AUTOIONIZING STATES IN THE ALKALI ATOMS WITH MICROSECOND LIFETIMES*

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In this note we report the existence of atomic energy levels in lithium, potassium, and rubidium which lie between the first and second ionization potentials and which are metastable against both radiation and autoionization with lifetimes in the microsecond region. Much shorter lived autoionizing levels in the same energy range in K and Rb have been previously observed by Beutler,[1] who attributed them to the excitation of an electron from the outermost closed shell of the atom. In addition, the ionization cross-section curves of many elements[2] have been found to exhibit "ultraionization" potentials which are also attributed to the same autoionizing excited-core states.

The selection rules for the autoionization of a discrete energy level lying above the ionization limit to a continuum level of the same energy via the Coulomb operator, $1/r$, require that the initial and final states have the same parity and J value.[3] If Russell-Sanders coupling holds, then L and S must also be conserved. Hence, an excited-core state arising from the excitation of a ground-state ($^2S_{1/2}$) alkali atom by electric dipole radiation will autoionize to the $^1S_0$ ground state of the ion and an outgoing electron in a continuum $k\,^2P_{1/2,3/2}$ state through the Coulomb interaction. The transition probability for this process is of the order of 10^{13}-10^{14} sec^{-1}. Configurations which violate the selection rules for autoionization through the Coulomb interaction cannot be reached from the atomic ground state through electric dipole excitation.

In lithium, the lowest excited-core states arise from the excitation of a $1s$ electron into either a $2s$ or a $2p$ orbital. In the other alkalis, an electron from the outermost p shell is raised to a d state in the same shell or an s or p state in the next higher shell, producing configurations such as (p^5sl). Beutler observed excited-core states by photoabsorption in the wavelength region 1200-600 Å. These states were necessarily odd-parity doublets with J values of 1/2 and 3/2. Quartet states violate the S selection rule for Coulomb autoionization, but only the level with maximum J will be truly metastable, since the other quartet J states many mix with the doublet states of the same J through magnetic interactions (spin-spin, spin-other orbit, etc.) and will be shorter lived. The lowest lying quartet state will also be metastable against radiation to lower atomic states which are necessarily doublets. Kroll[4] has suggested that these quartet states autoionize via the tensor part of the spin-spin interaction. The transition rate for this process is smaller by a factor of α^4 than the Coulomb autoionization rate, and the lifetime of the states is about 10^{-6} sec.

The simplest atoms exhibiting excited-core states are those of the lithium isoelectronic sequence (He^-, Li, Be^+, etc.). This system has been treated theoretically by several authors[5] who have shown that the lowest lying long-lived state is the $(1s2s2p)\,^4P_{5/2}$ state, in He^- lying 0.070 eV below the $^3S_1$ state of the atom, and in lithium, 6.4 eV below the $^3S_1$ level in the ion.[6] Pietenpol[7] has estimated that the spin-spin lifetime of these levels is 1.7×10^{-3} sec for He^- and 1.6×10^{-5} sec for Li. No calculations have been made on the energies of the excited-core states in the other alkalis because of the difficulty of obtaining even approximate wave functions. However, we do know the energies of the doublet states corresponding to the electronic configurations of interest here from Beutler's experimental results on K, Rb, and Cs. (The energies of these states in Li and Na were beyond the short-wavelength limit of his apparatus.) The lowest lying of these are shown in Fig. 1 for Rb, together with the parent states in the rubidium ion. The energy of the lowest excited-core doublet is 15.3 eV above the ground state in rubidium and 18.7 eV in potassium. From the positions of the parent states in the ion, one would expect that the levels of the $(4p^55s4d)$ configuration are lower than those of $(4p^55s5p)$. It is reasonable to expect that the quartets lie a few eV below the doublet states. Since the two configurations are optically connected, the higher one will not be metastable. The $(4p^55s4d)\,^4F_{9/2}$ state is the lowest lying quartet state and is therefore expected to be metastable against both radiation and autoionization. Metastable alkali atoms may be produced by exchange excitation of ground-state atoms.

