

Removal or Excitation of a 1s Electron in Kr II and Kr III

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Abstract. Relativistic configuration interaction calculations are done for Kr ions Kr II and Kr III. Transition energies and transition probabilities for 122 transitions between Kr II $4p^5 J = 1/2, 3/2 \rightarrow 1s 4p^6, 1s 4p^5 np$ ($n=5-8$) $J = 1/2, 3/2, 5/2$; 437 transitions between Kr III $4p^4 J = 0, 1, 2 \rightarrow 1s 4p^5, 1s 4p^4 np$ ($n=5-8$) $J = 0, 1, 2, 3$ have been calculated. These data have been used by experiment to reproduce the absorption spectrum of Kr II and Kr III and found to be in good agreement with their measurement. Also, the K-edge energy of neutral Kr, Kr II and Kr III has been calculated. The first is within 0.94 eV of an existing experiment, while the last two are calculated for the first time.

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1. Introduction

While atomic spectroscopy has never ceased being challenge from a fundamental viewpoint, currently there is substantial interest and need for theory with predictive power for inner-shell atomic absorption spectra due to high quality x-ray spectra of astrophysical objects obtained from the Chandra X-ray Observatory [1, 2] and the anticipated needs of x-ray free electron lasers (XFELs) where laser-produced laboratory plasmas can be studied [3]. The challenges to obtaining useful data in very complex environments are large, and reliable atomic spectra for various ionization states are a necessary starting point.

Experimentally, ionic krypton was chosen by the Argonne National Laboratory research group [4] because the behavior around the K-edge in neutral krypton had been previously well studied [5, 6, 7, 8] and it was well suited to the energy range of the beamline. Krypton is also an important element in controlled fusion experiments, where it is used as an ion density diagnostic [9]. The binding energy of the 1s electron in krypton is also of potential calibration interest in neutrino mass studies [10].

In order to aid in the interpretation of the observations [4], we were asked by a member [11] of the ANL research group to provide excitation and ionization energies, as well as transition probabilities associated with 1s electrons in the ground states of Kr II and Kr III. While the relative simplicity of the valence shell(s) structure (e.g. p^n

and $p^n p'$, $n=4, 5$) eases the treatment of correlation effects, the active participation of the 1s electron means that relativistic, QED, and relaxation effects will be important. Furthermore, the final states are all embedded in multiple continua, requiring that one calculates the shift and broadening of the final states arising from the interaction of the localized state and the continua in which it is embedded.

2. Methodology

Conceptually, we begin by separating the localized and continuum portions of the Kr II and Kr III final states, so that we may employ a relativistic form [12] of the Fano procedure [13]. In the present instance, our final states are of the form $1s 2s^2 \cdots 4p^n (p')$, and an adequate separation can be made if, in the language of configuration interaction, we exclude all 1s hole filling configurations (e.g. $2p^2 \rightarrow 1s x$) from the localized function. Separate calculations are done for each initial and final state, which means relaxation effects (~ 50 eV for removal or excitation of 1s electrons in Kr^{m+}) are automatically included. These arise because of the significant changes which occur in ALL Kr^{m+} radial functions upon ionization or excitation. Such effects are much smaller for removal (excitation) of outer electrons, as the radial functions of the deeper electrons are little affected by that process. Clearly the initial and final state radial basis will differ considerably, and we will have to account for non-orthogonality effects when calculating the transition probabilities [14].

2.1. Localized reference functions

The localized function is divided into two parts—a reference (ϕ) and a correlation part. Here, it is sufficient to take a single manifold $1s 2s^2 \cdots 4p^n (p')$ as the final state reference function, and $1s^2 2s^2 \cdots 4p^n$ as the ground state reference function. A manifold is defined to consist of all relativistic configurations reducing to the same non-relativistic configuration in the limit as $c \rightarrow \infty$.

The most general Hamiltonian used is the Dirac-Breit one, viz:

$$H = \sum_i h_D(i) + \sum_{i < j} \left[\frac{1}{r_{ij}} + h_B(i, j) \right] \quad (1)$$

where $h_D(i)$ is the one-electron Dirac Hamiltonian (with the nucleus treated as sphere of uniform proton charge distribution), and h_B is the two-electron relativistic (Breit) operator which may be divided into two parts [15], i.e. magnetic and retardation. Generally, the magnetic contribution is an order of magnitude larger than the retardation contribution.

Our reference wave function consists of a single manifold (which could be several relativistic configurations) built from a linear combination of Slater determinants, whose elements are spinors which in turn are 4-row column matrices with unknown radial functions (major and minor components) and relativistic-hydrogenic angular factors. The linear combination of determinants is forced to be an eigenstate of J^2 and J_z .

The remaining unknowns—the radial functions, and any undetermined Slater determinant coefficients are obtained by applying the energy variational principle, producing the Dirac-(Hartree)-Fock equations. These are solved using the algorithms of Desclaux [16, 17]. In the present instance, it is not necessary to include the Breit operator in the radial equations. Estimates of its contribution are made [16, 17] by applying first-order perturbation theory. For retardation effects, this will suffice. Corrections to the magnetic contributions will be made at the correlation stage (see section 2.2).

This algorithm [17] also supplies us with an estimate for QED effects (~ 10 eV) which include self-energy and vacuum polarization effects treated using the Welton picture [17, 18]. At the present time, it is not possible to treat QED effects more thoroughly (i.e. include the effects of exchange and correlation) for such complicated systems.

When one has two open subshells of the same symmetry, the normal Dirac-(Hartree)-Fock procedure may be ill-posed. This may happen for Kr^{m+} final states if both $1s\ 2s^2 \dots 4p^{n+1}$ and $1s\ 2s^2 \dots 4p^n\ p'$ can produce the same J . A practical solution to this problem—used here—is to select a J unique to $4p^n\ p'$, generate the radials, and use them for the desired J . The modest corrections needed because of the J change are incorporated in the correlation calculation.

