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# Photoionization of potassium

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**Abstract** · An analytic atomic independent particle model (IPM) potential is used to investigate the ground state photoionization cross section of the 4s electron of atomic potassium as a function of incident photon wavelength in the dipole length approximation . The spin-orbit interaction is included in the model potential and effects of core polarization have explicitly been considered The predicted photoionization cross sections are in better agreement with experiments than those of earlier calculations from threshold up to about 2600 Å

## 1. Introduction

Various theoretical studies have contributed to the increased understanding of spin-orbit interaction and core polarization effects in the photoionization of atomic potassium [1,2]. It has been repeatedly demonstrated through different studies that the electron exchange consideration and allowance for distorsion and polarization of the core alter the values of photoionization cross sections profoundly. In the case of potassium like sodium, rubidium and cesium, it was found that as the frequency of the incident radiation is increased above the spectral head, the cross section falls, reaches a minimum and then rises rapidly. The experimental work appears to have established accurate values of photoionization cross section of atomic potassium. The theoretical position is still not satisfactory. Even the calculations [1,3] using accurate wave functions which include the effect of electron exchange and allowance for distorsion and polarization of the core, are in poor agreement with experiment. These findings have consequently required a reconsideration of- potassium problem to see if the lack of

agreement with experiment could be removed. Weisheit [3] presented an alternate derivation of the core-polarization correction for potassium atom. He used a semi-emperical model potential which was based on the Hartree-Fock core potential with corrections for the core polarization and spin-orbit interactions. Hansen [4] investigated the influence of the core polarization in the model potentials and the transition matrix elements in alkali metal atoms and determined a complete set of their radiative life times for all these atoms up to the quantum member $n = 15$. Mansfield [5] studied the photoionization by the subvalence $s$ subshells of potassium along with other alkali atoms *viz* Rb and Cs confirming the importance of intra-subshell correction in such cases. All these features point towards the importance of undertaking the spin-orbit and core polarization phenomena in the studies of photoionization cross section of potassium atom. In the present case, we employ GSZ-IPM potential [6]. It is shown that in comparison to Hartree-Fock Stater (HFS) calculations, a simple two-parameter analytic GSZ-IPM potential has been very suitable choice to deal with atoms and electron – atom interactions [7,8]. Even in the case of atomic Li photoionization [9], we have found that the GSZ-IPM potential has been a good choice to investigate this problem at low photon energies. The photoionization cross sections of the 6s electron

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of cesium atom [10] have also been computed using this potential and it is shown that the variation of photoionization cross section with photoelectron energy is in better agreement with relaxed core result of Huang and Starace [11] than their frozen core results and also with the measurements of Cook *et al* [12] up to about 0.7 eV. Considering these findings, we investigate the photoionization of potassium atom incorporating the effect of spin-orbit interaction and core-polarization effect both because these studies demonstrate convincingly that the experimental photoabsorption can be explained with a reasonable treatment of these two effects . Recent literature survey also reveals that no such attempt using the aforesaid potential has been undertaken so far. It was therefore, considered worthwhile to study this problem .

## 2. Theory

The theory of interaction of radiation with matter enables us to formulate expressions which relate the oscillator strength and the integrated absorption cross section for a narrow line to appropriate matrix elements in the electric dipole approximation. The theoretical study of photoionization phenomenon however, requires that these relations should be extended so as to account for the fact that while the initial state is in discrete bound spectral level, the final state lies in the free continuous spectrum . The formula for the photoionization cross section $a_v$ of an N-electron atom due to a radiation of frequency $v$ [13] is given by

$$a_v = \frac{2\pi e^2 h^2}{m^2 c v} \int d\Omega_v \sum dr_N \, \psi_k(N) e^{ik_v \cdot r_j} p_j \psi_0(N) \qquad (1)$$

where $e$, $h$, $m$ and $c$ have their usual meaning. $\psi_0(N)$ and $\psi_k(N)$ are the initial and the final states of the atomic system respectively . $k_v$ is the photon momentum, $p_j$ and $r_j$ represent the momentum and position with respect to the target nucleus of the j-th electron respectively. $d\Omega_v$ indicates an integration variable over all directions of electron. If more than one final state is possible, a suitably weighted sum over such states must be introduced. In the visible region of the electromagnetic spectrum, $k_v \cdot r_j$ is of the order of $10^{-3}$ atomic unit and therefore, this exponential may be replaced by unity. Substituting numerical values of the various atomic constants, the above eq. (1) may the expressed as

$$a_v = 8.56 \times 10^{-19} \frac{1}{w(1+k^2)} S_{if} \quad \text{(in cm}^2\text{)}, \qquad (2)$$

where $I$ and $k^2$ are the ionization potential of the atomic $K$ and the kinetic energy of the photoelectron respectively (both given in Rydberg units) and from energy conservation, $h_v = I + k^2$ while $w$ is the statistical weight of the initial atomic state and for the case of alkali atoms in their ground state $2S_{1/2}$, it is unity .

