FORMATION OF SLOW ATOMIC NEGATIVE OXYGEN IONS IN COLLISIONS OF FAST PROTONS AND HYDROGEN ATOMS WITH O_2 MOLECULES

V. A. GUSEV, A. A. OKSYUK, Ya. M. FOGEL', and D. V. FILIPENKO

Physicotechnical Institute, Ukrainian Academy of Sciences

Submitted June 1, 1970

Zh. Eksp. Teor. Fiz. 59, 1909–1916 (December, 1970)

A procedure is developed for the investigation of processes of formation of slow negative ions in collisions of fast ions or atoms with gas molecules. The effective cross sections for the production of O^- ions in collisions of hydrogen ions and atoms with energy 3–50 keV with oxygen molecules are measured in relative units.

INTRODUCTION

IN collisions of singly-charged positive ions and atoms with diatomic molecules, slow atomic negative ions are produced as a result of the following two processes[1)]:

$$A^{0}_{+} + B_2 \to A^+ + B^- + B^+, \quad (1)$$

$$A^0 + B_2 \to A^+ + B_2^{-*} \to A^+ + B^- + B^*. \quad (2)$$

The process (1) is a direct dissociation of a diatomic molecule into a positive and a negative ion as a result of collision with a fast ion or atom. If the impinging particle has no electron shell (H^+, He^+, etc.) the process (1) is the only source of the slow ions B^-.

In process (2), the slow ions B^- are the result of the decay of the unstable molecular ion B_2^-, which is produced in turn when the target molecule captures an electron.

The process of dissociation of diatomic molecules by electron impact into positive and negative ions was observed in[1-7]. For collisions of heavy particles with gas molecules, this process has not been sufficiently well studied. Il'in, Afrosimov, and Fedorenko[8] gave the results of measurements of the effective cross section for the dissociation of the molecule O_2 into the ions O^- and O^+ by impact of the ions H^+ and H_2^+ at three values of the incoming-particle energy. Afrosimov and coworkers[9] estimated the effective cross section of the dissociation of the H_2 molecule into H^- and H^+ ions by proton impact. According to their data, the effective cross section of this process does not exceed 3×10^{-20} cm^2. Finally, Ogurtsov and Flaks[10] measured the effective cross sections for the production of C^-, O^-, and CO^- ions in the interaction of fast neon ions and atoms with CO molecules. They obtained cross sections $\sim 10^{-18}$, $\sim 10^{-19}$, and $\sim 10^{-20}$ cm^2 for the production of the ions O^-, C^-, and CO^-, respectively.

The formation of slow atomic negative ions in collisions between fast atoms and diatomic molecules has been somewhat better investigated, but still insufficiently[11-14].

Thus, the processes of formation of slow atomic negative ions in collisions between heavy particles and gas molecules have not yet been sufficiently well studied. This statement is particularly true with respect to process (1). On the other hand, a study of this process is of considerable interest, since it differs greatly from the other processes in which slow atomic ions are produced in molecular gases (dissociative charge exchange and dissociative ionization). A study of this process is useful also from the point of view of clarifying the general properties of the function $\sigma(v)$ (σ—effective cross section of a certain process of atomic collision, v—relative velocity of the colliding particles). The point lies in the fact that the formation of slow atomic negative ions in the process (1) can occur in many cases only along a single channel, and therefore the $\sigma(v)$ curves, which characterize this process, should have a particularly simple form, thereby greatly simplifying their analysis.

The purpose of our present and subsequent investigations is a detailed study of the regularities of process (1), which we wish to compare with the regularities in the formation of slow atomic negative ions by dissociative charge exchange (process (2)).

The first stage of these investigations is measurement of the effective cross sections for the production of O^- ions in collisions between fast protons or hydrogen atoms with O_2 molecules; the results of these measurements are reported in the present paper.

APPARATUS AND MEASUREMENT PROCEDURE

The measurements of the effective cross sections for the production of slow O^- ions were performed with the aid of the experimental setup described in[15]. The system for the extraction and beam shaping of the slow negative ions produced in the investigated gas is shown schematically in Fig. 1.