More details concerning some of the concepts discussed in this section can be found in the work of Indelicato and Lindroth for $K\alpha$ transitions [19], for example.

2.2. Correlation effects for localized function

We treat correlation using the Relativistic Configuration Interaction (RCI) method. With the reference function known, the FORM of a first-order wave function can be generated by making one and two electron excitations from the subshells occupied in the reference function into existing open subshells (e.g. $2p \rightarrow 4p$) or into new subshells, which we call virtuals (e.g. $1s^2 \rightarrow vp^2$).

We represent the radial portion of the virtuals with Relativistic Screened Hydrogenic Functions (RSH) with a single adjustable parameter Z^* , the effective charge. An estimate for Z^* may be obtained by matching the $\langle r \rangle$ of the virtual to that of the subshell it is replacing. Since each shell (common n) has a similar $\langle r \rangle$, we may expect that we would need a different virtual set for each originating shell. The estimated Z^* is adjusted during the RCI matrix diagonalization process by minimizing the energy of a specific root (generally the lowest). The use of RSH, where the major and minor radial components are determined by a single parameter (Z^*) prevents collapse into the “positron sea”—a problem encountered in early relativistic applications using basis sets.

The maximum azimuthal symmetry associated with “first-order” configurations possessing one virtual is $3l_{max}$, where l_{max} is the highest symmetry of the Dirac-Fock (DF) function being replaced. Experience has shown us that the same restriction is adequate for correlation configurations with two virtuals, although in this work, we

have included virtual symmetries as high as $l = 4$ ($l_{max}=1$ for Kr^{m+}).

As the size of our energy matrix is limited (to 20 000 currently [20]), and we have many levels to consider, it is important to include only those correlation effects which contribute substantially to energy differences (say > 0.05 eV) and/or to oscillator strengths. By using intermediate normalization for the wave function, it is possible to assign a specific energy contribution to each correlation configuration. This is only a “first-order” concept, but it suffices for our purposes.

One writes:

$$\Psi = \phi + \sum_i \frac{a_i}{a_\phi} \psi_i \quad (2)$$

where

$$\langle \phi | \Psi \rangle = 1 \quad (3)$$

The a_i 's are the RCI coefficients, and the energy contribution from ψ_i is

$$e_i = \frac{a_i}{a_\phi} H_{\phi,i} \quad (4)$$

Based on these formulae and our knowledge of shell structure, one may expect that the important contributors to energy differences in, for example, $1s^2 2s^2 \dots 4p^5 \rightarrow 1s 2s^2 \dots 4p^6$ would include double excitations from $1s^2$, $1s 2s$, $1s 2p$ (more of these in the ground state) and double excitations from $4p^2$ and $4s 4p$ (more of these in the final state). Excitations from $n=3$ electrons, for example, should be much smaller contributors to the desired energy difference. Specific examples will be given in the results section (e.g. 3.1.1)

In Kr II and Kr III, due to the large reference space and the core-valence correlations we put in, the matrix size easily outreaches the current limit of 20k of the RCI code [20]. The RCI matrix size can be substantially lowered by employing a formally first-order procedure which we call REDUCE [21, 22]. Essentially, one rotates the full basis set for the correlation manifold to maximize the number of zero matrix elements the rotated basis makes with the reference functions. The “zero” rotated functions are then discarded. Using only the Dirac-Coulomb Hamiltonian and assuming the major radial components are independent of j and the minor components are zero, each matrix element can be expressed as a linear combination of a small number (N) of radial integrals. For the rotated basis, the coefficient of each radial integral must vanish for as many functions as possible, subject to the condition that the basis remains orthonormal. Mathematically, one solves N equations in M unknowns (M is the number of basis functions, usually $M \gg N$). This underdetermined problem is solved by the singular value decomposition procedure of Press *et al* [23]. The size reduction can be great—for example, it was $\sim 18x$ times smaller for Kr III $1s 4s 4p^3 5p$ *vs* vp (v represents virtual subshells).

2.3. Shift of localized energy due to continuum interaction

The energy shift in the final state localized energy, E_{loc} , may be determined [12] by iteratively solving the equation:

$$E - E_{loc} = \sum_{n,i} \frac{|\langle \phi | H | \psi_{ni} \rangle|^2}{E - E_{ni}} + \sum_i P \int dE_i \frac{|\langle \phi | H | \psi_{E_i} \rangle|^2}{E - E_i} \quad (5)$$

Here E is the shifted energy, ϕ is the localized function, ψ_{E_i} is a function representing an open (continuum) channel, and ψ_{ni} represents a discrete Rydberg level (e.g. $2p^2 \rightarrow 1s4d$). The sum (integral) is over all functions excluded from the localized function, and P indicates the principle value taken for the integral.

Here, it seems sufficient to represent the localized function with just the reference function for Kr II and Kr III. Continuum solutions are generated by solving the frozen-core continuum Dirac-Fock radial equation (energy “ e ”) which includes correct structure, exchange, and orthogonality restrictions. The code that does this has been created by Perger and coworkers [24, 25].

2.4. Transition probabilities

We are concerned here with the strong transition probabilities of the electric dipole process. These are evaluated in two forms, the length and velocity, which would agree if the wave functions were exact (agreement is a necessary, but not a sufficient condition for wave function accuracy). Because the initial and final wave functions have different radial basis, non-orthogonality effects must be incorporated into the calculation of the transition probabilities. We do this using the methods of King *et al* [26], which over the years have been made dramatically more efficient [27] in such applications.

