Inner-shell ionization of potassium atoms ionized by a femtosecond laser

M. P. Hertlein,[1] H. Adaniya,[1] J. Amini,[1] C. Bressler,[2] B. Feinberg,[1] M. Kaiser,[2] N. Neumann,[1,3]
M. H. Prior,[1] and A. Belkacem[1]
[1]*Lawrence Berkeley National Laboratory, Berkeley, California, USA*
[2]*Laboratoire de Spectroscopie Ultrarapide, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*
[3]*Institut für Kernphysik, J.W. Goethe-Universität, Frankfurt am Main, D-60486 Frankfurt, Germany*
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With a femtosecond laser pulse we rapidly ionize potassium atoms (K^0) in the gas phase, generating potassium ions (K^+), and monitor the altered energy-level scheme with a subsequent hard x-ray pulse. Removal of the potassium 4*s* valence electron increases the binding energies of both the valence and the 1*s* core levels, and induces an ultrafast change of the 1*s*-4*p* x-ray transition energy by about 2.8 eV. We simultaneously observe a 50% increase in oscillator strength of K^+ over K^0 for that transition.

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Electrons in atoms and molecules are correlated, making the binding energy of an individual electron a function of its entire atomic environment. A change to this environment, such as the application of an external field or the removal of even a weakly bound valence electron, affects the entire system, including the deeply bound core levels.

This makes the energy levels within a single atom sensitive to the configuration, or simply the presence, of other electrons within the atom. Since the wave function of valence electrons partly extends deep into the ion core, their charge screening can even affect inner-shell electrons: Cubaynes *et al.* [1] has shown that the binding energy of 2*p* (*L*-shell) electrons in sodium changes by 2 eV, or about 5%, when the single 3*s* valence electron is excited to the 3*p* level. The influence of a valence electron extends even to the *K* shell: Comparison of measurements in carbon ions from Refs. [2,3] shows that the energy of transitions involving the *K* shell (1*s*-2*p* transition in C) differs by several electron volts for differently charged ions.

While these effects have been known for a long time theoretically [4], their experimental observation has been hampered due to several experimental limitations. Some information is available about the valence transition energies for ions (including some high charge states) [5,6], but extremely little is known for their deeper bound shells. The difficulties associated with dealing with potassium including its adverse contamination effects on ion and electron detectors [7] have limited the number of inner-shell photoionization potassium studies reported in the literature. The amount of data on potassium ions (K^+) is even more limited. The only study of inner-shell photoionization of singly charged potassium ions was an absorption measurement done in a crystal matrix by Gomilšek *et al.* [8]. However, because the proximity of other ions in the matrix induces chemical shifts, this study does not provide any results on *K*-shell x-ray transitions or oscillator strengths close to the *K* edge for the potassium ion, but instead focuses on two-electron transitions during *K*-shell photoionization.

In a previous study [9] we showed that the 4*s* valence electron of potassium plays a major role in the relaxation of a *K*-shell hole created by an x-ray pulse. In this work we use a femtosecond laser pulse to drive the 4*s* electron into a continuum state, and use hard x-ray pulses from a synchrotron to probe the photoinduced changes to the *K*-shell electrons. These changes occur on an extremely short time scale (much shorter than the 100-fs pulse width of our driving laser pulse), since inner-shell dynamics are typically fast enough [10] to follow valence configuration changes adiabatically. We present the first measurement of *K*-shell x-ray-absorption spectra of ionic potassium in the gas phase.

This experiment was performed at beamline 5.3.1 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. Hard x rays from a bending magnet pass through a Ge(111) double crystal monochromator with approximately 1:3000 energy resolution around 3.6 keV. The focal spot of the x-ray beam has a size of approximately 150×200 μm and is placed at the interaction region in the center of a vacuum chamber with less than 4×10^{-7} mbar background pressure.

