10^{-16} cm^2 and 11×10^{-16} cm^2 respectively.

(2) In ionization of air by protons and H_2^+ ions, about one-third of the secondary ions produced at the total-ionization maxima are atomic ions.

These experimental findings and the data on the ionization of inert gases by positive ions[3,10] indicate that the ionization mechanism in atomic collisions is different from that which operates in electron impact.

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