Some configurations may make a negligible contribution to energy differences but contribute significantly to transition probabilities. These may be identified by applying the First Order Theory of Oscillator Strengths (FOTOS [28]). Briefly, one applies the transition operator (e.g. \vec{r}) to an important configuration in one state to generate a configuration which might have to be included in the other, opposite parity, state. In the $1s^2 2s^2 \dots 4s^2 4p^5 \rightarrow 1s 2s^2 \dots 4s^2 4p^6$ transition, for example, application of \vec{r} to the initial state could generate $1s^2 2s^2 \dots 4s 4p^6$. However, for 1s hole states in Kr^{m+} , this is part of the continua which would be included in the discrete part of equation (5). We found such shell changing single de-excitations to have a small impact in this case.

2.5. Conversion coefficients

The energies we are dealing here are very large, so we have to be careful with the conversion factor from a.u. to eV. Since $1 \text{ a.u.} = 27.21139634 \text{ eV}$ is for infinite nuclear mass, we corrected it using $(1-m/M)$, so that $1 \text{ a.u.} = 27.21121986 \text{ eV}$. Given the energy separation between the Kr II ground state and $1s 2s^2 \dots 4p^6$, which is $\sim 527 \text{ a.u.}$, this makes a difference of $\sim 0.1 \text{ eV}$. We have used this corrected conversion factor throughout this work.

The ANL research group needs the $g_i B_{ik}$ values to interpret the absorption spectrum. In converting A_{ki} to B_{ik} , we found we had to correct the NIST book [29], as the coefficient factor of 6.01 in its formula seems to be wrong. Use of the Drake Handbook [30] led us to correct this to:

$$B_{ik} = 60.08\lambda^3 \frac{g_k}{g_i} A_{ki} \quad (6)$$

where λ is in Angstrom.

From this we get

$$gB = g_i \times B_{ik} = 60.08\lambda^3 g_k A_{ki} \quad (7)$$

3. Calculations

3.1. Transition energies and transition probabilities for Kr II

In both Kr II and Kr III, the final state levels are not LS pure. Therefore, we use “ rn ” to denote different levels from the same configuration, with the bottom level being $r1$. But for levels that are mixture of more than one configuration, and those lying above them, we just give their dominant configuration(s).

In Kr II, there are totally 122 electric dipole transitions from $1s^2 2s^2 \cdots 4p^5$ to $1s 2s^2 \cdots 4p^6$, $1s 2s^2 \cdots 4p^5 np$ ($n=5-8$). Table 1 gives 78 of them that have a large ($\geq 10^{10} s^{-1}$) transition probability.

In $J=1/2$ final state, the RCI radial functions for 1s, 2s, 2p, ..., 4p subshell are DF radials from $1s 2s^2 \cdots 4p^6$, while 5p radials are DF radials from $1s 2s^2 \cdots 4p^5 5p$ $J=1/2$. But when creating DF radials for 6p, 7p and 8p, no solution was found (see section 2.1). Instead, we created np $j=1/2$, $j=3/2$ radials separately: $np_{1/2}$ from $(1s 2s^2 \cdots 4p^5)_{J_c=2} np$ $J=5/2$, $np_{3/2}$ from $(1s 2s^2 \cdots 4p^5)_{J_c=0} np$ $J=3/2$. The discrepancy from the actual np radials is corrected by the symmetry preserving single excitation $np \rightarrow vp$ in the RCI procedure. There was no such problem with the radials in $J=5/2$ and $J=3/2$ final states.

3.1.1. Transition energies We started with the transition $1s^2 2s^2 \cdots 4p^5 \rightarrow 1s 2s^2 \cdots 4p^6 \ ^2S_{1/2}$. The following excitations were found to be energetically most important:

$4p \rightarrow f, 4s \rightarrow d$	(only found in $4p^5$)
$4p^2 \rightarrow vp^2, vd^2, vf^2, vg^2, vd\ vg$	(differential contribution ~ 1.253 eV)
$4s\ 4p \rightarrow vsvp, vpv d, vd\ v f, v f\ v g$	(differential contribution ~ 0.232 eV)
$1s\ 2p \rightarrow vsvp, vpv d, vd\ v f; 1s\ 2s \rightarrow vs^2, vp^2$	(differential contribution ~ 0.522 eV)
$1s^2 \rightarrow vs^2, vp^2, vd^2$	(~ 0.820 eV, only found in $4p^5$)

To represent the above correlation, 5 sets of RSH functions were used for the initial states ($J=1/2, 3/2$) and 4 sets were used for the final state.

At this stage, we calculated the splitting between the $J=1/2$ and $J=3/2$ initial states. The splitting was found to be 0.652 eV, whereas Moore’s table gives 5371 cm^{-1} [31], i.e. about 0.666 eV. This indicates there may be missing correlation of about 0.014

eV in the $J=3/2$ ground state. So instead of using the RCI result, we obtained the transition energy of the $J=3/2$ ground state to $1s\ 2s^2 \cdots 4p^6\ ^2S_{1/2}$ by adding 0.666 eV to the corresponding transition energy of the $J=1/2$ initial state.

About 1/3 of the correlation energy from exciting two 4p electrons in $1s\ 2s^2 \cdots 4p^6$ goes to the transition energy. Since our angular space was truncated at $l = 4$, we estimated the contribution from $l \geq 5$ by extrapolating correlation energies of the computed l 's. The l dependence is approximately l^{-5} for $4p^2 \rightarrow vl^2$ and $(l+2)^{-5}$ for $4p^2 \rightarrow vl\ v(l+2)$. The total net contribution from $l \geq 5$ to the transition energy is about 0.056 eV. This will decrease the transition energy. We also extrapolated the correlation energies from exciting two 1s electrons which are only found in $1s^2\ 2s^2 \cdots 4p^5$. But this turned out to be very small and therefore was not included.

