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IONIZING COLLISIONS OF ELECTRONS WITH IONS AND ATOMS

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The method of intersecting ion and electron beams has been used to measure the cross sections for single ionization of the ions Hg^+, Xe^+, Kr^+, Ar^+, Ne^+, Hg^{2+}, Xe^{2+}, Kr^{2+}, and Ar^{2+}. The parent ions were obtained by ionization of the neutral atoms by a primary beam of electrons. The variation of the secondary ionization cross sections with the electron energy in the primary beam has been determined. It is shown that the ionization of neutral atoms by electron impact is accompanied by formation of metastable excited ions with single, double, or triple charge. It is also shown that, for an accelerating voltage of 2800 V, the existence of background in a mass spectrometer is due mainly to various ionization processes in which the metastable excited ions take part.

1. INTRODUCTION

KNOWLEDGE of the cross sections for excitation and ionization of ions by electrons is necessary for study of gas discharge plasmas and various astrophysical phenomena. Recently Burgess[1], Hill[2], Schwartz and Zirin[3], and Malik and Trefftz[4] have made theoretical evaluations of the ionization cross sections of various positive ions by electrons in the Born approximation and by the distorted wave method. These authors have assumed that the parent ions are in their ground states.

The direct experimental study of the ionization of positive ions by electrons has been described only in two papers. Dolder, Harrison, and Thoneman[5] measured the ionization cross section of He^+ ions from the ground state as a function of the bombarding electron energy. In our earlier paper[6] we reported briefly the results of our studies of the ionization of singly and doubly charged ions of Hg, Xe, Kr, Ar, and Ne by electron impact. In actual plasma phenomena, ionization of excited atoms[7] and ions by electrons can play an important role, particularly for ions with a large number of electrons. The purpose of the present study is the experimental investigation of ionizing collisions of electrons with different multiply charged positive ions formed by the ionization of neutral atoms by electron impact.

2. EXPERIMENTAL METHOD

The investigations were made by means of intersecting ion and electron beams in a double mass spectrometer in which an electron gun was placed between two magnetic analyzers (Fig. 1). The ions under study were obtained from an ion source in which neutral gas atoms were ionized by electron impact. The ions, accelerated by a 2800 volt potential in the ion source, passed through the first analyzer which focused onto slit S_1 an ion beam with a definite value of m/e (ratio of ion mass m to ion charge e). The analyzed ion beam was intersected at right angles by an electron beam from an electron gun. Ions formed in collisions of the parent ions with the electrons were analyzed according to m/e value by the second analyzer and recorded by a detector. The electron gun was constructed from the electrodes of a 6P3S beam tetrode with an oxide cathode, and produced an electron beam in the shape of a flat ribbon with a cross

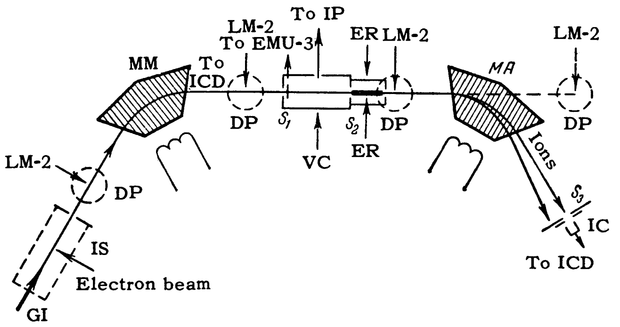

FIG. 1. Diagram of the double mass spectrometer with the electron gun: MM—mass monochromator (first analyzer); MA—mass analyzer (second analyzer); S_1, S_2, S_3—slits; EG—electron gun; ER—electron ribbon; IS—ion source (GI—gas inlet); IC—ion collector; DP—diffusion pump TsVL-100; IP—ion pump type ENS-1; VC—vacuum chamber; IG—ionization gauge type LM-2; ICD—ion current detector, type SI-01.

section of 0.2 × 3 cm. The electron current to the electron collector could be adjusted from 1 to 20 mA, and the electron energy from 10 to 500 eV. During the measurements the gas pressure was 5×10^{-6} mm Hg in the region between the ion source and slit S_1, 1×10^{-7} mm Hg between slits S_1 and S_2, and 1×10^{-6} mm Hg between slits S_2 and S_3. The ion current measurements were made with an ÉMU-3 electrometer amplifier and a Faraday cup collector or with a secondary emission multiplier (SEM), depending on the magnitude of the current being measured.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The ions Hg^+, Xe^+, Kr^+, Ar^+, Ne^+, Hg^{2+}, Xe^{2+}, Kr^{2+}, Ar^{2+}, and Xe^{3+}, obtained from ionization of the corresponding neutral atoms in the source by electrons of energy E_1, were ionized by electrons in the region of the electron gun. From the variation in the yield of secondary ions in the single ionization processes

