## LONG-LIVED HIGHLY EXCITED STATES OF POSITIVE IONS

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Experimental data are reported on the "stripping" and ionization of He<sup>+</sup>, Xe<sup>+</sup>, Xe<sup>2+</sup>, and  $Xe^{3+}$  ions near a metal surface. It is shown that highly excited ions are present in beams of these ions and that their states are close to a continuous spectrum. These ion states are long lived. It is noted that such states can be found also in some other ions.

**I** T is known<sup>[1]</sup> that the lifetimes  $T_{nl}$  of the quantum states of the hydrogen atom increase with increase of the principal quantum number n. For a fixed azimuthal quantum number l, we have  $T_{nl} \propto n^3$ , and the average lifetime  $T_n$  of the n-th quantum state increases with increase of n much faster:  $T_n \propto n^{4.5}$ . From this, we can expect that all the highly excited quantum states of the H atom and the He<sup>+</sup> ion are long-lived. It is clear that the highest quantum states lie near the corresponding ionization thresholds:  $\approx 13.5$  eV for the H atom and  $\approx 79$  eV for the He<sup>+</sup> ion.

To detect long-lived highly excited states of ions, we used the method of second impact, based on the dependence [2,3] of the inelastic process cross section on the ionic quantum state.

One of the possible inelastic processes, which is convenient for the detection of highly excited ions, forms the basis of the earlier used method of second ionization<sup>[4,5]</sup> by one of the following three processes.

1. The ionization of ions by electron impact:

$$A^{k+} + e \to A^{(k+1)+} + 2e,$$
 (1)

where k is the ion charge. This has been used to detect the presence of metastable highly excited ions using their large ionization cross section, the change of this cross section with the ion state, [4] and the values of the ionization potentials of the ions. [5]

2. The ionization of ions on collision with atoms and molecules in the region of low ion energies: <sup>[5]</sup>

$$A^{k+} + A \to A^{(k+1)+} + A + e.$$
 (2)

3. The ionization of ions near metal surfaces: <sup>[5]</sup>

$$A^{k+} \to A^{(k+1)+} + e. \tag{3}$$

In the present paper, we shall present briefly

the results of experiments carried out to prove the existence of highly excited long-lived states of He<sup>+</sup>, Ne<sup>+</sup>, Ar<sup>+</sup>, Kr<sup>+</sup>, Xe<sup>+</sup>, Hg<sup>+</sup>, Kr<sup>2+</sup>, Xe<sup>2+</sup>, and Xe<sup>3+</sup> ions. These states, as will be shown below, lie quite close to the continuous spectrum.

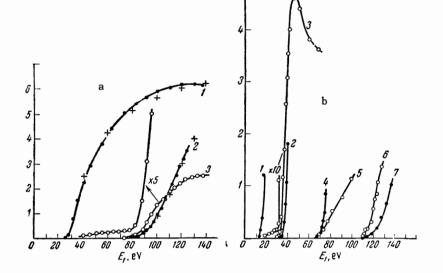
The work was carried out on a double mass spectrometer.<sup>[5]</sup> The composition of a beam of ions after excitation was controlled by varying the energy  $E_1$  of the electrons which ionized the gas in the ion source. The voltages used to accelerate electrons in the ion source were recorded to within  $\approx 0.5$  V. The scatter of the electron energies amounted to  $\approx 0.3$  eV.

The figure shows the dependences of the He<sup>+</sup>,  $He^{2+}$ ,  $Xe^{+}$ ,  $Xe^{2+}$ ,  $Xe^{3+}$ , and  $Xe^{4+}$  ion currents on the electron energy  $E_1$ . The curves drawn through the black dots represent the formation of ions in the processes

$$A^{0} + e \rightarrow A^{k+} + (k+1)e.$$
 (4)

The curves drawn through the open circles represent the formation of ions with the corresponding charge in the processes (2) and (3). Similar dependences were obtained for all the ions listed above.