Next we calculated transitions to $1s\ 2s^2 \cdots 4p^5\ np$ ($n=5-8$) $J=1/2$. The idea is to find energy differences between $1s\ 2s^2 \cdots 4p^5\ np\ J=1/2$ and $1s\ 2s^2 \cdots 4p^6\ ^2S_{1/2}$, then add them to the transition energy of the ground state to the last. This reduces the amount of correlation that we need to include. For the first step, we did one RCI calculation with $1s\ 2s^2 \cdots 4p^6$, $1s\ 2s^2 \cdots 4p^5\ np$ ($n=5-8$) $J=1/2$ in the reference space. Since their deep core orbitals have same occupation numbers and have similar radials, only excitations from the shallow core of 4s and 4p, and the valence np need to be included when constructing the wave function. Two sets of RSH functions were used to represent these correlation effects. The following excitations are differentially big (> 0.05 eV):

$$4p^2 \rightarrow xp^2, vd^2, vf^2, vg^2, vdv g$$

$$4s\ 4p \rightarrow vsxp, xpv d, vdv f$$

$$4p \rightarrow xp, vf$$

$$4s \rightarrow vs, vd$$

(xp denotes both np and vp)

Next we calculated transitions to $1s\ 2s^2 \cdots 4p^5\ np$ ($n=5-8$) $J=3/2$ final states. We first positioned the $J=3/2$ final state levels relative to the bottom level of $1s\ 2s^2 \cdots 4p^5\ 5p\ J=1/2$ by doing a RCI calculation for each of the J states. Again, in RCI runs it's only necessary to have excitations from 4p and np only. Then we added to them the corresponding transition energy to the $1s\ 2s^2 \cdots 4p^5\ 5p\ J=1/2$ bottom level.

The transition energies to $J=5/2$ final states were obtained in the same way except that in the first step, we included excitations not only from 4p subshell, but also those from the 4s subshell. This is because $4s\ np \rightarrow 4p\ vs$ is allowed in $J=3/2$, but not in $J=5/2$, and it contributes ~ 0.085 eV to the energy difference.

3.1.2. Other corrections to transition energies In addition to relaxation and correlation effects, there are other significant many-body effects. These include the Auger effect, the Breit effect and the QED effect.

The Auger effect was evaluated using formula (5). For the integral, the localized function in the bra and ket was represented by the corresponding reference function only. The wave function for the Auger electron was tabulated at more than forty energy values up to 3 500 a.u. ($\sim 10\ 000$ eV). The matrix elements were evaluated using an improved

suite of continuum codes [24, 25]. They were interpolated with an approximate function using Mathematica. The difficulty with integrating over a pole can be treated by a method suggested in reference [32], but we chose to use a simpler one: leaving out an interval symmetric about the pole, approximating the principal-value integral with two normal integrals over two different ranges, and decreasing the width of the remaining interval until convergence in the sum of the two normal integrals is reached. Using the localized reference energy of $1s\ 2s^2 \cdots 4p^6$ before the shift as the starting value for E , the shift was found to be always less than 1 eV. On the other hand, the value of the integral remains almost the same while changing E by several tens of eV. Thus the shift was determined without solving equation (5) iteratively.

Table 2 lists all the channels we have tested. The choice of the channels was guided by the table for autoionization widths by Chen *et al* [33]. We began with the largest ones in that table and stopped our calculations where the shifts were found to be several orders of magnitude smaller than the dominant channel.

The shift due to interaction with the discrete channels, i.e. the sum in formula (5), was also tested but was found to be tiny. It's therefore not included in table 2.

Finally, the total shift in $1s\ 2s^2 \cdots 4p^6$ is ~ 0.256 eV. All transition energies were increased by the same amount accordingly. Changes in $n \geq 4$ subshell occupations have negligible impact on the shift.

The retardation and QED effects were calculated using Desclaux's program [17]. This code also produces the magnetic Breit effect at DF level. But the Breit correlation effect was big and must be included. So at the final stage of the RCI calculation, the magnetic Breit operator was introduced into the Hamiltonian and the energy matrix re-diagonalized. Though not explicitly shown in table 1, one can get an idea of the magnitude of these effects from table 4, the edge energy table. These effects vary only slightly among the 1s hole states and among the initial states.

Due to the limit on matrix size, we estimated the effect of opening the inner core of 3s, 3p, 3d subshells in small separate calculations. As expected, for $1s^2\ 2s^2 \cdots 4p^5 \rightarrow 1s\ 2s^2 \cdots 4p^6$, correlation from double excitations of 1s (3s,3p,3d) increases the transition energy (by 0.078 eV), while correlation from double excitations of (3s,3p,3d) 4p decreases it (by 0.266 eV). These correlation contributions have been added to all transitions where applicable.

3.1.3. Transition probabilities A_{ki} For the transition probability run, our wave function for both the initial and final state includes only excitations from 4s, 4p, and np. The intermediate run showed that $1s^2\ 2s^2 \cdots 4p^4\ vp$ in the initial state and $1s\ 2s^2 \cdots 4p^5\ vp$ in the final state make big contributions. This is not surprising as both configurations are predicted by FOTOS (First Order Theory of Oscillator Strength) to be important [28]. So we correlated them with all of the big excitations (i.e. included some second-order effects) and came up with improved wave functions for transition probability calculations. In most cases, the impact on the big A_{ki} 's is a change of less than 10%. There are some exceptions, for example, in transitions from the $J=3/2$ ground state to

$J=1/2$ upper states, correlating these two FOTOS configurations changes one A_{ki} by +29% and another by -20%. However, the sum of the nearby A_{ki} 's is almost preserved, which is expected [34]. Thus the changes are due to redistribution of A_{ki} 's among the transitions.

Except for the above configurations, we tested all other configurations predicted by FOTOS, but none of them has an effect of more than 5% and therefore were not included in the wave functions.