This system consists of five flat electrodes, each a disc of 40 mm diameter. Electrodes 1 and 2, in the space between which the beam of incoming particles enters, form the collision chamber proper. The slow negative ions produced in the collision chamber are moved by the electric field due to the extraction potential difference V_{extr} (which is smoothly adjustable from 0 to 175 V) applied between electrodes 1 and 2 through a slit in the second electrode into the space between the

[1)] In principle, the ions B^- can also be produced in the process $A^+ + B_2 \to A^{++} + B_2^{-*} \to A^{++} + B^- + B^*$. However, owing to the large resonance defect of this process, its effective cross section is small compared with that of the process (2).

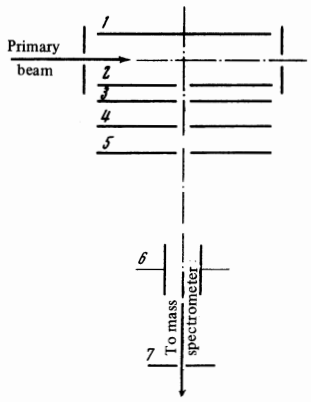

FIG. 1. System for the production of the beam of secondary ions. The slit dimensions in the electrodes of the extraction system are as follows: electrode 2–1.5 × 7 mm; electrodes 3, 4, and 5–1 × 7 mm. Distances between electrodes of the extraction system: between 1 and 2–10 mm, between 2 and 3–3 mm, between 3 and 4 and between 4 and 5–5 mm.

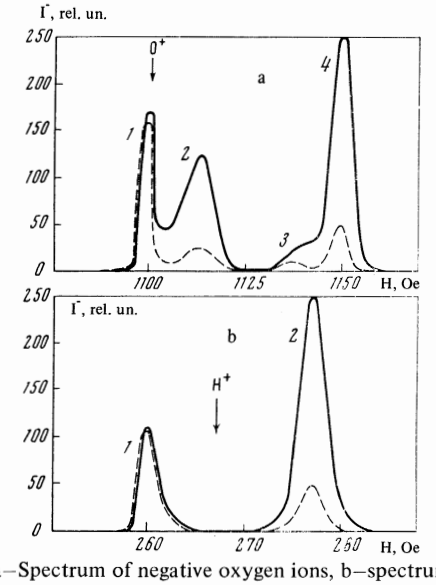

FIG. 2. a–Spectrum of negative oxygen ions, b–spectrum of negative hydrogen ions. Solid curves–solid first electrode, dashed–reticular first electrode.

electrodes 3, 4, and 5. The collision chamber is under an accelerating potential V_{acc} equal to 1500 V, relative to the grounded electrode 3. The beam of negative ions passing through the slit in the electrode 3 is focused with the aid of a focusing potential $V_{foc} \approx 1000$ V applied to electrode 4, and then passes through a slit in the grounded electrode 5 and strikes the slit 7 of the mass spectrometer. The negative-ion beam trajectory is corrected in the space between the system of electrodes 1–5 and the slit 7 by the electric field of parallelepiped-plate capacitor 6. The dimensions of the slits in the electrodes of the extraction system and the distances between the electrodes of the extraction and negative-ion-beam shaping systems are given in the caption of Fig. 1.

In measuring the effective cross sections for the production of slow negative ions, it must be kept in mind that the investigated negative ions can result not only from collisions between the incoming-beam particles and the gas molecules, but also in the following processes:

1) In collisions between the secondary electrons knocked out by the incoming-beam particles from the edges of the entrance and exit slits of the collision chamber, and the molecules of the investigated gas.

2. In collisions between the secondary electrons produced in the collision-chamber gas and the molecules of this gas.

3. In processes occurring when the surface of the first electrode of the collision chamber is bombarded by positive ions produced in the collision-chamber gas by the incoming-beam particles. These positive ions, accelerated in the electric field produced by the extraction voltage applied to the collision-chamber electrodes, can produce, by charge exchange and by secondary ion-ion emission on the surface of the first electrode, negative ions having the same nature as the negative ions produced in the collision-chamber gas by passage of the primary-beam particles through the chamber[2)]. The negative ions produced on the surface of the first electrode by the field of the extraction potential difference are accelerated towards the slit of the second collision-chamber electrode and are registered ultimately by the mass-spectrometer receiver.