The x rays initially pass through a 2-mm-diameter hole drilled at an angle of 45° through the center of a dielectric laser mirror positioned 45 cm upstream of the interaction region (Fig. 1). The larger, converging laser beam is reflected off the mirror, enters the interaction region in a collinear geometry, and comes to a focus about 3 cm downstream of the interaction region. The amplified $Ti:Al_2O_3$ laser system produces 800-nm, 1.6-mJ, 120-fs pulses at 1-kHz repetition rate, and is phase locked [11] to the frequency of the ALS

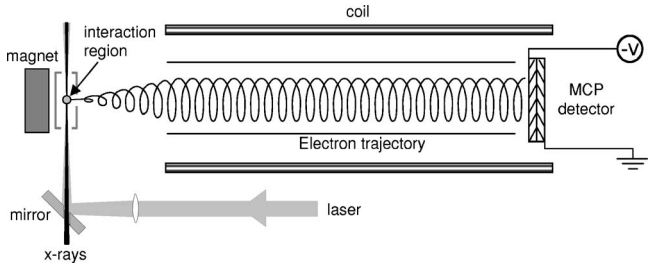

FIG. 1. Schematic of the experimental setup with time-of-flight (TOF) tube. The permanent magnet and the coil provide the magnetic-field gradient that turns and guides electrons from the interaction region towards the detector. The interaction region with the potassium is enclosed except for the photon and electron access holes.

storage ring (500 MHz), producing laser pulses synchronized to the x-ray pulse train with variable time delay (accurate to about 1 ps). The laser beam is focused approximately 3 cm downstream in order to match x-ray and laser beam sizes at the interaction region.

The interaction region marks the source of a magnetic bottle time-of-flight (TOF) spectrometer for detection of energetic Auger electrons produced in the potassium vapor. Although our setup incorporates permanent magnets [12,13], the principle of operation of the spectrometer is similar to the one described in Ref. [14].

The magnetic bottle design enhances the collection efficiency of the isotropically emitted Auger electrons by several orders of magnitude, by guiding them towards the detector microchannel plate (MCP) detector at the end of the tube (Fig. 1) while minimizing differences in time-of-flight for electrons emitted into different directions. Electrons emitted from the interaction region (3-kG field) are turned adiabatically by the strong magnetic gradient towards the TOF tube, where the 100-G magnetic field produced by the coil guides them towards the MCP. The front side of the MCP is biased to −400 V to reject low energy electrons, and only potassium *K-LL* Auger electrons, and primary photoelectrons ejected from the *L* and *M* shells, are energetic enough to reach the front of the MCP to be detected.

The TOF spectrometer has a temporal resolution of about 2 ns for electrons with 3-keV kinetic energy. An effusive oven just below the beams, operated at a temperature near 240 °C, emits gas phase potassium atoms, producing about 10^{11} atoms/cm^3 at the interaction region. To minimize contamination of the vacuum chamber by potassium, the oven is surrounded by a cooled copper enclosure with small access holes for the beams and the Auger electrons.

X-ray-absorption spectra are recorded by scanning the x-ray energies and recording the *K-LL* Auger electron yield at 2-kHz repetition rate, while the laser excites the gas at 1 kHz. This data acquisition strategy has been employed before in time-resolved XAFS measurements [15].

The $1s$-$4p$ transition in atomic K^0 is accessed near 3607.9 eV with a width of 0.74 eV [8], corresponding to a core-hole lifetime of about 1 fs. The resulting $1s$ core hole is primarily filled by $2p$ electrons through an Auger process. Our experimental setup rejects all low-energy electrons, and the *K-LL* Auger electrons dominate the measured count rate. Photoelectrons produced by direct ionization from the *L* and *M* shells only contribute to a flat background, since the cross section for their production does not change appreciably in the x-ray energy range near 3600 eV.

The gray points in Fig. 2 show the static x-ray absorption spectrum (XAS) of atomic potassium. The observed absorption bands reproduce the features of a conventional XAS measurement [8] and those obtained in total ion production rate studies [9]. The $1s$-$4p$ transition at 3607.9 eV is the most dominant feature. Its observed width of about 2.2 eV represents a convolution between the natural linewidth [8] and the x-ray monochromator bandwidth. Higher-lying $1s$-np Rydberg transitions exhibit similar widths, and thus merge into a broad continuum at higher energies due to their closer spacing. Above the ionization potential (IP) of atomic K^0 (IP=3611 eV), Auger electrons are produced after $1s$ excitations to the continuum, and after multielectron excitations (e.g., transitions to the $[1s4s]^{-1}4p5s$ state) which appear as overlapping broad bands in the continuum region [8].