$$B^+ + e \rightarrow B^{2+} + 2e, \tag{1}$$

$$B^{2+} + e \rightarrow B^{3+} + 2e \tag{2}$$

(B^+ is the ion under investigation) as a function of the energy E_2 of the electrons from the gun, we determined the maximum ionization probabilities of the ions in question for $E_2 = E_{max}$. The experimental absolute cross sections for single ionization of the ions were calculated from the formula

$$\sigma_e = \frac{J^{(n+1)+}}{J^{n+}} \frac{n}{n+1} \frac{1}{J_e} \frac{ev_- V}{\sqrt{v_-^2 + V^2}} h, \tag{3}$$

where J^{n+} is the current of the parent ions, $J^{(n+1)+}$ is the current of ions obtained from ionization of the parent ions, n and (n+1) are the ionization multiplicities of the parent and secondary ions, J_e is the current of electrons intersecting the ion beam, e is the electronic charge, v_- and V are the respective velocities of the electron and ion, and h is the thickness of the electron beam, which is equal to the thickness of the ion beam.

Table I lists the experimental cross sections for single ionization of the ions studied for E_1 = 150 eV and $E_2 = E_{max}$, computed from formula (3) using our earlier data[6] and new measurements. The errors in the values listed are ±20% for the heavier ions and ±30% for Ar^+, Ar^{2+}, and Ne^+. Incomplete intersection of the electron and ion beams and nonuniformities in the beams can occur in the experiment. Therefore all the values of σ_e found may prove to be too low. An estimate of this factor gives a figure of 10%. The second line of Table I lists values of the theoretical ionization cross sections σ_t of the respective ions from their ground states, at the peak of the ionization curves. These values were computed from the formulas of Drawin[8] and Gryzinski[9]. Since the results obtained according to [8] and [9] agree closely, we have listed in Table I the average of these two calculations (for Hg^+ and Hg^{2+}, σ_t was computed only according to [8]). Table I also lists the ionization potentials of the respective ions from their ground states[10].

We can see from Table I that

1) the ionization cross section σ_e of the heavy ions, regardless of their charge (Hg^+, Xe^+, Kr^+, Hg^{2+}, Xe^{2+}, Kr^{2+}) is larger than σ_e for the light ions (A^+, Ne^+);

2) for a number of the ions listed, σ_e is larger than σ_t and does not always follow the variation of σ_t.

We found that the magnitudes and the variation of the cross sections for single ionization in the second electron collision depend noticeably on the energy E_1 of the electrons which ionize the neutral atoms in the ion source. Figure 2 shows a curve of the single ionization probability of Xe^+ ions as a function of E_1. The energy and current of the

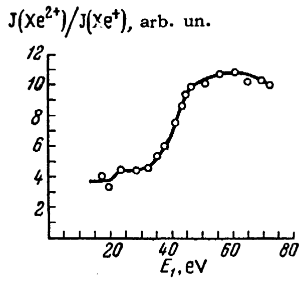

FIG. 2. Ratio of secondary to parent ion current as a function of ion source electron energy E_1, for E_2 = const. In plotting the curve, background was not taken into account.

Table I

Ions	Hg^+	Xe^+	Kr^+	Ar^+	Ne^+	Hg^{2+}	Xe^{2+}	Kr^{2+}	Ar^{2+}
σ_e, 10^{-16} cm^2	4.2	5.6	7.0	1.4	0.4	6.0	5.4	1.6	2.0
σ_t, 10^{-16} cm^2	2.0	2.0	1.5	1.1	0.5	0.6	0.8	0.6	0.5
V_i, eV	18.5	21.18	24.28	27.64	40.67	32.4	31.33	35.71	40.9

electron beam from the gun were held constant in this case (E_2 = 150 eV, J_e = 10 mA). The variation of the ionization cross section of the other ions with E_1 has basically the same shape as the curve of Fig. 2.

Figure 3 shows the variation of σ_e with E_2 for Kr^+ ions for two values of E_1. It is clear from Fig. 3 that, with an increase of E_1, the potential at which Kr^{2+} ions appear in the second electron collision is shifted towards lower values of E_2, the position of the peak of the curve is also shifted to lower E_2, and the height of the peak increases markedly. A similar shift in the ionization threshold potential occurs for Xe^+ ions. Thus, for example, if Xe^+ ions, formed by electrons with E_1 = 30 eV in the ion source, are ionized, the process $Xe^+ + e \rightarrow Xe^{2+} + 2e$ has a threshold at E_2 = 20 eV, which agrees satisfactorily with the known single ionization potential [10] of the Xe^+ ion (about 21.2 eV). If E_1 = 60 eV, then this process commences at an energy E_2 = 10 eV or perhaps even lower.