4. In collisions between the negative ions from the surfaces of the electrodes when negative ions pass through the slit of the beam-shaping system.

To prevent the secondary electrons knocked out by the incoming-beam particles from the edges of the entrance and exit slits of the collision chamber from entering the region from which the slow secondary ions are drawn into the beam-shaping system, a positive potential of 500 V was applied to the slit in order to block the secondary electrons.

We investigated the dependence of the current i of the slow negative ions on the incoming-particle-beam current I and on the gas pressure p in the collision chamber. The effective cross sections for the production of the slow negative ions were measured at values of I and p within the limits of the linear sections of the i(I) and i(p) dependences, thereby eliminating the contribution made to the slow-negative-ion current by collisions between the gas molecules and the secondary electrons produced in the gas.

To separate the negative ions to be investigated from the negative ions having the same nature but produced on the surface of the first electrode on the collision chamber or on the slits of the slow-negative-ion beam shaping system, we investigated the mass spectra of the slow negative and positive ions produced by the passage of a beam of 20-keV protons through hydrogen and oxygen. These spectra are shown in Fig. 2a (oxygen) and Fig. 2b (hydrogen). They were obtained in each case by using two forms of the first electrode of the secondary-ion-beam shaping system: in the form of a solid disc (solid lines) and in the form of a grid having a transparency of 80% (dashed lines).

As seen from Fig. 2a, four peaks are observed in the mass spectrum of the negative ions produced in oxygen. When the solid first electrode of the shaping beam is replaced by a reticular one, the height of the first peak remains unchanged, whereas the heights of the second

[2)]The possibility of producing on the surface of the first electrode negative ions having the same nature as the ions produced in the collision-chamber gas was kindly pointed out to us by M. N. Panov and Yu. A. Mamaev of the Physicotechnical Institute of the USSR Academy of Sciences, to whom the authors are sincerely grateful.

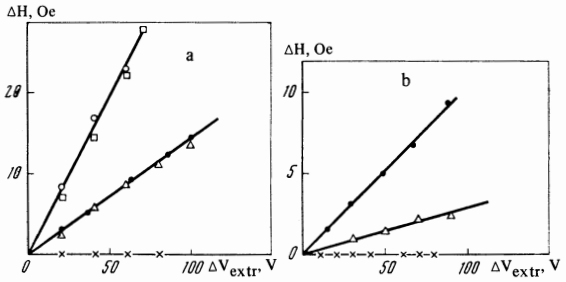

FIG. 3. a–Plot of $\Delta H = f(\Delta V_{extr})$ for the peaks of the negative spectrum of oxygen: ●–first peak of negative spectrum, Δ–peak of O^+ ions, □–second peak of negative spectrum, X–third peak of negative spectrum: ○–fourth peak of negative spectrum. b–Plot of $\Delta H = f(\Delta V_{extr})$ for peaks of the negative spectrum of hydrogen: ●–second peak of negative spectrum, Δ–peak of H^+ ions, X–first peak of negative spectrum.

and fourth peaks decrease by an approximate factor of 5. This indicates that the negative ions of the second and fourth peaks of the spectrum are produced in processes occurring on the surface of the first electrode of the extraction system.

The arrow in Fig. 2a marks the value of the magnetic field intensity corresponding to the peak of the O^+ ions and coinciding in magnitude with the field intensity for the first peak of the negative spectrum.

