Measurement of the photoionization cross section for the $6p\ ^2P_{3/2}$ state of potassium using a time-of-flight mass spectrometer

Ahmad Yar and Raheel Ali
Atomic and molecular Physics Laboratory, Department of Physics, Quaid-i-Azam University, 45320 Islamabad, Pakistan

M. Aslam Baig*
National Center for Physics, Quaid-i-Azam University Campus, 45320 Islamabad, Pakistan
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The photoionization cross sections for the $6p\ ^2P_{3/2}$ excited state of potassium have been measured using a two-step selective excitation and ionization technique in conjunction with an atomic-beam source and a time-of-flight (TOF) mass spectrometer. The cross sections of photoionization have been measured at three ionizing laser wavelengths, 1064, 689.53, and 532 nm, as 4.80 ± 0.31, 3.59 ± 0.18, and 2.69 ± 0.22 Mb, respectively, and the number density has been determined as 2×10^{11} cm^{-3}. The presently measured experimental values of the photoionization cross sections are in excellent agreement with the theoretical calculations.

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I. INTRODUCTION

The photoionization from the excited states of atomic systems provides an opportunity to investigate the dynamic interplay among many-body electron-electron correlations and relativistic effects. Cross sections are also important as applied data because photoionization takes place in many physical systems, including a large variety of astrophysical systems, the upper atmosphere, and different types of laboratory plasma. The alkali-metal atoms are particularly motivating because sufficient vapor densities can be attained at moderate temperatures. Moreover, their excitation energies are very low, and high populations of the selectively excited levels can easily be accomplished with the available narrow bandwidth dye lasers that made studies of photoexcitation and photoionization from the excited states of alkali-metal atoms more attractive. The photoionization from the low-lying states of potassium has been studied theoretically and experimentally by a number of groups [1–13]. There are few experimental or theoretical data available for photoionization from the excited states near and above the first ionization threshold.

Theoretically, Moskvin [1] used the quantum defect method to calculate the photoionization cross section for the $4p$ state of potassium. Aymar *et al.* [2] calculated the photoionization cross section for the s, p, and d Rydberg states of Li, Na, and K using the parametric central potential in the framework of a single-electron nonrelativistic model. Petrov *et al.* [3] reported the partial and total photoionization cross section of potassium using a configuration interaction technique with Pauli-Fock orbitals. Stone and Kim [4] presented calculations for the electron impact excitation cross sections from the ground state to the np levels of sodium ($3 \leqslant n \leqslant 11$) and potassium ($4 \leqslant n \leqslant 12$). Savukov [5] carried out calculations of photoionization cross sections for alkali-metal atoms in the framework of relativistic many-body perturbation theory (RMBPT) using quasicontinuum B-spline orbitals. Recently, Zatsarinny and Tayal [6] calculated the photoionization using a Dirac-based B-spline R matrix from the $4s$ ground and $4p$, $5s$–$7s$, and $3d$–$5d$ excited states of potassium. McKay *et al.* [7] reported the laser cooling and trapping of neutral potassium on an open transition.

The experimental work on potassium was pioneered by Driver [8], who reported the photoionization cross section for the $3p$ subshell from the ionization limit at 50 to 32 nm. Nygaard *et al.* [10] initiated the measurements of the photoionization cross sections of potassium from the $4p$ excited state using the two-step photoionization technique and compared them with the theoretically calculated values [1]. Burkhardt *et al.* [11] determined the photoionization cross sections and the atomic densities for the resonance levels of sodium, barium, and potassium by utilizing the saturation technique. Feng and Zhang [12] measured the photoionization cross section from the $7p$ excited state of potassium using the method of ionization saturation. Recently, Amin *et al.* [13] reported the photoionization cross sections from the $4p\ ^2P_{1/2,3/2}$, $5d\ ^2D_{5/2,3/2}$, and $7s\ ^2S_{1/2}$ excited states of potassium using the saturation technique and a thermionic diode ion detector.