The figure (a) shows satisfactory agreement of our ionization curves for He with the data of Fox.<sup>[6]</sup> We can see from the curves that the ion currents of the doubly, triply and quadruply charged ions, formed in the processes (2) and (3), rise sharply near the appearance potentials of the ions whose charge is one unit larger than that of the initial ions. Taking into account the error due to the large difference (a factor of about  $10^5$ ) between the intensities of the primary ions and the ions formed in the processes (2) and (3), we may conclude that the differences in the threshold energies do not exceed 0.5-1 eV. The differences between the threshold Dependence of the ion currents (in arbitrary units) on the energy of electrons  $E_1$  which ionize He<sup>0</sup> and Xe<sup>0</sup> atoms in an ion source (arrows with numbers indicate the parts of the curves near thresholds which are plotted on larger scale); a) ionization of helium: 1) He<sup>0</sup> + e  $\rightarrow$  He<sup>+</sup> + 2e; 2) He<sup>0</sup> + e  $\rightarrow$  He<sup>2+</sup> + 3e; 3) He<sup>+</sup>  $\rightarrow$  He<sup>2+</sup> + e; the cross represents Fox's data;<sup>[6]</sup> b) ionization of xenon: 1) Xe<sup>0</sup> + e  $\rightarrow$  Xe<sup>+</sup> + 2e; 2) Xe<sup>0</sup> + e  $\rightarrow$  Xe<sup>2+</sup> + 3e; 3) Xe<sup>+</sup>  $\rightarrow$  Xe<sup>2+</sup> + e; 4) Xe<sup>0</sup> + e  $\rightarrow$  Xe<sup>3+</sup> + 4e; 5) Xe<sup>2+</sup>  $\rightarrow$  Xe<sup>3+</sup> + e; 6) Xe<sup>3+</sup>  $\rightarrow$  Xe<sup>4+</sup> + e; 7) Xe<sup>0</sup> +  $e \rightarrow$  Xe<sup>4+</sup> + 5e.



energies for all the processes investigated by us

$$\begin{array}{ccc} \mathrm{He^{+} \rightarrow He^{2+}, & \mathrm{Ne^{+} \rightarrow Ne^{2+}, & \mathrm{Ar^{+} \rightarrow Ar^{2+}, & \mathrm{Kr^{+} \rightarrow Kr^{2+}, \\ \mathrm{Xe^{+} \rightarrow Xe^{2+}, & \mathrm{Hg^{+} \rightarrow Hg^{2+}, & \mathrm{Kr^{2+} \rightarrow Kr^{3+}, & \mathrm{Xe^{2+} \rightarrow Xe^{3+}, \\ \mathrm{Xe^{3+} \rightarrow Xe^{4+}} \end{array}} \end{array}$$

and the appearance potentials of the ions with the corresponding charge  $(2^+, 3^+, 4^+)$  in the processes (4), lie within the same limits.

The figure shows also that curves denoted by 3 do not decrease to zero on reduction of the electron energy below the region where the He<sup>2+</sup> and Xe<sup>2+</sup> ion currents change rapidly in the processes (2) and (3). These tails of the curves 3 are due to the "stripping" of the singly charged nonexcited ions or those excited to lower states in the electron energy region below  $\approx$ 79 eV for He<sup>+</sup> and  $\approx$  33 eV for Xe<sup>+</sup>. In the latter case, there is a slight discontinuity in the curve near 24 eV, which is due to the appearance in the beam of metastable ions of known<sup>[7]</sup> states <sup>4</sup>D(23.96 eV), <sup>4</sup>F(24.38 eV), <sup>4</sup>F<sub>9/2</sub> (24.45 eV), <sup>2</sup>F<sub>9/2</sub>(26.37 eV).

Special experiments carried out for the purpose of eliminating other possible processes showed that the sharp rise of the intensity of the secondary ions formed in the processes (2) and (3), near the closelying ionization potenials of the corresponding atoms, was due to the appearance, in the primary ion beams, of highly excited ions having various charges. These excited ions were long-lived ( $\approx 10^{-6}-10^{-5}$  sec) and were very likely to be ionized in the processes (1)-(3).

The results reported above confirm and supplement the results of earlier  $work^{[4,5]}$  in which large ionization cross sections were obtained and explained by the presence of a fraction of highly excited ions in the beams. Recently, there has been a report<sup>[8]</sup> of the existence of highly excited  $Ar^+$  ions formed in argon by the process (2). This report confirms our previous conclusions<sup>[4,5]</sup> and is in agreement with the results reported in the present communication.

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<sup>3</sup>D. R. Bates, Atomic and Molecular Processes, New York (1962).

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<sup>5</sup> Latypov, Kupriyanov, and Tunitskiĭ, JETP **46**, 833 (1964), Soviet Phys. JETP **19**, 570 (1964).

<sup>6</sup> R. E. Fox, Advances in Mass Spectrometry (ed. by J. D. Waldron), New York, 1959, p. 397.

<sup>7</sup>C. E. Moore, Atomic Energy Levels, National Bureau of Standards Publ. No. 467, 1-3, Government Printing Office, Washington, 1949-1958.

<sup>8</sup>J. W. McGowan and L. Kerwin, Can. J. Phys. 41, 1535 (1963).

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