For a more detailed elucidation of the nature of the negative-spectrum peaks, we investigated the function $\Delta H = f(\Delta V_{extr})$, which represents the variation of the magnetic field intensity corresponding to the top of the peak with variation of the extraction voltage. Here $\Delta H_i = H_{max} - H_i$, $\Delta V^i_{extr} = V^{max}_{extr} - V^i_{extr}$, where H_{max} is the magnetic field intensity corresponding to the top of the investigated peak at the maximum value of the extraction voltage V^{max}_{extr}. Figures 3a and 3b show plots of $\Delta H = f(\Delta V_{extr})$ for oxygen and hydrogen, respectively. Since the ions are produced in the gas in a region lying halfway between the electrodes of the collision chamber, their energy on leaving the beam-shaping system will be equal to $e[V_{acc} + (V_{extr}/2)]$. The negative ions produced on the surface of the first electrode of the collision chamber can acquire at the exit from the beam-shaping system, owing to charge exchange of the slow positive ions, an energy $e(V_{acc} + kV_{extr})$, where the coefficient k is equal to 3/2 if the slow ions are elastically scattered during the charge exchange. On the other hand, if the collisions between the slow ions and the surface of the first electrode are inelastic, then k can assume arbitrary values smaller than 3/2, down to k = 1. The negative ions produced on the surface of the first electrode by secondary ion emission will have an energy $e(V_{acc} + V_{extr}) + E_i$, where E_i is the initial kinetic energy of the knocked-out negative ions. The energy of the ions produced outside the collision chamber (on the slits of the shaping-system electrodes) will be independent of V_{extr}.

Figure 3a shows plots of $\Delta H = f(\Delta V_{extr})$ for all the peaks of the negative spectrum of oxygen and for the peak of the O^+ ions. As seen from this figure, the slopes of the plots of $\Delta H = f(\Delta V_{extr})$ for the second and fourth peaks of the spectrum are approximately 2.5 times larger than for the first peak of the negative spectrum and for the peak of the O^+ ions. The agreement between the plots of $\Delta H = f(\Delta V_{extr})$ for the second and fourth peaks of the spectrum indicates that the coefficients k in the formula for the energy are close in magnitude for ions producing the second and fourth peaks of the spectrum. The magnetic field intensity at which the third peak of the spectrum appears is independent of the extracting potential difference.

On the basis of the foregoing measurements it can be concluded that the first peak of the mass spectrum shown in Fig. 2a corresponds to O^- ions produced in the collision chamber by dissociation of the O_2 molecule into a positive ion and a negative ion as a result of proton impact. The second and fourth peaks of the mass spectrum correspond to the negative ions produced on the surface of the first electrode of the collision chamber. The third peak of the negative spectrum is apparently produced by ions knocked out from the surface of the second electrode of the extraction system by the negative secondary-ion beam passing through the slits of the electrodes.

Similar methodical investigations of the peaks of the negative spectrum of hydrogen, the results of which are shown in Figs. 2b and 3b, allow us to conclude that the first peak of the spectrum of Fig. 2b corresponds to H^- ions produced on the surface of the second electrode of the extraction system. The second peak of the negative spectrum is due to H^- ions produced in processes occurring on the surface of the first electrode of the extraction system. Thus, it was impossible to observe in the mass spectrum of the negative ions the peak corresponding to the H^- ions produced in the collision chamber as a result of the dissociation of the hydrogen molecules into positive and negative hydrogen ions. It appears that in bombardment of molecular hydrogen by 20-keV protons, the effective cross section of this process does not exceed 5×10^{-21} cm^2, which is the lower limit of the sensitivity of our experimental setup.

The methodological measurements performed show that it is possible to investigate processes (1) and (2) in molecular oxygen. The results of this investigation are reported in the next section of the article.

EXPERIMENTAL RESULTS AND DISCUSSION

When protons pass through oxygen, O^- ions are produced only as a result of process (1). We shall designate the effective cross section of this process by $\sigma^{\pm}_{O^-}$.

In the case of passage of hydrogen atoms through oxygen, the O^- ions are produced as a result of either process (1) or process (2). The total effective cross section $\sigma^0_{O^-}$ for the production of O^- ions in oxygen by passage of hydrogen atoms is given by the formula

$$\sigma_{O^-}{}^0 = \sigma_{O^-}^{diss} + \sigma_{O^-}^{c.e.}, \qquad (3)$$

where $\sigma^{diss}_{O^-}$ and $\sigma^{c.e.}_{O^-}$ are the effective cross sections of the processes (1) and (2) in collisions of hydrogen atoms with O_2 molecules.