Another big effect is from the magnetic Breit operator. We tested its impact on the A_{ki} 's for transitions to $J=3/2$ final states. For most transitions, the Breit effect changes the A_{ki} 's by $\sim 10\%$. But for a few others, the change is much larger and even more than 100%. Usually these are transitions to lower levels of $1s\ 2s^2 \cdots 4p^5\ 5p\ J=3/2$, or to higher levels of $J=3/2$ final state where the mixing between $1s\ 2s^2 \cdots 4p^5\ 7p$ and $1s\ 2s^2 \cdots 4p^5\ 8p$ is changed a lot by the Breit effect. In either case, the sum of the A_{ki} 's of all nearby transitions is nearly preserved. Therefore, the Breit operator redistributes the A_{ki} 's among nearby transitions.

3.2. Transition Energies and Transition Probabilities for Kr III

Calculations for Kr III are very similar to those for Kr II. Results for transition energies and transition probabilities of the 118 largest transitions are listed in table 3.

3.2.1. Transition energies For Kr III, we computed electric dipole transitions from $1s^2\ 2s^2 \cdots 4p^4\ J = 0, 1, 2$ to $1s\ 2s^2 \cdots 4p^5\ J = 0, 1, 2$, $1s\ 2s^2 \cdots 4p^4\ np\ (n=5-8)\ J=0, 1, 2, 3$. For the upper states, 50 $J=1$ levels, 52 $J=2$ levels, 28 $J=3$ levels and 24 $J=0$ levels were obtained. This necessitated increasing the number of roots allowed in RCI [20] from 30 to 60. A total of 437 $E1$ transitions connecting these levels were calculated.

We started with calculating transition energies between $1s^2\ 2s^2 \cdots 4p^4$ states and $1s\ 2s^2 \cdots 4p^5$ states. For both states, excitations from 1s, 2s, 2p, 4s, 4p and outermost np electrons were included in the wave functions. A total of 5 RSH functions per symmetry were used except that 6 were used for symmetry f and 4 were used for symmetry g.

The correlation effects from opening 3s, 3p and 3d subshell were estimated separately in small calculations. Correlation from double excitations of 1s (3s,3p,3d) and (3s,3p,3d) 4p makes a net contribution decreasing the transition energy by 0.069 eV. This effect is smaller than that in Kr II, as now there is one less 4p electron in each state. As for the energy shift in $1s\ 2s^2 \cdots 4p^5$ due to the Auger effect, we used our results for Kr II $1s\ 2s^2 \cdots 4p^6$. Comparing the average radii of all the inner subshells 1s, 2s, ..., 3d between Kr II $1s\ 2s^2 \cdots 4p^6$ and Kr III $1s\ 2s^2 \cdots 4p^5$, the differences are less than 0.1%. So the radials are very similar. According to results for Kr II, none of those big channels involves orbitals beyond 3p. Therefore it's safe to assume that the matrix element in the integrand of formula (5) should be almost the same for Kr III. As to the denominator of the integrand, it's true that positions of the pole in Kr III are different from those in Kr II. But this has turned out to have very little effect: the

poles in Kr III are within about 109 eV of the corresponding poles in Kr II. We shifted the positions of the pole in Kr II by ~ 109 eV, and the change in energy shift is always less than 0.5 meV for all the big channels. Combining the above two factors, we assume that in Kr III the energy shift is 0.256 eV, the same as in Kr II.

The magnetic Breit correlation effects are included by introducing the magnetic Breit operator into the Hamiltonian at the final stage of the calculation, then diagonalizing the energy matrix. To speed up calculations, we applied the “partial” Breit technique [35]. The Breit effects are calculated for all the matrix elements containing reference configurations and all diagonal matrix elements, but excluded for the matrix elements involving two different correlation configurations. The savings in CPU time can reach 60%. For Kr II, we have tested the error made by using “partial” Breit. For Kr II $1s\ 2s^2 \cdots 4p^5\ np\ J = 1/2$ upper states, using “partial” Breit and including only the reference space as the Breit reference space, caused significant changes in the top 6 nearly degenerate levels; for the remaining lower levels, this introduced an error of 0.0008–0.0017 eV in the energy differences whose values are larger than 19 eV. Then we calculated transition probabilities using this “partial” Breit wave function. Except for transitions to the top 6 “problem” levels, A_{ki} ’s for other levels were very close to those obtained using the full Breit, especially the bigger one’s where the changes are all within 1.5%. Moreover, if we enlarged the Breit reference space by including in it those single excitations from 4p, the maximum change in the energy difference became 0.0003 eV. The problem with the top 6 A_{ki} ’s disappeared and the bigger A_{ki} ’s were changed by less than 1.0%. So as long as “partial” Breit is used for non-degenerate energy levels, it introduces no big error in both transition energies and A_{ki} ’s.

The Breit effects differ among the $1s\ 2s^2 \cdots 4p^5$ levels. For example, they differ by 0.054 eV between $J = 2$ and $J = 0$ levels.

The retardation and the QED effects were almost the same among the initial state levels. The difference is less than 5 meV and thus was neglected. This is true with the final state levels too. The net effect to transition energy is: the retardation effect increases it by 1.644 eV, QED effects decrease it by 10.789 eV.

All of the above effects have been added to transition energies for $1s^2\ 2s^2 \cdots 4p^4 \rightarrow 1s\ 2s^2 \cdots 4p^5$.

As in Kr II, transition energies to the $1s\ 2s^2 \cdots 4p^4\ np$ levels were obtained on the basis of transition energies to $1s\ 2s^2 \cdots 4p^5$ levels. For each total J of $1s\ 2s^2 \cdots 4p^4\ np$, we did separate RCI calculations (including also $1s\ 2s^2 \cdots 4p^5$ in the reference space except in $J=3$) where only excitations from 4s, 4p and np are included. Two RSH functions per symmetry (symmetry f and g have only 1) were used to capture most of the correlation energy. The effect of the magnetic Breit operator can be large: it can change the energy difference relative to $1s\ 2s^2 \cdots 4p^5$ from +0.020 eV to -0.118 eV (“+” means to increase, “-” means to decrease). For example, in the $J=3$ upper state, the splitting between $1s\ 2s^2 \cdots 4p^4\ 7p\ r6$ and $1s\ 2s^2 \cdots 4p^4\ 8p\ r4$ used to be 0.0008 eV, but after including the Breit operator, the two levels flipped and their splitting became 0.0327 eV. The Breit operator also causes a big mixing between $1s\ 2s^2 \cdots 4p^5\ 7p$ and

1s 2s² ... 4p⁵ 8p in some higher levels.

