Mass-spectrometer study of metastable autoionization states of lithium and potassium atoms

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The mass-spectrometer method has been used to study the formation of excited atoms of lithium and potassium in various long-lived states (lifetime $\gtrsim 10^{-6}$ sec), among which are both the well known autoionization quartet states and new quartet and doublet states.

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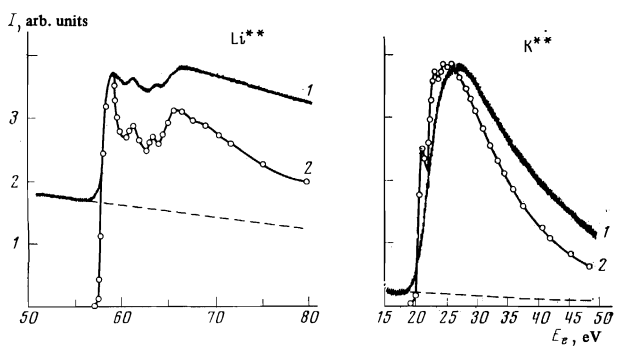
In this article we report new results obtained in study of long-lived (lifetime $\sim 10^{-6}$ sec) excited atoms in a mass spectrometer with a two-chamber ion source of the type described previously[1, 2] to which has been added a furnace producing an atomic beam. Atoms of lithium and potassium were excited in the first chamber by electrons of controlled energy and passed into the second chamber, where they were converted to ions as a result of slow autoionization. The ions Li^+ and K^+ arising in the second chamber were extracted, accelerated to 3 keV, and analyzed in mass-to-charge ratio by the magnetic field of the mass spectrometer. Ions produced in the first chamber in direct ionization and also as the result of fast autoionization of the atoms were removed from the beam by the transverse electric field of a set of deflecting plates placed between the first and second chambers. Only neutral particles could enter the second chamber, which was located a distance of 1 cm from the first.

This technique for studying metastable atoms of lithium and potassium excited to the quartet ionization states $Li^{**}(1s2s2p)^4P_J$ and $K^{**}(3p^54s3d)^4F_J$ is used here for the first time. Previously these atoms have been studied by measurement of the current of electrons or ions directly in the chamber where the autoionization occurred.[3]

Some of the data obtained, together with the results of Feldman and Novick,[3] are given in the figure. We can see the similar behavior of the curves characterizing the excitation functions of the long-lived states of lithium and potassium atoms. For example, for lithium the entire structure is reproduced. There are four distinct peaks. However, no such structure was observed in the excitation function of potassium in our case. The existing single broad peak, which evidently is a superposition of several unresolved narrower peaks, is shifted toward higher electron energies. The drop in the excitation functions of lithium and potassium in the region of high electron energies occurs significantly more slowly than according to the data of Feldman and Novick.[3]



Excitation functions of long-lived autoionization states of lithium and potassium: 1–present work, 2–ref. 3.

These differences in the excitation functions cannot be explained by the effect of highly excited atoms occurring with a large n ($n \gtrsim 10$) in the hydrogen-like states $Li^*(1s^2nl)^2L_J$ and $K^*(3p^6nl)^2L_J$. Atoms of this type, as shown in ref. 4, are ionized near a metallic surface and in an electric field, and also in collisions with molecules of thermal energies.[5] The Li^+ and K^+ ions produced in these processes make a contribution (shown by the dashed line in the figure) to the measured ion current.

To reduce the contribution of highly excited hydrogen-like atoms, an electric field of strength up to $\sim 10^4$ V/cm was applied between the deflecting electrodes. With this field, as a result of ionization, the flux of highly excited atoms was greatly decreased. However, it could not be avoided completely, since part of the atoms in states with low n ($n \sim 10$) were not ionized in the field during their time of flight, and at the same time they were sufficiently long-lived to reach the second chamber (particularly in the case of lithium). The contribution was taken into account on the basis of the excitation functions obtained by us by the method described in ref. 4 for highly excited hydrogen-like states of the lithium and potassium atoms. These functions have peaks at ~7 eV for lithium and ~5 eV for potassium, i.e., near their ionization limits, and then they fall monotonically as in ref. 3. Other experimental conditions were also varied, in particular, the oven temperature, the pressure (admission of gas), and the electron current.

Analysis of all the experiments carried out leads to the conclusion that for single collisions of electrons with atoms of lithium and potassium, three groups of highly excited long-lived states are formed, which are easily distinguished in energy and structure:

1) The hydrogen-like states $Li^*(1s^2nl)^2L_J$ and $K^*(3p^6nl)^2L_J$ with $n \gtrsim 10$. Their excitation energy is small ($Li^* \sim 5$ eV, $K^* \sim 4$ eV), and their lifetimes increase with n as n^3.

2) The metastable quarted ionization states $Li^{**}(1s2s2p)^4P_J$ and $K^{**}(3p^54s3d)^4F_J$, which have a high excitation energy ($Li^{**} \sim 57$ eV, $K^{**} \sim 20$ eV) and lifetime ($Li^{**} \sim 5.1 \times 10^{-6}$ sec, $K^{**} \sim 9 \times 10^{-5}$ sec).[3]

3) The hydrogen-like autoionization quartet states $Li^{***}(1s2snl)^4L_J$ and $K^{***}(3p^54snl)^4L_J$, which have still higher excitation ($Li^{***} \gtrsim 64$ eV, $K^{***} \gtrsim 24$ eV), since in the limit as $n \to \infty$ they converge to the first excited triplet states of the ions $Li^+(1s2s)^3S$ and $K^+(3p^54s)$, and also those of the doublet states $Li^{***}(1s2lnl')^2L_J$ and $K^{***}(3p^54lnl')^2L_J$ for which Coulomb autoionization is forbidden.[6]

Atoms in the hydrogen-like autoionization states belonging to the third group, like the atoms Li** and K**, have two excited electrons, in contrast to the atoms Li* and K* in which only one valence electron is excited. In contrast to the Li** and K** atoms, and like the atoms Li* and K*, they have only one electron excited in states with large n. For $n \gtrsim 10$ they will be sufficiently long-lived to appear experimentally, since Coulomb autoionization is forbidden for them by the selection rules[3, 6] and the probabilities of radiative transitions to lower states fall of as n^{-3} as a result of the hydrogen-like nature of these highly excited states.[6, 7]

In these experiments metastable autoionization quartet states of the lithium and potassium atoms were formed as the result of an exchange collision with an electron, i.e., a collision in which the incident electron replaces an atomic electron with opposite spin direction. The excitation functions of these states are characterized by a sharp rise in the cross section for excitation at threshold and a rapid drop of the excitation function on reaching a sharp peak located near threshold.[8] The excitation functions of states formed without exchange are characterized by a slow rise after the threshold and a slow drop on reaching the peak. In the present case the doublet autoionization states are of this type; their excitation functions should have peaks which are broader than for the quartets and located at higher incident-electron energies, and a less rapid falloff. In the work of Feldman and Novick[3] these states and the hydrogen-like quartet autoionization states were not observed, as a result of their deactivation in the electric field and on traversal of a long pathlength (3–12 cm) from the point of excitation to the point of detection.

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