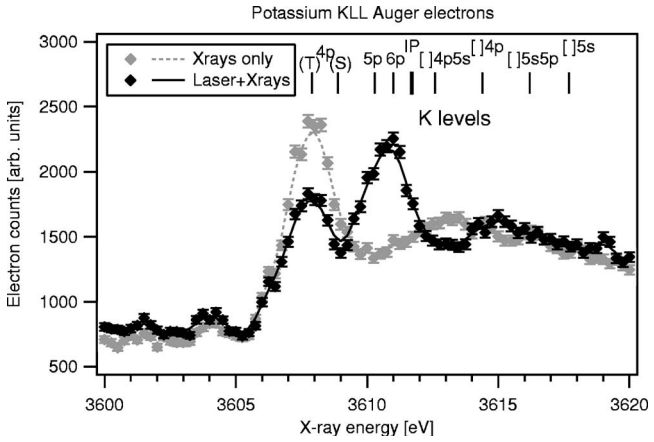

FIG. 2. Energetic electron production as a function of x-ray photon energy, for potassium atoms (gray) and for an atom-ion mix (black) produced by a laser pulse crossing the sample region several ns before the x-ray probe. The solid lines are three-point smoothed data. Indicated on top are the positions of the *K*-shell resonances for the potassium atom,[8] with T and S marking the triplet and singlet $4p$ resonance positions, and square brackets denoting a $1s4s$ double core hole.

Figure 2 also shows the XAS 2 ns after interaction with the laser pulse. The spectrum, originating from a superposition of atomic and singly ionized potassium, displays a prominent new absorption peak 2.8 eV above the atomic $1s$-$4p$ resonance, originating from the blueshifted $1s$-$4p$ transition in K^+. To obtain the XAS of K^+, we subtract a fraction f of the atomic XAS from the observed mixed spectrum, and adjust f such that the atomic $4p$ resonance completely disappears. Figure 3 shows the resulting spectrum obtained for $f=38\%$, corresponding to the bare potassium ion K^+ spectrum.

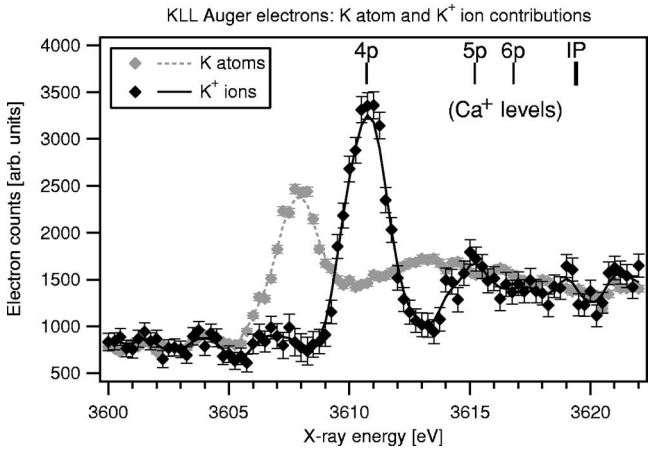

FIG. 3. X-ray absorption of atomic (K^0) and ionic (K^+) potassium in the gas phase as a function of x-ray photon energy, measured via *K-LL* Auger electron yield. The solid lines are three-point smoothed data. Indicated on top are the energies of valence transition levels for a Ca^+ ion, shifted to align the Ca^+ $4p$ level with the K^+ $4p$ presonance.

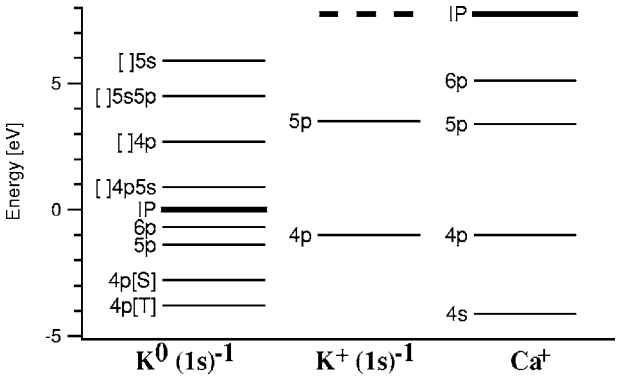

FIG. 4. Energy levels of the potassium atom, and of the singly charged potassium and calcium ions. The left column shows the relative energy levels for 1*s*-*np* excitation of the K atom [8,9]. The center column shows the equivalent observed energy levels for the singly charged K ion. The right column shows the 4*s*-*np* excitation levels of the singly charged calcium ion [5,6], shifted in energy to match the 4*p* level of K^+.

This result is the first measurement of the 1*s*-4*p* transition energy for K^+ in the gas phase. The blueshift of the 1*s*-4*p* transition is due to the missing 4*s* valence electron, which reduces the electronic screening of both the 1*s* and 4*p* orbitals, though by different amounts.