3.2.2. Transition probabilities As in Kr II, the magnetic Breit operator and some FOTOS configurations have a big impact on transition probabilities. With the magnetic Breit operator “turned on” in both states for the big A_{ki} ’s, the changes range from almost zero to 56%. There are even several transitions whose changes are bigger than 65%. However, the sum of A_{ki} ’s of all the transitions is almost preserved, i.e. the A_{ki} ’s are redistributed among the transitions. The big changes are usually accompanied by a big change in the dominant contribution to the dipole matrix element. Part of the reason, according to our observation during the calculation, is that the magnetic Breit operator changes the mixing of 1s 2s² ... 4p⁴ 7p into 1s 2s² ... 4p⁴ 8p, or vice versa; it changes also the LS compositions of some of the levels. For example, in 1s² 2s² ... 4p⁴ ¹D₂ → 1s 2s² ... 4p⁴ 5p r5 $J=3$, magnetic Breit effects increase the A_{ki} by 33%. Our analysis table shows that contribution from 1s 2s² ... 4p⁴ 5p r5 increases by 15%. Also, a small test run at the DF level shows that the magnetic Breit operator increases the percentage composition of ¹F₃ in 1s 2s² ... 4p⁴ 5p r5 by 9%. This is the only term that’s responsible for the $E1$ transition between 1s² 2s² ... 4p⁴ ¹D₂ and 1s 2s² ... 4p⁴ 5p r5 $J=3$.

Kr III 1s 2s² ... 4p⁵ $J=1$ produces two LS terms: ³P₁, ¹P₁. But the two $J=1$ levels are not LS pure. A small calculation at the DF level demonstrated this. Moreover, the A_{ki} ’s for transitions to these two $J=1$ levels are always of the same order as can be seen from table 3. This is another manifestation that these two levels are not LS pure.

In table 1 and table 3, the smaller A_{ki} ’s are omitted due to lack of space, but they are available upon request.

3.3. K Edge Energies for Kr I, Kr II and Kr III

Our calculated three K edge energies together with the individual contributions are listed in table 4. Also listed are the experimental and other theoretical results. The estimated net contributions from double excitations of 1s (3s,3p,3d) and (3s,3p,3d) 4p are included where applicable. We assume the Auger shift is the same for the three 1s hole states, based on the same argument made in section 3.2.1.. We used the following expression to find K edge energy for Kr I:

$$\text{edge energy} = \Delta E_{1s4p^6-4p^5 \ ^2P_{3/2}} + \Delta E_{4p^5 \ ^2P_{3/2}-4p^6 \ ^1S_0}$$

where the first term gives the K shell transition energy of Kr II, which has been calculated by RCI. The second term gives the binding energy of the 4p electron in the Kr atom, which was directly taken from Moore’s table [31]. Therefore, in table 4, all entries under “Kr I ” are for the first term, i.e., the transition energy for 1s² 2s² ... 4p⁵ ²P_{3/2} → 1s 2s² ... 4p⁶, except for the first one, which includes the experimental binding energy of the 4p electron. The experimental value was obtained using the same idea as the above expression, though they have taken more than one combination of transition and binding energies and taken the weighted average value as the final result.

Indeed, our value agrees well with the experimental value—it’s about 0.94 eV bigger. This edge energy was calculated by Indelicato *et al* [36] before. Our value is only about 0.06 eV larger than theirs. Though there is no specific data for individual contributions in their paper to compare with, the way they took into account of the retardation effect, the QED corrections was essentially the same as ours. For the Auger effect and correlation, they used the complex rotation method and many body perturbation theory, but the Coulomb and Magnetic correlation contributions were obtained by extrapolation of calculations for some selected elements [19, 36].

Experimentally, edge energies can be measured in two different ways: by critical absorption edge measurement or by X-ray photoelectron measurement. The first method gives approximately the edge position but theoretical corrections must be made for fine structure effects in the edge. Also, the thickness of the absorber can displace the observed edge. Therefore, this method is considered to be less precise than the second one. Sufficient care must be taken for its results to be competitive with that of the photoelectron method. In the photoelectron measurement, however, one has to take into account of the work function of the spectrometer which suffers from some uncertainty. In addition to these “direct” measurements of the edge energy, there are also some “indirect” methods that provide a good estimate of the edge energy. One is to combine experimental inner-shell transition energies with experimental outer-shell binding energies that are more amenable to accurate measurements. Due to the extensive database for the latter, there are redundant routes to edge determinations. Therefore, the final estimated edge energy is taken as the weighted average of several determinations. Another method is to use the photoabsorption spectrum to determine the energy difference between the closed-core state and the X-ray excited state, then relate the energy to the vacuum level by means of the corresponding spectroscopic series.

For Kr I, we were able to find the “direct” K edge energies only in Bearden’s database [37] which were rescaled a decade ago [38]. Other values we found all belonged to the “indirect” catalogue and they agree very well with each other (they differ by 0.1 eV if rounded to the first digit after the decimal) [10]. Therefore, in table 4 we listed the “indirect” value given in reference [38] as the experimental data.

