OBSERVATION OF HIGHLY EXCITED HYDROGENLIKE STATES OF Ca^+, Sr^+, Ba^+, *AND* Mg^+ *IONS*

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It is shown that in collisions between electrons and Ca, Sr, Ba, or Mg atoms highly excited hydrogenlike states (Rydberg states) of singly-charged ions are formed as a result of (1) stripping of one outer electron and excitation of another outer electron to a state with high principal quantum number n, or (2) excitation of an inner electron to a high-n state followed by rapid autoionization. Rydberg states have also been observed in doubly-charged Ca^{2+}, Sr^{2+}, and Ba^{2+} ions.

EXPERIMENTAL results described in this communication indicate that in electron-atom collisions highly-excited hydrogenlike states of multielectron ions can result from either (1) the stripping of one outer electron and the excitation of another outer electron to a state possessing a high value of the principal quantum number n, or (2) the excitation of one inner electron to a high-n state followed by rapid autoionization.

In this investigation with a mass spectrometer a 70% transparent copper grid was positioned between the ion source and the analyzer. Ions formed in electron beam collisions with atoms were accelerated at V = 3.1 kV and passed through the fine grid; here some of the singly-charged ions (A^+) became doubly-charged ions (A^{2+}) when the highly excited hydrogenlike ions were ionized close to the metallic surface.[1] A low voltage $V_g \sim 100-400$ V was applied to the grid.

To determine the processes producing highly excited Ca^+, Sr^+, Mg^+, and Ba^+ ions an investigation was performed, to determine the influence of electron energy and current strength on the intensity of singly charged ions (A^+) that are produced when electrons collide with Ca, Sr, Mg, and Ba atoms in an ion source:

$$A + e \rightarrow A^+ + 2e, \qquad (1)$$

and of doubly charged ions (A^{2+}) produced from highly excited singly charged Ca^+, Sr^+, Mg^+, and Ba^+ ions close to the metallic (Me) surface of the grid:

$$A^+ + Me \rightarrow A^{2+} + Me. \qquad (2)$$

The accompanying figure shows some of the observed dependences. All ion intensities depend linearly on the electron current in the region 0.15–0.8 mA. The intensities of doubly charged ions are directly proportional to the intensities of the corresponding singly charged ions. The curves reveal that the Ca^{2+} and Sr^{2+} currents resulting from the corresponding A^+ ions through process (2) begin to appear only when the electron energy approaches (with ~0.5-eV accuracy) the detachment energy of two outer s electrons. Consequently, at the given electron energy, in the singly charged beams the highly excited Ca^+ and Sr^+ ions are produced by interactions between an incident electron and two outer electrons ($4s^2$ in the case of Ca and $5s^2$ in the case of Sr). One of these outer electrons is stripped off, while the other electron is excited to a state with high n and some one among different values of l, the azimuthal quantum number. The doubly-charged ion intensity rises steeply when the electron energy approaches (with ~ 1.5-eV accuracy) the binding energy of an inner electron ($3p^6$ in Ca and $4p^6$ in Sr). At this energy a new production of highly excited singly charged ions is initiated as incoming electrons interact with inner electrons of the atoms; one inner p electron is excited into a high-n state, thus producing a highly excited atom of Ca ($3p^5 4s^2 nl$) or Sr ($4p^5 5s^2 nl$). Coulomb interaction between the s and p shells causes these atoms to decay rapidly through autoionization,[3] leaving the highly excited singly charged ions Ca^+ ($3p^6 nl$) or Sr^+ ($4p^6 nl$) where only one electron exists in a high-n state. The probability of autoionization through ejection of the nl electron varies as n^{-3} and is therefore small for high n.

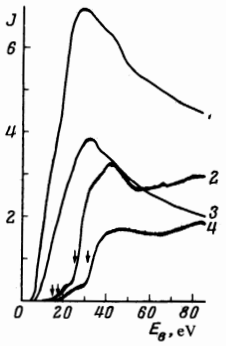
The doubly charged ions Ba^{2+} and Mg^{2+} are produced from singly charged ions via process (2) at two electron energies: Ba^{2+} at ~ 15.4 and 20.8 eV, and Mg^{2+} at ~ 22 and 56 ± 3 eV. The higher values are close to the binding energies of inner p electrons.

It has thus been found that highly excited hydrogenlike states of the investigated singly charged ions result mainly from two processes in electron-atom collisions: 1) ionization and the excitement of outer s electrons, and (2) excitation of one inner p electron. The forms of curves 2 and 4 in the figure indicate that other processes also participate in the formation of highly excited singly charged ions.

In accordance with [4] it can be concluded that in electron collisions with Ca and Sr atoms two types of long-lived highly excited Ca^+ and Sr^+ states are produced:

1. Hydrogenlike states with one excited electron. These ions are converted into doubly charged ions only by some external influence such as an interaction with a metallic surface.

2. Autoionizing states with two excited electrons. The lowest autoionizing states of Ca^+ and Sr^+ appear to be analogous to postulated[5] metastable autoionizing states of the respective isoelectronic atoms K and Rb. In this case the autoionizing quartet state ($4p^5 4d5s\,^4F_{9/2}$) of Sr^+ should be metastable. This state results when one $5s^2$ electron is detached and one $4p^6$ electron is excited



Dependence of ion current I (in arbitrary units) on electron energy E_e: 1) Sr^+, 2) Sr^{2+}, 3) Ca^+, 4) Ca^{2+}. The arrows mark the detachment energies of the two outer electrons and one inner electron.[2] The curves were recorded automatically using an electronic potentiometer, with $\sim 2 \times 10^{-7}$ Torr pressure at the grid and total electron currents of 0.4 and 0.8 mA in the ionization of Ca and Sr, respectively.

into a 4d state with exchange. At higher incident electron energies this atomic electron can be excited into still higher nl states. With higher values of n we can have highly excited hydrogenlike ionic states with two excited electrons, one of which is in the 5s state and the other is in a higher-n state.

In the case of barium we have not observed any appreciable production of metastable autoionizing states in Ba^+. Highly excited Ba^+ is converted into doubly charged Ba^{2+} through interaction with a metallic surface and therefore has hydrogenlike states.

We have also observed that highly excited hydrogenlike Ca^{2+}, Sr^{2+}, and Ba^{2+} can be converted into the corresponding triply charged ions in the vicinity of a metallic surface.

The maximum yield of doubly charged ions A^{2+} produced in process (2) is ~ 0.003, 0.005, 0.006, and 0.008% of the maximum yield of singly charged ions Mg^+, Ca^+, Sr^+, and Ba^+, respectively, in process (1). The A^{2+} yield from the autoionization of Ca^+ and Sr^+ is two to three times greater. Only a very small fraction of the highly excited singly charged ions are transformed into doubly charged ions via process (2). We can therefore expect that when electrons collide with Mg, Ca, Sr, and Ba atoms at least 1–2% of the singly charged ions will be formed in long-lived highly excited states.

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2