We measured, in relative units, the effective cross sections $\sigma^+_{O^-}$ and $\sigma^0_{O^-}$ for collisions of protons and hydrogen atoms of energy 3–50 keV with O_2 molecules.

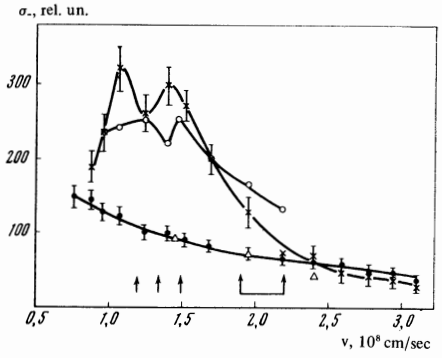

FIG. 4. Plots of $\sigma_{O^-}^{+}(v)$ and $\sigma_{O^-}^{0}(v)$ for the pairs H^+-O_2 and H^0-O_2: ●—protons in oxygen, X—hydrogen atoms in oxygen, Δ—results of [8], O—results of [14]. The arrows mark the velocity region in which the maxima of the process $H^0 + O_2 \rightarrow H^+ + O^- + O^*$ should be located (the O atom in the ground state as well as in all the excited states).

Plots of the effective cross sections $\sigma_{O^-}^{+}$ and $\sigma_{O^-}^{0}$ against the velocity of the incoming particles are shown in Fig. 4. The same figure shows plots of $\sigma_{O^-}^{0}(v)$ obtained in[14]. The three values of the effective cross section $\sigma_{O^-}^{+}$ obtained in[8] are also shown in Fig. 4. These values of $\sigma_{O^-}^{+}$ are made to agree with the $\sigma_{O^-}^{+}(v)$ curve obtained in the present paper at the point corresponding to a proton energy of 20 keV. As seen from Fig. 4, the results of the earlier measurements of the effective cross sections $\sigma_{O^-}^{+}$ and $\sigma_{O^-}^{0}$ are in satisfactory agreement with the results of the measurements reported in the present article.

The $\sigma_{O^-}^{+}(v)$ and $\sigma_{O^-}^{0}(v)$ curves differ strongly in the incoming-particle velocity interval $(1-2) \times 10^8$ cm/sec. In this velocity region, the effective cross section $\sigma_{O^-}^{0}$ is several times larger than $\sigma_{O^-}^{+}$. However, with increasing incoming-particle velocity the differences between $\sigma_{O^-}^{+}$ and $\sigma_{O^-}^{0}$ and between their velocity dependences disappear.

The observed differences in the form of the $\sigma_{O^-}^{+}(v)$ and $\sigma_{O^-}^{0}(v)$ curves can be explained on the basis of the adiabatic maximum rule of Hasted and Massey. According to this rule, the velocity v_{max} corresponding to the maximum of the effective cross section of the process is determined by the equation $v_{max} \approx a|\Delta E|_\infty/h$, where a is the radius of the interaction forces between the colliding particles, $|\Delta E|_\infty$ is the resonance defect of the process or the distance between the potential curves of the initial and final states of the system of colliding particles at an infinitely large distance between them, and h is Planck's constant.

As shown in[10], the value of a for the charge exchange processes (2) is ~ 3 Å. By calculating the resonance defects for the processes (2), in which the oxygen atom is produced not only in the ground state but also in different excited states, and by using the value a = 3 Å, we can determine v_{max} for different channels of the process (2). The values of v_{max} calculated in this manner are indicated by the arrows in Fig. 4.