Our K edge energy for Kr III was calculated in the same way as for Kr I, except that Kr III $1s\ 2s^2 \dots 4p^5\ ^3P_2$ was used as the intermediate state. The edge energy for Kr II was obtained by finding the energy difference between $1s\ 2s^2 \dots 4p^5\ ^3P_2$ and $1s^2\ 2s^2 \dots 4p^5\ ^2P_{3/2}$ directly. Though there is no measurement for the K edge energies of Kr II and Kr III, estimates can be made for them [39]. From [6, 40], the energy for ejecting both a 1s and 4p electron from Kr atom is estimated to be 14353.8 eV with at least 1 eV uncertainty. Since the binding energy of 4p electron in Kr atom is 14.0 eV [31], the 1s ionization energy of Kr II can therefore be estimated as 14340 eV with at least 1 eV uncertainty. This is included in table 4 as the experimental value. For the K edge energy of Kr III, one can make use of the “Z+1 approximation”, in which it’s assumed that the potential experienced by the high-lying 1s-excited state of Kr III is similar to the potential experienced by corresponding valence-excited state of Rb III. The binding

energy of the 4p electron in Kr III $1s\ 2s^2 \cdots 4p^5$ is thus estimated to be 39.7 eV [31]. Combining with the above 14353.8 eV, the energy required to remove one 1s electron and two 4p electron from Kr atom is estimated to be 14393.5 eV. Since about 38.6 eV [31] is required to remove two 4p electrons from the Kr atom, the rough estimated K edge energy for Kr III is thus 14354.9 eV with unknown uncertainty, quite close to our RCI result of 14356.150 eV.

Another way to test the reliability of our results is to work backwards. Using our values for Kr I and Kr II in table 4, we derived the energy difference between Kr III $1s \cdots 4p^5$ and Kr II $1s \cdots 4p^6$ in the following way: From table 4

$$E(1s \cdots 4p^5) - E(1s^2 \cdots 4p^5) = 14341.353 \text{ eV};$$

$$E(1s \cdots 4p^6) - E(1s^2 \cdots 4p^6) = 14328.127 \text{ eV},$$

Subtracting these two equations and rearranging the terms, we get:

$$E(1s \cdots 4p^5) - E(1s \cdots 4p^6) = 13.226 \text{ eV} + [E(1s^2 \cdots 4p^5) - E(1s^2 \cdots 4p^6)]$$

The energy difference in the bracket is found to be ~ 14.000 eV from Moore's table [31]. Thus for Kr,

$$E(1s \cdots 4p^5) - E(1s \cdots 4p^6) = 27.226 \text{ eV}.$$

This, as predicted by the "Z+1 approximation", should be approximately the same as the 4p ionization energy of Rb II, which is ~ 27.506 eV [31]. Indeed, the two numbers are very close. Following the same idea, we derived for Kr the energy difference $E(1s \cdots 4p^4) - E(1s \cdots 4p^5)$ to be 39.369 eV, while the corresponding "Z+1 approximation" value for Rb III is ~ 39.675 eV. We thus believe that our edge energies for Kr II and Kr III are reliable enough to serve as good starting points in any future work.

4. Conclusion

The Relativistic Configuration Interaction methodology has been used to calculate K-shell transition energies and transition probabilities for 122 $E1$ transitions in Kr II, and 437 transitions in Kr III. The agreement between the transition forms is excellent, averaging 1.34% in Kr II and 2.34% in Kr III. These data have been used to interpret absorption spectrum for a mixture of Kr II and Kr III and have been found to be in good agreement with measurement [4]. Relaxation effects, QED effects, correlation and Breit effects, are all essential for accurate transition energies. The good agreement in K-edge energy for Kr atom between our value and another theoretical work and experiment, indicates that the above effects and Auger effects have been well accounted for. The bulk of the remaining difference (~ 1 eV) may be with QED effects. Higher order terms which are $1/Z$ times those included would yield one order of magnitude correction ~ 1 eV for $Z \approx 36$. QED accuracies at this level are not yet possible for any but one and two electron atoms (ions).

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Table 1. Photoexcitation Transition Energies (in eV) and Transition Probabilities (in 10^{10} s^{-1}) for Kr II

Final State	Transition Energy	A_{ki}		
		Vel. Form	Len. Form	Average
$4p^5 \ ^2P_{1/2} \rightarrow J=3/2$				
1s $4p^5$ 5p r4	14333.900	6.36	6.29	6.33
1s $4p^5$ 5p r5	14334.475	92.77	91.72	92.24
1s $4p^5$ 5p r6	14334.534	81.52	80.71	81.12
1s $4p^5$ 5p r7	14334.659	77.85	77.11	77.48
1s $4p^5$ 6p r4	14337.448	1.58	1.57	1.58
1s $4p^5$ 6p r5	14338.134	16.06	15.92	15.99
1s $4p^5$ 6p r6	14338.172	35.95	35.53	35.74
1s $4p^5$ 6p r7	14338.230	33.64	33.36	33.50
1s $4p^5$ 7p r5	14339.644	9.28	9.20	9.24
1s $4p^5$ 7p r6	14339.699	6.03	5.95	5.99
1s $4p^5$ 8p r4	14339.710	16.87	16.69	16.78
1s $4p^5$ 7p r7	14339.739	9.72	9.65	9.68
1s $4p^5$ 8p r5	14340.418	5.86	5.81	5.83
1s $4p^5$ 8p r6	14340.488	8.96	8.85	8.90
1s $4p^5$ 8p r7	14340.504	9.06	8.99	9.03
$4p^5 \ ^2P_{1/2} \rightarrow J=1/2$				
1s $4p^6$	14313.461	878.28	868.26	873.27
1s $4p^5$ 5p r1	14332.791	14.20	14.08	14.14
1s $4p^5$ 5p r2	14333.240	4.24	4.21	4.23
1s $4p^5$ 5p r3	14333.598	10.55	10.42	10.48
1s $4p^5$ 5p r4	14333.886	37.88	37.61	37.74
1s $4p^5$ 5p r5	14334.055	161.68	160.75	161.21
1s $4p^5$ 5p r6	14334.400	13.44	13.39	13.41
1s $4p^5$ 6p r2	14336.819	1.90	1.87	1.89
1s $4p^5$ 6p r4	14337.549	18.30	18.08	18.19
1s $4p^5$ 6p r5	14337.636	47.80	47.26	47.53
1s $4p^5$ 6p r6	14337.744	11.49	11.37	11.43
1s $4p^5$ 7p r1	14338.216	1.64	1.63	1.63
1s $4p^5$ 7p r4	14339.076	8.45	8.35	8.40
1s $4p^5$ (7p+8p)	14339.116	5.92	5.84	5.88
1s $4p^5$ (7p+8p)	14339.176	20.88	20.65	20.76
1s $4p^5$ (7p+8p)	14339.241	2.07	2.05	2.06
1s $4p^5$ 8p r4	14339.863	4.05	4.00	4.03
1s $4p^5$ 8p r5	14339.937	14.54	14.35	14.44
1s $4p^5$ 8p r6	14339.966	2.48	2.46	2.47
$4p^5 \ ^2P_{3/2} \rightarrow J=5/2$				
1s $4p^5$ 5p r1	14334.177	82.32	81.53	81.92
1s $4p^5$ 5p r2	14334.333	158.61	156.61	157.61
1s $4p^5$ 5p r3	14334.492	21.94	21.68	21.81
1s $4p^5$ 5p r4	14335.278	1.23	1.21	1.22