Although only the relative shift between the levels is immediately visible, it is nevertheless possible to extract the individual shifts in binding energy through comparison with the quasi-isoelectronic Ca^+ ion: A core electron in the K^+ potassium ion that is promoted to a 4*p* or higher *np* level initially sees a doubly charged core with a filled $n=3$ shell; a similar environment is seen by the single valence electron in a Ca^+ calcium ion when it is excited to higher levels. The energy spacings between 1*s*-*np* resonances in K^+ therefore closely approximate the spacings between 4*s*-*np* transitions in Ca^+, with increasing agreement for higher *n* where the quantum defect becomes negligible.

Figure 3 shows the energy levels of Ca^+, shifted so the 4*p* level matches the 4*p* peak of K^+. The K^+ peak seen at 3615 eV matches in position with the Ca^+ 5*p* level, and can therefore be attributed to the K^+ 1*s*-5*p* transition. The analogy is further illustrated in Fig. 4, showing the energy positions for the 1*s* core transitions in neutral K^0 and ionic K^+, and for the 4*s* valence transitions in Ca^+ ions. This correspondence allows us to determine the individual 1*s* core and valence level shifts directly from experimental data. Comparison of K^+ and Ca^+ levels indicates that the *K*-shell ionization edge of K^+ is located at about 3619.4 eV, meaning that the 1*s* electron binding energy is increased by 7.7 eV over the atom. This size of the 1*s* shift, determined from our experimental measurements, agrees with a theoretically predicted value of about 7.25 eV, obtained from self-consistent field calculations [16]. The K^+ 4*p* electron is therefore bound by about 8.7 eV, which is a 4.9 eV increase over the atom. The resulting 2.8 eV increase for the 1*s*-4*p* transition agrees reasonably well with a theoretical estimate of about 2.6 eV [17].

Interestingly, we also observe a significant change in oscillator strength for the 1*s*-4*p* transition when going from K^0 to K^+. Figure 3 shows that the 4*p* peak intensity in the potassium ion spectrum is about 50% (±10%) larger than for the neutral atom. This has been attributed to the high sensitivity to charge screening. Theoretical studies indicate that the oscillator strength varies approximately as the fifth power of the ratio of effective nuclear charges seen by the electron in the final and initial states of the transition [18]. Hence even a small change in core charge screening can cause a large change in cross section.

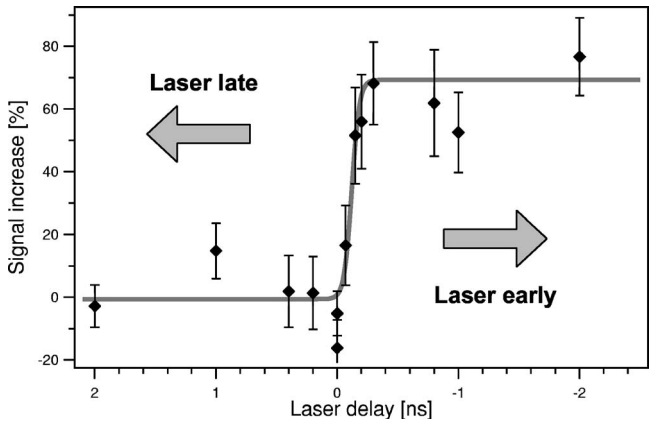

FIG. 5. Change in electron production in potassium after interaction with an ionizing laser pulse and x-ray photons of 3611-eV energy, as a function of laser delay. The solid line is an arctangent fit to the data, with width 68 ps (±20 ps).

Because of the time scales involved for the core hole decay, it is expected that the core and valence levels shift their energetic eigenvalues on a subfemtosecond time scale following removal of a valence electron, thus much faster than the pulse width of the exciting laser. We may also expect that core and valence electrons adjust to their new equilibrium energies on different time scales, which opens up interesting experimental future possibilities with attosecond pulsed laser and x-ray sources. In this work, we are limited by the pulse width of the x rays. This is illustrated in Fig. 5, where we scan the time delay between laser and x-ray pulses while monitoring the Auger electron yield at 3611 eV, corresponding to the ionic K^+ 1*s*-4*p* transition. When the laser precedes or overlaps the x-ray pulse, the laser effectively induces a 70% increase in cross section at this x-ray energy. The observed step function corresponds to a pulse width of 68 ps (±20 ps), reflecting the (full width half maximum) pulse length of the x rays produced by the ALS.