In addition to the measurement of the photoionization cross section, structural and parametric studies of potassium as an alkali metal have been carried out by many groups [14–17]. Huang and Wang [14] reported the oscillator strengths for the principal series $np\ ^2P_{1/2,3/2}$ of potassium and also reported the photoionization cross section at the ionization limit. Subsequently, Wang and Shirinzadeh [15] calibrated the oscillator strength measurements against the lifetime of the $4s \rightarrow 4p$ transition of potassium and also reported the value of the photoionization cross section at the series limit. Barrienttos and Martin [16] studied the oscillator-strength distribution between the discrete and continuous regions of the spectrum of the alkali elements Li, Na, K, Rb, and Cs using the quantum defect orbital (QDO) approach. More recently, Borovik [17] measured the autoionization cross section of potassium atoms excited by electron impact in the energy range from the first autoionization threshold at 18.72 to 202 eV.

There are no experimental data on the photoionization cross section from the $6p$ excited state of potassium despite the

*Author to whom corresponding should be addressed: baig@qau.edu.pk, aslam@ncp.edu.pk, baig77@gmail.com

availability of extensive theoretical calculations for the np ($n = 4$–10) excited sates of potassium [2]. The objectives of the present work were to measure the photoionization cross section from the $6p$ state of potassium in the vicinity of the first ionization threshold and to compare it with the theoretical calculations to validate the absolute values. This work continues our experimental studies [18–27] on the photoionization for the excited states of atoms. We report here measurements of the photoionization cross sections from the $6p\ ^2P_{3/2}$ excited state of potassium at three different ionizing lasers wavelengths above the first ionization threshold using two-step photoionization saturation techniques in conjunction with a time-of-flight (TOF) mass spectrometer. The measured values are found to be in excellent agreement with the theoretical calculations.

II. EXPERIMENTAL DETAILS

The experimental setup to measure the photoionization cross sections from the $6p\ ^2P_{3/2}$ state of potassium is the same as described by Saleem *et al.* [18–20], Rafiq *et al.* [21], and Kalyar *et al.* [22] for the measurements of the photoionization cross section of lithium, magnesium, and barium, respectively. It comprised a linear TOF mass spectrometer, an atomic-beam apparatus, and a Nd:YAG laser pumped dye lasers system. The atomic-beam apparatus was specifically designed for the potassium vapors, keeping in mind its physical properties such as thermal velocity, boiling temperature, and mean free path. The laser system comprised of a Q-switched pulsed Nd:YAG laser coupled with a second-harmonic-generation (SHG) module for producing a 532-nm laser, capable of delivering energy of ≈450 mJ. It operates at 10 Hz with a pulse duration of ≈5 ns. About 70% of the available power of the SHG (532 nm) of the Nd:YAG laser was used to pump the TDL-90 (Quantel) dye laser. LDS-698 dye dissolved in methanol was used to charge the dye laser, which was tuned at 689.53 nm. The bandwidth of the dye laser was $\leqslant 0.1\ \text{cm}^{-1}$, and the output laser energy was about 300 μJ. The frequency-doubled output of the dye laser at 344.76 nm with about 60 μJ of energy was used in the first step to populate the $6p\ ^2P_{3/2}$ level. For the second step, we used three laser wavelengths, 1064, 689.53, and 532 nm, to photoionize the atoms. The exciting laser beam, having a diameter of 4.5 mm, filled the entire atomic-beam diameter in the ionization or extraction region of the TOF mass spectrometer. The ionizer laser beam was focused at the center of the above-mentioned region with a plano-convex lens with a focal length of 50 cm. It enabled making the ionizing volume as nearly cylindrical as possible over the ion collection length, which was equal to the calculated diameter (4 mm) of the atomic beam in the interaction region. Both laser pulses were linearly polarized with a parallel polarization axis.

The potassium sample was loaded in the oven placed in a vacuum chamber and then evacuated up to $\sim 10^{-6}$ mbar. The oven was heated at a constant temperature of ≈465 K. A well-collimated atomic beam of potassium was produced that traveled from the lower to the upper part of the vacuum chamber and passed through the center of the ionization or extraction region of the TOF mass spectrometer where it interacts orthogonally with the exciting and the ionizing laser beams. Since both laser beams originate from the same Nd:YAG laser, we nevertheless confirmed the temporal overlap with a photodiode. Interaction of the laser beams with the atomic beam produces potassium ions that were detected by a Channeltron. The TOF detector produces voltage signals of potassium ions across a 50 Ω resistor, which was converted to the number of ions produced. The detector's linearity is very important while measuring the photoionization cross section. An optimum operating voltage was determined for the Channeltron corresponding to the maximum available laser intensity in order to get the true photoion signals. The temporal overlapping of the exciting and the ionizing lasers is also essential and was adjusted using an optical delay line and confirmed with a PIN photodiode.