The quantity of our concern is

$$S_{if} = 4 \sum_j \left| \psi_k^*(N) \nabla_N \psi_0(N) dr_N \right|^2. \qquad (3)$$

The sum is over final states and

$$= \sum_{i=1}^{N} \qquad (4)$$

$$p_j = i \nabla_j \qquad (5)$$

Using the commutation relation

$$[H, r_N] = -\nabla_N \qquad (6)$$

and remembering that

$$r_N = \sum_{r=1}^{N} r_j, \qquad (7)$$

where $r_j$ is the position vector of the j-th electron with respect to the target nucleus, the reduction in formula (3) can at once be effected to give

$$S_{if} = (I + k^2) |\sigma_L|^2, \qquad (8)$$

where $\sigma_L = \int \psi_k^*(N) r_N \psi_0(N) dr_N \qquad (9)$

is called the length form of the matrix element. $\psi_0(N)$ and $\psi_k(N)$ are the initial and the final states of the atomic system respectively. The remaining problem consists in finding sufficiently good approximation to the many body wave function. Zero order calculations assume that the electrons are separable *i.e.* the correlation plays no role. In such case, $\psi_0$ and $\psi_k$ may be represented by linear combination of Slater determinants composed of one electron spin orbitals . If we consider the core to be inert, then for alkali atoms, a single such determinant suffices. Therefore, we get on simplification, the following final expression for the photoionization cross section of potassium atom :

$$= 0.856 \times 10^{-20} (I + k^2) \left| \int P_{kp}(r) \, rP_{4s}(r) dr \right|^2 \quad \text{(in cm}^2\text{)}. \quad (10)$$

Here, $P_{kp}(r)$ is the radial wave function of the free (continuum) state electron with momentum $k$ and $P_{4s}$ is the radial ground state (*i.e.* bound state) wave function. In order to complete the calculation, $P_{4s}(r)$ and $P_{kp}(r)$ have to be found and the matrix element computed. As the electron correlations are crucial enough to play an important role, the core-polarization effect must be included. The expression for the dipole transition moment is consequently modified to account for polarization of the alkali core by the valence electron. The dipole operator $r$ in the eq. (10) is replaced by the following corrected operator $Q(r)$ due to Weisheit [3].

$$Q(r) = r\left[1 - \frac{\alpha_d}{r^3}\left\{1 - \exp-\left(\frac{r}{r_c}\right)\right\}\right] \quad (11)$$

where $r_c$ is an effective core radius cut off and $\alpha_d$ is the static dipole core polarizability. This correction for the core polarization in the dipole matrix element has been determined by additional fit to precise and experimental photoionization data. The values of $\alpha_d$ and $r_c$ for $K$ atom in the present calculation are taken from the Table 1 of Hansen [4].

Using eq. (11), the eq. (10) now becomes

$$a_v = 0.856 \times 10^{-20}(I + k^2)M^2 \quad (\text{in cm}^2), \quad (12)$$

where

$$M = \int \bar{P}_{4s}(r)\, Q(r)\, P_{kp}(r)\, dr. \quad (13)$$

When the effect of the spin orbit perturbation of the free state photoelectron wave function is considered, then there are two slightly different wave functions for the final $j$ values (1/2 and 3/2) with corresponding matrix elements $M_1$ and $M_3$. The total photo ionization cross section from the ground state of potassium is therefore obtained by adding together the two corresponding cross section due to transition to degenerate $j = 1/2$ and $j = 3/2$ continuum levels at each value of the photo-ejected electron momentum k. Thus, the resulting expression for the total photoionization cross section ( in cm$^2$) will be given by

$$a_v = 0.856 \times 10^{-20}(I + k^2)\left(\frac{1}{2}M_1^2 + \frac{2}{3}M_3^2\right) \quad (14)$$

Here, $M_1$ and $M_3$ are

$$M_1 = \int P_{4s}(r)\, Q(r)\, p_{k,1/2}(r)\, dr \quad (15)$$

and

$$M_3 = \int P_{4s}(r)\, Q(r)\, p_{k,1/3}(r)\, dr. \quad (16)$$

The use is made of the tables of Clementi and Roetti [14] for getting the normalized ground state radial wave function $P_{4s}(r)$ for the atomic $K$. The differential wave equation satisfied by $P_{kp}(r)$ is given by

$$\frac{d}{dr} + k^2 - 2/r^2 + V(r)\left|P_{kp}(r) = 0. \quad (17)$$

The potential $V(r)$ in which the radial part of the free state wave function is generated is composed of three terms.

$$V(r) = V_g(r) + V_p(r) + V_{so}(r). \quad (18)$$

Here, $V_g$ is the G S Z-I P M potential [6] having the following form:

$$V_g(r) = \frac{2(N-2)}{r}\left[(z-1)\left(H\left(e^{r/d} - 1\right) + 1\right)^{-1} + 1\right] \quad (19)$$

where $Z$ is the number of nuclear protons, $N$ is the number of core electrons, $r$ is the radial distance from the nucleus, $d$ and $H$ are the adjustable parameters. $V_p$ is the core-polarization potential [4]. It accounts for the polarization of the core by the valence electron and it is of the following form. It also includes the effect of induced core moments on the outer electron.