This work exploits time-resolved x-ray-absorption spectroscopy (detecting *K-LL* Auger electrons) to observe singly ionized K^+ in the gas phase, and to directly study the energy-level shifts between K^0 and K^+. We show that an ultrashort laser pulse can induce a fast modification of the cross sections and energies of core electron transitions. We demonstrate that the 1*s* core-level binding energy increases by 7.9 eV upon removal of the 4*s* valence electron, while the 4*p* level shifts by only 4.8 eV, resulting in the observed 2.8 eV blueshift for the 1*s*-4*p* transition. In addition, we find that the oscillator strength of the transition is enhanced by 50% in K^+ due to the reduced core-hole screening from the removed 4*s* electron.

Our measurement is generally limited by the x-ray pulse width of about 70 ps; with the availability of ultrafast x rays, the temporal measurement could be significantly improved. Alternatively, using a laser to drive reversible changes in the valence electron structure, such as bound-bound transitions in potassium (e.g., $4s$-$5p$), would allow probing the induced inner-shell level shifts in the time domain. Alternatively, we are exploring the possibility to include the measurement of the Auger electron energies. Since these electrons are ejected on a subfemtosecond time scale, by analyzing the photoelectron energies in the atom and ion of Auger electrons from different shells (which are emitted at slightly different times) we can already gain insight to the time scale of dynamic energetic shifts. This add-on would propel studies into the attosecond time domain, and provide deeper insight into basic atomic physical processes.

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[1] D. Cubaynes, J. M. Bizau, F. J. Wuilleumier, B. Carré, and F. Gounand, Phys. Rev. Lett. **63**, 2460 (1989).
[2] A. S. Schlachter *et al.*, J. Phys. B **37**, L103 (2004).
[3] S. W. Scully *et al.*, J. Phys. B **38**, 1967 (2005).
[4] I. Lindgren, J. Electron Spectrosc. Relat. Phenom. **77**, 370 (2004).
[5] C. E. Moore, *Atomic Energy Levels as Derived from the Analyses of Optical Spectra*, National Bureau of Standards Circular 467, National Standard Reference Data Series, National Bureau of Standards (US) 35, 1971 (Washington, DC).
[6] Atomic Spectra Database, (http://physics.nist.gov/PhysRefData/ASD/index.html) National Institute of Standards and Technology.
[7] H. G. Berry, Y. Azuma, P. L. Cowan, D. S. Gemmell, T. LeBrun, and M. Ya Amusia, Nucl. Instrum. Methods Phys. Res. B **98**, 25 (1995).
[8] J. P. Gomilšek, A. Kodre, I. Arčon, and R. Prešeren, Phys. Rev. A **64**, 022508 (2001).
[9] M. P. Hertlein, H. Adaniya, K. Cole, B. Feinberg, J. Maddi, M. H. Prior, R. Schriel, and A. Belkacem, Phys. Rev. A **71**, 022702 (2005).
[10] M. Drescher, M. Hentschel, R. Kienberger, M. Uiberacker, V. Yakovlev, A. Scrinzi, Th. Westerwalbesloh, U. Kleineberg, U. Heinzmann, and F. Krausz, Nature (London) **419**, 803 (2002).
[11] M. J. W. Rodwell, D. M. Bloom, and K. J. Weingarten, IEEE J. Quantum Electron. **25**, 817 (1989).
[12] H. Handschuh, G. Ganteför, and W. Eberhardt, Rev. Sci. Instrum. **66**, 3838 (1995).
[13] J. H. D. Eland, O. Vieuxmaire, T. Kinugawa, P. Lablanquie, R. I. Hall, and F. Penent, Phys. Rev. Lett. **90**, 053003 (2003).
[14] P. Kruit and F. H. Read, J. Phys. E **16**, 313 (1983).
[15] M. Saes, C. Bressler, R. Abela, D. Grolimund, S. L. Johnson, P. A. Heimann, and M. Chergui, Phys. Rev. Lett. **90**, 047403 (2003).
[16] I. Lindgren, J. Electron Spectrosc. Relat. Phenom. **137**, 59 (2004).
[17] X.-M. Tong, (private communication).
[18] M. Ya Amusia, A. S. Baltenkov, and G. I. Zhuravleva, J. Phys. B **29**, L151 (1996).