III. RESULTS AND DISCUSSION

In order to measure the photoionization cross sections from the $6p^2P_{3/2}$ excited state above the first ionization threshold of potassium, we have used a two-step excitation- ionization technique. According to the dipole transition selection rules in LS coupling [$\Delta\ell = \pm 1$, $\Delta S = 0$, $\Delta J = 0, \pm 1$, and $\Delta L = 0$, ± 1 (even $\leftrightarrow$ odd, odd $\leftrightarrow$ even)], the first-step excited levels are

$$4s\ ^2S_{1/2} \xrightarrow{\hbar\omega} np\ ^2P_{1/2,\ 3/2}.$$

The atoms from the $4s\ ^2S_{1/2}$ ground state are promoted to the $6p\ ^2P_{3/2}$ level using a dye laser tuned at 344.76 nm. This wavelength was obtained by frequency doubling the dye laser output at 689.53 nm using a beta barium borate (BBO) crystal. The laser light is linearly polarized, with a polarization vector in the z direction. The $4s\ ^2S_{1/2}$ level possesses $m_J = \pm 1/2$ states, whereas the $6p\ ^2P_{3/2}$ level possesses $m_J = \pm 3/2$ and $\pm 1/2$ states. With the linearly polarized laser light, the assessable transitions follow the $\Delta m_J = 0$ selection rule; therefore only transitions to the $m_J = \pm 1/2$ states are allowed. In the second step, the atoms from the $6p\ ^2P_{3/2}$ level are ionized at three laser wavelengths, 1064, 689.53, and 532 nm. The ionizing laser is also linearly polarized, and its polarization direction is kept parallel to that of the first-step dye laser. The ionization from the $6p\ ^2P_{3/2}$ level approaches the εs and εd continuum channels.

$$4s\ ^2S_{1/2} \xrightarrow{\hbar\omega} 6p\ ^2P_{3/2} \xrightarrow{\hbar\omega} \varepsilon s\ ^2S_{1/2} \xrightarrow{\hbar\omega} \varepsilon d\ ^2D_{3/2,5/2}.$$

Thus, we can promote atoms from the ground state to the continuum using the two-step excitation-photoionization technique. As the transition in the first step is saturated, the time-dependent number densities in the ground and the excited states are equally distributed accordingly:

$$N_{\text{Ground}}(t) = N_{\text{Excited}}(t) = 1/2\, N_{\text{Total}}(t). \tag{1}$$

In the second step, the atoms from the $6p$ excited state are photoionized by the ionizing laser; thus the ionization rate from this state is given by the relation

$$dN_{\text{Excited}}(t)/dt = -R_{\text{ion}} N_{\text{Ecited}}(t) = -R_{\text{ion}} N_{\text{Total}}(t)/2. \tag{2}$$

Here, R_{ion} is the rate of ionization from the excited state, which is related to the photoionization cross section, the intensity, and

energy of the ionizing laser as

$$R_{\text{ion}} = \frac{I(t)\,\sigma}{\hbar\omega}. \tag{3}$$

Here σ (cm^2) is the cross section of photoionization from the excited state to the continuum channels at the ionizing laser wavelength, I (W/cm^2) is the time-dependent intensity, and hω (J) is the photon energy of the ionizing laser. Rate equations involving number densities in the ground state, excited state, and the ionization channels have been solved to derive a relation for the number of ions produced as a function of the intensity of the ionizing laser. This method has been described by a number of researchers [11,18–29] and has been widely used for the measurement of the photoionization cross section of lithium isotopes [18–20] and of the excited states of alkali and alkaline earth metals [18–32]. Saturation is explained by the fact that as the intensity of the ionizing laser is increased, the ion signal keeps on increasing until the point at which any further increase in the ionizing laser intensity will not increase the ion signal. At this point total ionization of the excited atoms takes place, and saturation in the ion signal is achieved. The rate-equation solution yields a relation between the voltage signal V_S and the photoionization cross section [11], [22–25]:

$$V_S = \frac{eN_0VR}{\Delta t}\left[1 - \exp\left(-\frac{\sigma\,E}{2\hbar\omega\,A}\right)\right]. \tag{4}$$