$$V_p(r) = \frac{\alpha_d}{r^4}\left[1 - \exp(r/r_c)^6\right] + \frac{(\alpha_q - 3\beta a_0)}{r^6}\left[1 - \exp(-r/r_c)^{10}\right], \quad (20)$$

where $\alpha_q$ is quadrupole polarizability and $\beta$ is the nonadiabatic correction of the core polarizability and $a_0$ is the Bohr radius. $V_{so}(r)$, which is the Dirac form of the spin-orbit potential [4] is taken to be

$$V_{so}(r) = \frac{\alpha^2}{2}\frac{1}{r}\frac{d}{dr}\left(V_p + V_g\right)\left[1 + \frac{\alpha^2}{4}\left(V_p + V_g\right)\right]^{-} (L.S). \quad (21)$$

Here, $\alpha$ is the fine structure constant. The term in the bigger bracket in eq. (21) is an additional relativistic correction to account for the proper behaviour of the spin-orbit interaction near the origin. The eq. (17) has been solved numerically using Numerov's method. The numerically generated continua are normalized by Stewart's method [15]. The integration occurring in the normalization of continua is done by Gauss quadrature rule. A finer initial radial interval dr as small as $10^{-6}$ Å, is employed to ensure the accuracy in the numerical integration of the photoionization matrix elements $M_1$ and $M_3$ by Simpson quadrature rule. The computer program has been so adjusted that radial interval dr keeps on doubling each time after every 1000 steps up to a considerable radial distance beyond which the contribution is found to be negligibly small.

## 3. Results and discussion

Our calculation for the ground state photoionization cross section of 4$s$ electron of atomic potassium as a function of photon wavelength is shown in Figure 1. The result is compared with the measurements and also with the earlier theoretical calculations. The predicted cross sections are in fairly good agreement with the two sets of measured data [16,17] in the range of photon wavelengths considered. The present predicted minima in the photoionization cross section of the potassium atom is at 2725 Å and its value is $1.3 \times 10^{-21}$ cm$^2$ as against the two sets of the corresponding measured values of (i) 2675 ± 75 Å and 2 × 10$^{-21}$ cm$^2$ due to Hudson and Carter [16] and (ii) 2725 ± 75 Å and (4 ± 2) × 10$^{-21}$ cm$^2$ due to Marr and Greek [17]. The

corresponding two sets of the computed these values are, however, (i) 2720 Å and 0.22 × $10^{-21}$ cm$^2$ due to Weisheit and Dalgarno [1] and (ii) 2700 Å and 0.3 × $10^{-21}$ cm$^2$ due to Seaton [18] . The present result is therefore, better than both of these earlier theoretical predictions [1, 18] and when compared with the measured data . We therefore, conclude that the present method that includes the core polarization as well as the spin-orbit effects is found to provide a good estimate of photoionization cross section of 4s electron of potassium atom at low photon energy. Similar results have been obtained for the
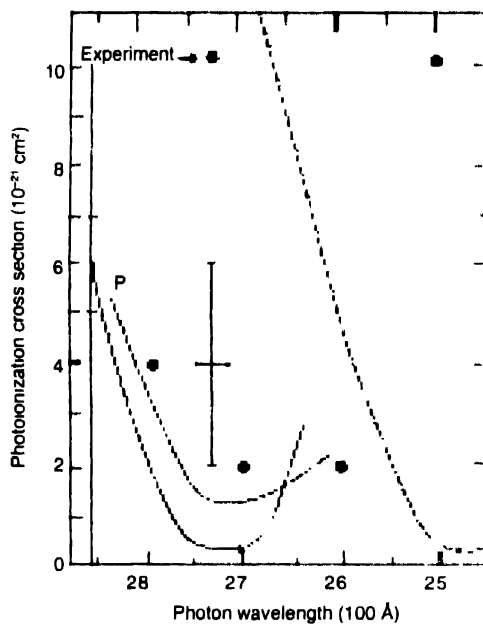


**Figure 1.** Ground state photoionization cross section of 4s electron of atomic potassium versus photon wavelength.

(i) Curve P . Present calculation ; (ii) The filled circle Measurement of Hudson & Carter [16] , (iii) The solid curve Calculation of Weisheit and Dalgarno with the core polarization correction [1] , (iv) The dashed curve · Calculation of Weisheit and Dalgarno without core polarization correction [1]

The bars represent threshold and minimum values due to Marr and Greek [17] while the cross mark indicates the photoionization cross section minimum for atomic potassium due to Seaton [18] All curves except the curve P are taken from the Figure 1 of the paper by Weisheit and Dalgarno [1]

case of Li and Cs atoms [9,10] using the present model. It is shown that GSZ-IPM potential has been a good choice to deal with the photoionization of atomic Li [9] and Cs atom [10] at low photon energies. Therefore in conclusion, the present method which is simple in nature, is indeed encouraging to investigate the photoionization for alkalis. This model may be further verified by using more accurate potential which includes physics of correlation phenomena in a more effective way.

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