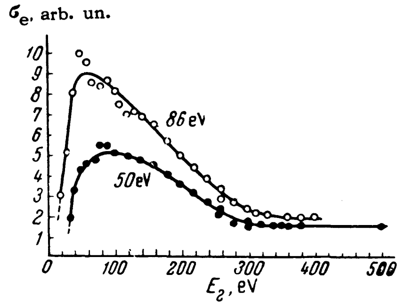

FIG. 3. Kr^+ single ionization cross section as a function of electron gun energy E_2 for E_1 = 50 eV and E_1 = 86 eV.

On the basis of the facts given above we can draw the following conclusion: In the ionization of neutral atoms by electrons whose energy E_1 is above a definite minimum value, a fraction of the ions are formed in metastable excited states; the presence of such ions is manifest in the values of their ionization cross sections in a second electron impact and in other phenomena discussed in this paper. From the data of Table I it is clear that for Ne^+ the experimental ionization cross section σ_e is close to the theoretical cross section σ_t. Evidently, strongly excited Ne^+ ions are not present in the Ne^+ ion beam in sufficient quantity to change the ionization cross section appreciably. Consequently, the formation of metastable states of Ne^+ with lifetimes greater than $\approx 10^{-5}$ sec (the time of flight of an ion from the ion source to the electron gun) occurs with a low probability. This observation agrees with the data of Hagstrum.[11]

Table II. Atomic and ionic energy states of xenon

	Level	Energy, eV
Ground state of Xe atom	$^1S_0$	0
Ground state of Xe^+ ion	$^2P_{3/2}$	12.13
Metastable states of Xe^+ ion	$^2P_{1/2}$	13.44
	$^4D_{7/2}$	23.96
	$^4F_{7/2}$	24.38
	$^4F_{9/2}$	24.45
	$^2F_{7/2}$	26.37
Ground state of Xe^{2+} ion	$^3P_2$	33.34

Various metastable states of the ions listed in Table I are known from the work of Hagstrum and others [11-13]. Let us discuss, for example, the Xe^+ ion. Table II lists several states of Xe, Xe^+, and Xe^{2+} and their energies as given by Hagstrum [11] and Koch and Lindholm [12]. Xe^+ ions in the metastable states $^4D_{7/2}$, $^4F_{7/2}$, $^4F_{9/2}$, and $^2F_{7/2}$ should be formed in the ion source for electron energies E_1 = 24—26 eV. We can see from Fig. 2 that a rapid rise in the ionization cross section of Xe^+ in the second electron impact begins at energies $E_1 \approx 33$ eV, although some rise is visible at $E_1 \approx 25$ eV. From these data we can conclude that in our experiments the Xe^+ ion beam contains, in addition to ions in the ground state, ions in the metastable excited states listed in Table II and ions in still higher energy states.

The formation of metastable excited states in ions with many electrons can occur by at least three processes.

1. The incident electron singly ionizes a neutral atom by removing an electron from an inner shell. The singly charged ion formed can remain in a highly excited metastable state or go by radiative transition to lower metastable levels. In the formation of doubly, triply, or more highly charged ions, single ionization of the parent atom must be accompanied by Auger transitions with the loss of one or more electrons.

2. Metastable ions can be formed by removal of one or more electrons from the outer shell by the incident electron, with simultaneous excitation of at least one of the bound electrons.

3. In the ionization region of the ion source, charge-exchange processes of the type $B^{n+} + B \rightarrow B^{(n-1)+*} + B^+$ can lead to the formation of metastable ions ($B^{(n-1)+*}$ is an excited ion, n = 2, 3, 4). Our results and also those of Hagstrum [11] show that the yield of metastable ions depends weakly

on the ion source gas pressure. Therefore metastable ion formation by charge-exchange processes is not important under the conditions of our experiment.

In view of the absence of the necessary data, we are not in a position to describe quantitatively all possible processes of metastable ion formation. Qualitative considerations require us to postulate that, of the mechanisms discussed for metastable ion formation, the first one is apparently the most probable.

The existence of metastable excited ions is also revealed in studies of the yield of ions of different ionization multiplicities in ionizing collisions of electrons with the parent ions. In Fig. 4 the relative cross sections are plotted for formation of Xe ions with charges from 2 to 6 in ionization of Xe^+, as a function of the electron energy E_2. The cross sections for production of Xe^{2+} ions at the peak of the ionization curve is taken as unity. Comparison of the "ion spectrum" of Fig. 4 with the Xe "ion spectrum" obtain by Fox[14] in ionization of neutral Xe atoms by electrons shows a larger relative yield of ions with removal of a single electron from the parent ion than from the neutral atom. The same holds true for the "ion spectra" obtained by Kupriyanov and Latypov[6] in the multiple ionization of Hg^+ and Kr^+. It is clear that the excitation energy of the metastable Hg^+ and Xe^+ ions affects the single ionization cross sections more strongly than those for multiple ionization.