In the present experiment, a neutral beam of

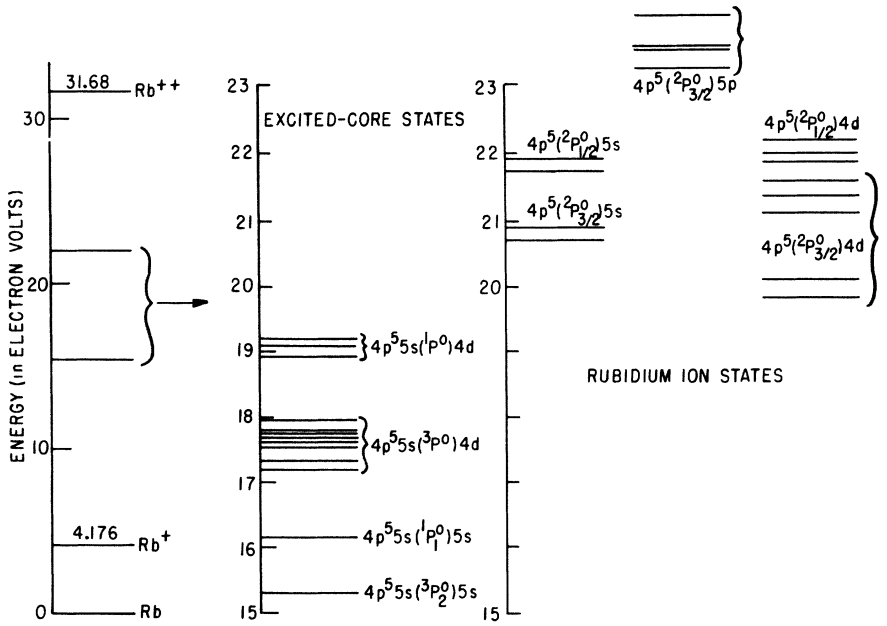

FIG. 1. Energy-level diagram for rubidium showing the lower doublet excited-core states observed by Beutler and some of the low-lying ionic states.

atoms is excited by electron bombardment. Charged particles are removed from the beam by suitable magnetic and electric fields (see Fig. 2). A detector cage is located 3 cm from the center of the bombardment region and long-lived autoionizing atoms are detected by collecting either the ions or the electrons emitted in their decay inside the cage. Excitation curves for lithium, potassium, and rubidium are given in Fig. 3. The same excitation function is obtained with either electron or ion collection. The lithium curve exhibits a threshold at 56 ± 1 eV rising sharply to a maximum (characteristic of exchange excitation) at 58 eV, corresponding to a production cross section of 10^{-19} cm^2. Wu and Shen[5] estimated the energy of the $(1s2s2p)\,^4P_{5/2}$ state in Li at 57.99 eV. The structure observed is attributed to higher

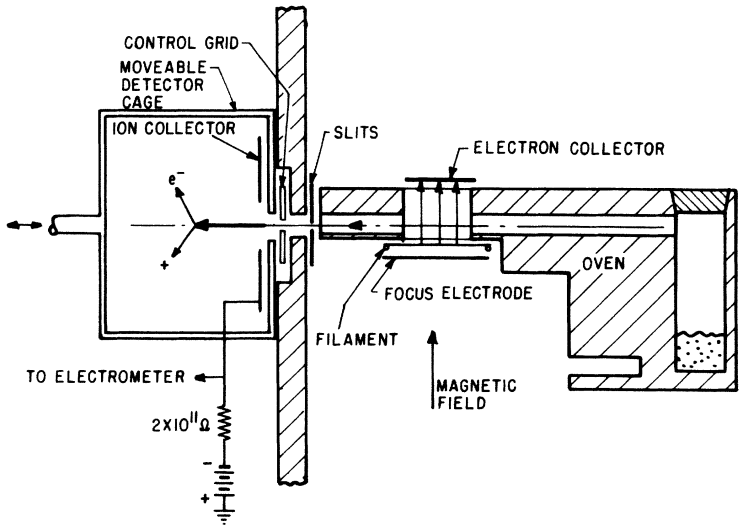

FIG. 2. Schematic diagram of the apparatus.

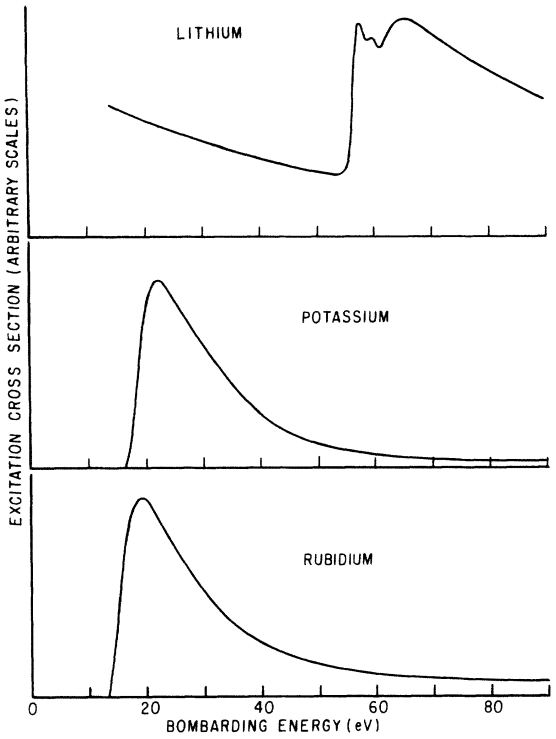

FIG. 3. Excitation functions for the long-lived autoionizing states in lithium, potassium, and rubidium. The collector was biased to collect positive ions.

excited-core states which radiate to the $(1s2s2p)\,^4P_{5/2}$ level in a time short compared with the autoionization lifetime. Several unassigned lines in the spectrum of Li II may be due to such radiative transitions between excited-core quartet states of the atom.[8] The energy thresholds for K and Rb are at 17.5 ± 1 and 14.2 ± 1 eV respectively, both below the lowest doublet excited-core state observed by Beutler. The excitation curves have the characteristic shape for exchange excitation but with no observable structure, and the maximum corresponds to a cross section of about 10^{-18} cm^2. The background below 55 eV on the lithium curve is dependent on the voltage applied to the control grid mounted on front of the detector cage, and may be completely suppressed at several kilovolts without any appreciable change in the magnitude of the metastable signal.