An examination of Fig. 4 shows that the two maxima on the $\sigma_{O^-}^{0}(v)$ curve lie in the velocity region predicted by the adiabatic maximum rule. We can conclude from this that in the velocity region $(1-2) \times 10^8$ cm/sec the contribution made to the total effective cross section $\sigma_{O^-}^{0}$ by the effective cross section $\sigma_{O^-}^{c.e.}$ of the charge-exchange process (2) is quite appreciable. As is well known, the effective charge-exchange cross section decreases rapidly with increasing velocity. In the velocity region $v > 2.5 \times 10^8$ cm/sec, the effective cross section $\sigma_{O^-}^{c.e.}$ becomes sufficiently small and the total effective cross section $\sigma_{O^-}^{0}$ approaches the effective cross section $\sigma_{O^-}^{diss}$. If this reasoning is valid, then it can be concluded from the identical course of the $\sigma_{O^-}^{+}(v)$ and $\sigma_{O^-}^{0}(v)$ curves in the velocity region $v > 2.5 \times 10^8$ cm/sec that the effective cross section of the process for the dissociation of the molecule O_2 into ions O^+ and O^- depends little on the charge state of the incoming particle.

As seen from Fig. 4, the effective cross section $\sigma_{O^-}^{+}$ increases monotonically with decreasing velocity of the incoming particle. This means that the maximum of the $\sigma_{O^-}^{+}(v)$ curve lies in the velocity region $v < 7 \times 10^7$ cm/sec. On the other hand, for the process (1) we have $\Delta E_\infty = -17.2$ eV. If a = 3 Å for this process, too, then the maximum of the $\sigma_{O^-}^{+}(v)$ curve should occur in the region $v \approx 1.2 \times 10^8$ cm/sec. The absence of a maximum on the $\sigma_{O^-}^{+}(v)$ curve in this velocity region indicates that a < 3 Å for process (1).

In conclusion, it must be emphasized that the course of the $\sigma_{O^-}^{+}(v)$ curve in the investigated velocity interval differs significantly from the course of the $\sigma(v)$ curves for dissociative ionization. Further investigations of the process (1) using other incoming particles and target molecules will show the extent to which this conclusion is general and what its meaning is.

[1] H. Guitbier and H. Nehert, Zs. Naturforsch., 9a, 335, 1954.
[2] R. E. Fox, J. Chem. Phys., 26, 1281, 1957.
[3] V. I. Khvostenko and V. M. Dukel'skiĭ, Zh. Eksp. Teor. Fiz. 33, 851 (1957) [Sov. Phys.-JETP 6, 657 (1958)].
[4] R. Thorburn, Proc. Phys. Soc. 73, 122, 1959.
[5] G. J. Schulz, Phys. Rev. 113, 816, 1959.
[6] D. Rapp and D. D. Briglia, J. Chem. Phys. 43, 1480, 1965.
[7] P. J. Chantry and G. J. Schulz, Phys. Rev. 156, 134, 1967.
[8] R. N. Il'in, V. V. Afrosimov, and N. V. Fedorenko, Zh. Eksp. Teor. Fiz. 36, 41 (1959) [Sov. Phys.-JETP 9, 29 (1959)].
[9] V. V. Afrosimov, G. A. Leĭko, Yu. A. Mamaev, and M. M. Panov, ibid. 56, 1204 (1969) [29, 648 (1969)].
[10] G. N. Ogurtsov and I. P. Flaks, Zh. Tekh. Fiz. 36, 117 (1966) [Sov. Phys.-Tech. Phys. 11, 84 (1966)].
[11] T. M. Donahue and F. Hushfar, Nature, 186, 1038, 1960.
[12] T. M. Donahue and F. Hushfar, Phys. Rev. 124, 138, 1961.
[13] A. M. Bukhteev, Yu. F. Bydin, and V. M. Dukel'skiĭ, Zh. Tekh. Fiz. 31, 688 (1961) [Sov. Phys.-Tech. Phys. 6, 496 (1961)].
[14] D. V. Pilipenko and Ya. M. Fogel', Zh. Eksp. Teor. Fiz. 48, 404 (1965) [Sov. Phys.-JETP 21, 266 (1965)].
[15] V. A. Gusev, G. N. Polyakova, and Ya. M. Fogel', ibid. 55, 2128 (1968) [28, 1126 (1969)].
[16] M. C. Poulizac, J. Desesquelles, and M. Dufay, Ann. d'Astrophys., 30, 301, 1967.

Translated by J. G. Adashko
215