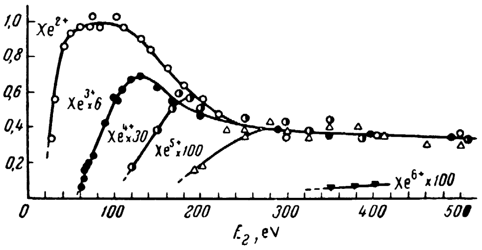

FIG. 4. Relative production cross sections of Xe^{n+} ions ($n = 2 - 6$) as a function of E_2 in the processes $Xe^+ + e \to Xe^{n+} + ne$ ($E_1 = 150$ eV).

It should be noted that the curves of ionization probability corresponding to process (1) (for example, Figs. 3 and 4) have a complex structure in the region of the peak, which is systematically reproduced in experiment. We have drawn smooth curves through all the experimental points. Fox [14,15], in studies of the multiple ionization of the neutral atoms Ne, Ar, Kr, and Xe, has shown that the multiple ionization cross section is a linear function of the excess of the incident electron energy over the ionization potentials. Fox suggested that multiple ionization of atoms by electron impact can be explained mainly as the result of the removal of an electron from an inner orbit and the resulting Auger transitions. This conclusion seems natural in the light of the work of Burhop[16] and Melton[17]. This is in agreement with the mechanism which we have suggested as the most probable for the formation of metastable excited ions.

Investigations of the yield of secondary ions in the single ionization processes (1) and (2) are interrelated with the treatment of a background which is found to be superposed on the current of B^{2+} ions (for ionization of singly charged ions) and B^{3+} ions (for ionization of doubly charged ions). We observed this background in the ionization of all the ions listed in Table I. A detailed study of the origin and behavior of the background for various experimental conditions has allowed us to make corrections to the measured ionization cross sections and has confirmed the existence of metastable excitation in the parent ions.

The main sources of background in studies of the ionization of ions are the following: a) a fraction of the parent ions accelerated by the 2800 volt potential are singly ionized near the surface of slit S_1 (Fig. 1) and, passing through the region of the electron gun and the second analyzer magnet, are counted as the result of processes (1) and (2); b) a fraction of the parent ions are singly ionized in collisions with the residual gas ("stripping") in the region between the two magnetic analyzers and are counted as the result of processes (1) and (2).

Studies of the ionization of the parent ions at the edges of slit S_1 were made with the electron gun turned off. It was shown that the part of the background due to (a) above appears only at electron energies E_1 in the ion source for which highly excited ions are formed, and depends strongly on the width of slit S_1. The part of the background due to stripping of the parent ions in the gas in the apparatus (case (b)) was somewhat smaller than the part connected with processes at the edges of slit S_1. This was shown by study of the dependence of the background on the pressure in the different parts of the system. In measurements of ion currents near the peaks of the ionization curves for the various ions, the background in most cases did not exceed 20% of the total current.

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[1] A. Burgess, Astrophys. J. **132**, 503 (1960).

[2] E. R. Hill, Aust. J. Sci. Res. **4A**, 437 (1951).

[3] S. Schwartz and H. Zirin, Astrophys. J. **130**, 384 (1959).
[4] F. B. Malik and E. Trefftz, Z. Naturforsch. **16a**, 583 (1961).
[5] Dolder, Harrison, and Thoneman, Proc. Roy. Soc. (London) **A264**, 367 (1961).
[6] S. E. Kupriyanov and Z. Z. Latypov, JETP **45**, 815 (1963), Soviet Phys. JETP **18**, 558 (1964).
[7] Biberman, Toropkin, and Ul'yanov, ZhTF **32**, 827 (1962), Soviet Phys. Tech. Phys. **7**, 605 (1963).
[8] H.-W. Drawin, Z. Physik **164**, 513 (1961).
[9] M. Gryzinski, Phys. Rev. **115**, 374 (1959).
[10] G. W. Kaye and T. H. Laby, Tables of Physical and Chemical Constants and Some Mathematical Functions, 10th ed., London, New York, Longmans, Green, 1948.
[11] H. D. Hagstrum, Phys. Rev. **104**, 309 (1956).
[12] H. von Koch and E. Lindholm, Arkiv Fysik **19**, 123 (1961).
[13] P. Wilmenius and E. Lindholm, Arkiv Fysik **21**, 97 (1962).
[14] R. E. Fox, J. Chem. Phys. **33**, 200 (1960).
[15] Advances in Mass Spectrometry, edited by J. Waldron, Pergamon, 1959, p. 397.
[16] E. H. S. Burhop, The Auger Effect, Camb. Univ. Press, 1952.
[17] C. E. Melton, J. Chem. Phys. **37**, 562 (1962).

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