The lifetimes of these long-lived atomic states were determined by measuring the ion current with the detector at different distances from the source. The aperture to the detector cage was fixed so that the entire beam would enter the cage for all detector positions so that no geometrical correction would be necessary. The control grid was placed at a positive potential to keep ions resulting from the decay of autoionizing atoms outside the cage from entering the detector. A typical decay plot for lithium is given in Fig. 4(a). In extracting the lifetime from this data, we have allowed for the Maxwellian velocity distribution of the atoms.[9] The results are for Li, $\tau = 5.1 \pm 1$ μsec; K, $\tau = 90 \pm 20$ μsec; Rb, $\tau = 75 \pm 20$ μsec. There was no significant change in the apparent lifetime as the residual pressure in the system varied from 10^{-5} to 5×10^{-7} Torr, indicating negligible collision quenching. The lithium lifetime is in reasonably good agreement with Pietenpol's

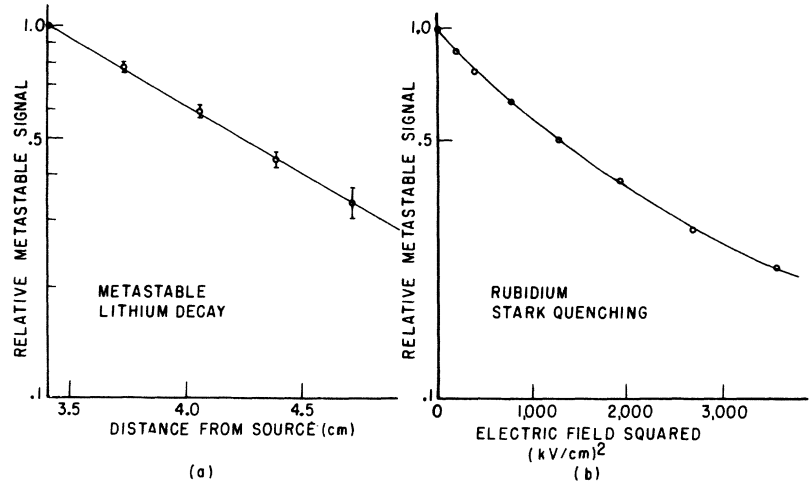

FIG. 4. Decay of the metastable alkali atoms: (a) spontaneous decay in flight of the $(1s2s2p)\,^4P_{5/2}$ state of lithium; (b) electric-field-induced decay of rubidium.

estimate.

The quenching effect of an external electric field was investigated by introducing a field over a 1-cm length of beam path in front of the detector. The Stark quenching observed in rubidium is shown in Fig. 4(b). A smaller effect was observed in potassium, and none in lithium. Since the electric field mixes the metastable state with neighboring states of opposite parity, same spin, and total J differing by 0 or ± 1, one might expect a significant decrease in the lifetime of metastable atoms if the neighboring states satisfying these selection rules are shorter lived. Examples of such neighboring states are $(4p^5 5s4f)\,{}^4G_{9/2,7/2}$ in Rb and $(1s2p^2)\,{}^4P_{3/2}$ in Li. Wu and Shen have estimated that the energy separation between the $(1s2p^2)\,{}^4P_{3/2}$ and $(1s2s2p)\,{}^4P_{5/2}$ states in Li is 3.43 eV. This large separation probably accounts for the absence of an observable quenching effect at the highest field attainable in our apparatus (150 000 V/cm). In K and Rb the neighboring short-lived states are probably much closer to the metastable state.

Further experiments employing the techniques of resonance spectroscopy and magnetic deflection are necessary for complete identification of the observed states, and are in progress in our laboratory. It is also desirable to extend the work of Beutler to shorter wavelengths so that the energies of the excited-core doublet states in lithium and sodium can be determined.[10]

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VARIATIONAL THEORY OF THREE-BODY ELECTRON-ION RECOMBINATION RATES*

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The rate of three-body electron-ion recombination

$$A^+ + e^- + e^- \rightarrow A + e^-$$

is calculated from a classical variational theory, which has proved successful in determining atomic recombination rates in the presence of repulsive third bodies.[1] The above mechanism, in which an electron acts as a third body removing the recombination energy, is known to be important at high electron densities and low temperatures when radiative transitions are unimportant.

A classical solution may be justified only when the deBroglie wavelength is smaller than the characteristic range of the interaction. The appropriate range here is Thomson's radius,[2] $2e^2/3kT$, at which the potential energy of the recombining pair is equal to the kinetic energy, and inside which two ions have a high probability of recombining. Based on this dimension a classical