Here, Δt(s) is the full width at half maximum of the photoion's signal, e (C) is the electronic charge, R (Ω) is the load resistor, V (cm^3) is the laser-interaction volume, N_0 (cm^{-3}) is the number density of atoms in the excited state, A (cm^2) is the area of cross section of the ionizing laser, $\hbar\omega$ (J) is the energy of the ionizing photon, E (J) is the energy of the ionizing laser pulse, and σ (Mb) is the photoionization cross section of the excited state. All the quantities in this relation are known, except N_0 and σ, which can be extracted by the least-squares fit of Eq. (4) to the experimental data. The above equation shows that the ion signal becomes saturated if the energy density of the ionizing laser is infinite. Accurate determination of the photoionization cross section and number density demands accurate measurements of the ionizing laser energy density as well as the characterization of the spatial profiles of both the exciting and the ionizing laser pulses in the interaction region. An aperture with a diameter of ≈3.8 mm was placed in the path of the exciting laser, whereas another aperture with a smaller diameter, ≈2.6 mm, was placed in the path of the ionizing laser. Since the diameter of the ionizing laser is kept smaller than that of the exciting laser beam, it reduces the problems associated with the spatial overlap of the laser beams in the interaction region. A lens with a long focal length of 50 cm was also used in the path of the ionizing laser to meet the power requirements for saturation. The measurements of the spatial profiles of both the exciting and the ionizing laser beams were carried out with two beam splitters placed before the entrance to the interaction region by scanning a PIN photodiode across their diameters. The intensity distribution of both laser beams was found to be Gaussian. Furthermore, by detecting ions rather than photoelectrons, we avoided the normalization problems arising from the angular distribution of the electrons [33].

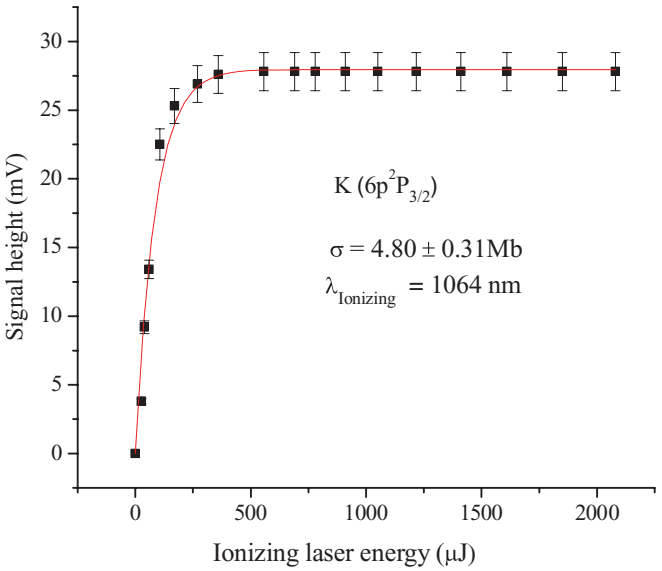

FIG. 1. (Color online) Photoionization cross section data at the 1064-nm ionizing laser wavelength from the $6p\ ^2P_{3/2}$ state of potassium.

In Fig. 1, we present the photoionization data for the photoionization from the $6p\ ^2P_{3/2}$ state of potassium using the ionizing laser wavelength at 1064 nm. It is evident from Fig. 1 that at lower energy of the ionizing laser, the change in the signal height is very fast; with a further increase in the ionizing laser energy (intensity) it deviates and tends to approach saturation. The solid squares are the experimental data points; the error bars show ≈5% uncertainty. The solid line is the least-squares fit of Eq. (4) to the experimental data, which yields the value of the cross section σ as 4.80 ± 0.31 Mb at the 1064-nm ionizing laser wave lengths and the number density N_0 as 2×10^{11} cm^{-3}. Similarly, in the next set of two experiments, we have recorded the ionization signal from the

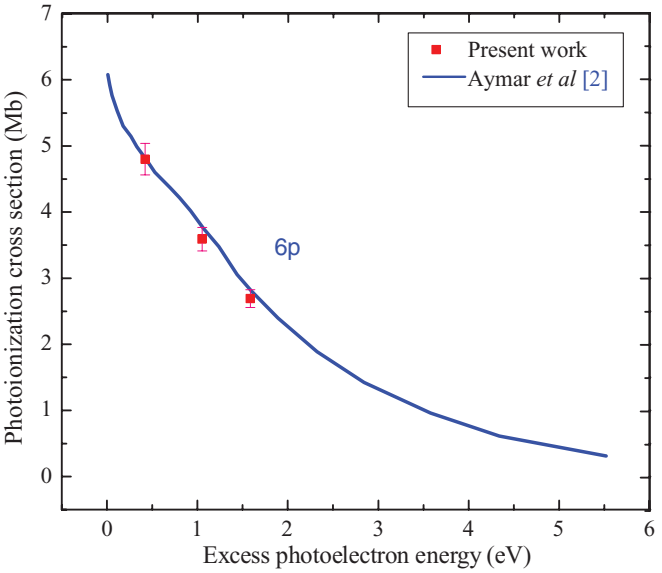

FIG. 2. (Color online) Comparison of the photoionization cross sections (Mb) as a function of excess photoelectron energy for the $6p\ ^2P_{3/2}$ state of potassium.

TABLE I. Comparison of the photoionization cross sections measured from the $6p\ ^2P_{3/2}$ excited state of potassium with the theoretically calculated values.

Present work (experiment)			Previous work (theory)[a]	
Cross section σ (Mb)	Ionizing laser (nm)	Excess energy (eV)	Cross section σ (Mb)	Ionizing laser (nm)
4.80 ± 0.31	1064	0.421	4.76	1064
3.59 ± 0.18	689.53	1.053	3.68	689
2.69 ± 0.22	532	1.586	2.78	532

[a]The theoretical results are obtained from the published data curves reported by Aymar *et al.* [2].

$6p\ ^2P_{3/2}$ state using the ionizing laser at 689.53 and 532 nm. We remark that such a complete saturation of ionization as Eq. (4) illustrates is possible only if the ionizing laser energy (intensity) approaches infinity.

The fitting procedure of the curves of Eq. (4) to the experimental data points yields the photoionization cross sections from the $6p\ ^2P_{3/2}$ excited state as 4.80 ± 0.31, 3.59 ± 0.18, and 2.69 ± 0.22 Mb at ionizing laser wavelengths of 1064, 689.53, and 532, respectively. The main sources of uncertainty in the measurement of the cross section are the uncertainties in the laser energy measurement and the cross-sectional area of the ionizer laser beam in the interaction region. The uncertainties in the energy measurements are due to the energy meter ($\pm 3\%$) and pulse-to-pulse variations in the laser energy ($\pm 5\%$). Additional uncertainty comes from the area measurement of the spatial beam profile of the ionizer laser beam ($\pm 10\%$). The maximum overall uncertainty in the determination of the absolute cross section is $\approx 15\%$.

The results of our experiments involving the measurements of photoionization cross sections from the $6p\ ^2P_{3/2}$ state of potassium at three different ionizing wavelengths (1064, 689.53, and 532 nm) are reported. For comparison of our experimental results, the theoretical data of photoionization cross sections from the $6p$ state of potassium, as shown in Fig. 2, have been obtained from the published curve of the data reported by Aymar *et al.* [2]. The solid line represents the theoretical data, whereas the solid squares are the present experimental results. Evidently, the measured values of the photoionization cross sections are in excellent agreement with the theoretical calculations of Aymar *et al.* [2].

A comparison of the measured photoionization cross sections from the $6p\ ^2P_{3/2}$ excited states of potassium (in Mb) with the existing theoretical values is given in Table I, showing excellent agreement. Thus, the present experimental results appear to validate the theoretical results.

In conclusion, we have been able to obtain the absolute values of the photoionization cross sections from the $6p\ ^2P_{3/2}$ excited state of potassium in the energy region above the first ionization threshold up to 1.58 eV at three ionizing lasers wavelengths. The photoionization cross section is higher near the ionization limit and decreases as the ionizing laser wavelength decreases. This behavior is very different from that observed for the photoionization from the $4p$ excited state. The presently measured values of the photoionization cross section are found to be in excellent agreement with the theoretical calculations. It will be interesting to have more experimental data at higher excess energies to validate further the theoretical calculations.

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