Final State	Transition Energy	A_{ki}		
		Vel. Form	Len. Form	Average
$4p^5 \ ^2P_{3/2} \rightarrow J=5/2$				
1s $4p^5$ 6p r1	14337.861	32.77	32.46	32.61
1s $4p^5$ 6p r2	14337.926	25.80	25.79	25.80
1s $4p^5$ 6p r3	14338.097	26.25	26.18	26.21
1s $4p^5$ 6p r4	14338.904	1.10	1.10	1.10
1s $4p^5$ 7p r1	14339.380	15.85	15.70	15.77
1s $4p^5$ 7p r2	14339.411	9.69	9.73	9.71
1s $4p^5$ 7p r3	14339.605	13.47	13.48	13.47
1s $4p^5$ 8p r1	14340.159	8.81	8.73	8.77
1s $4p^5$ 8p r2	14340.177	5.06	5.10	5.08
1s $4p^5$ 8p r3	14340.382	7.66	7.68	7.67
$4p^5 \ ^2P_{3/2} \rightarrow J=3/2$				
1s $4p^5$ 5p r2	14334.292	32.32	32.02	32.17
1s $4p^5$ 5p r3	14334.428	137.22	135.81	136.52
1s $4p^5$ 5p r4	14334.566	71.74	71.10	71.42
1s $4p^5$ 5p r7	14335.325	6.22	6.17	6.19
1s $4p^5$ 6p r2	14337.897	40.80	40.44	40.62
1s $4p^5$ 6p r3	14338.060	27.36	27.08	27.22
1s $4p^5$ 6p r4	14338.114	16.46	16.34	16.40
1s $4p^5$ 7p r2	14339.389	23.62	23.42	23.52
1s $4p^5$ 7p r3	14339.578	11.34	11.23	11.28
1s $4p^5$ 7p r4	14339.603	6.77	6.73	6.75
1s $4p^5$ 8p r2	14340.159	15.43	15.31	15.37
1s $4p^5$ 8p r3	14340.356	6.33	6.27	6.30
1s $4p^5$ 7p r7	14340.405	3.39	3.37	3.38
$4p^5 \ ^2P_{3/2} \rightarrow J=1/2$				
1s $4p^6$	14314.127	1700.89	1683.52	1692.20
1s $4p^5$ 5p r1	14333.457	209.82	208.29	209.06
1s $4p^5$ 5p r2	14333.906	1.26	1.28	1.27
1s $4p^5$ 5p r3	14334.264	3.23	3.25	3.24
1s $4p^5$ 5p r4	14334.552	1.31	1.31	1.31
1s $4p^5$ 5p r5	14334.721	6.42	6.40	6.41
1s $4p^5$ 5p r6	14335.066	17.22	16.98	17.10
1s $4p^5$ 6p r1	14337.357	61.62	60.90	61.26
1s $4p^5$ 6p r2	14337.485	5.68	5.59	5.63
1s $4p^5$ 6p r6	14338.410	9.05	8.94	8.99
1s $4p^5$ 7p r1	14338.882	16.21	16.04	16.12
1s $4p^5$ 7p r2	14339.011	10.93	10.79	10.86
1s $4p^5$ 8p r1	14339.628	11.15	11.01	11.08
1s $4p^5$ (7p+8p)	14339.782	3.83	3.78	3.80
1s $4p^5$ (7p+8p)	14339.842	2.33	2.31	2.32
1s $4p^5$ (7p+8p)	14339.907	2.16	2.13	2.14
1s $4p^5$ 8p r6	14340.632	1.93	1.91	1.92

Table 2. Contributions to energy shift from each channel that is connected to Kr II 1s 4p⁶ state via K-shell Auger transition.

Labels used by Chen <i>et al.</i> [33]	Channel	Shift (eV)
L ₂ L ₂ , L ₂ L ₃ , L ₃ L ₃	(1s ² 2s ² 2p ⁴ ... 4p ⁶) ¹ D ₂ εd	0.1550
	(1s ² 2s ² 2p ⁴ ... 4p ⁶) ¹ S ₀ εs	0.0197
L ₁ L ₂ , L ₁ L ₃	(1s ² 2s 2p ⁵ ... 4p ⁶) ³ P εp	0.0544
	(1s ² 2s 2p ⁵ ... 4p ⁶) ¹ P ₁ εp	-0.0166
L ₂ M ₂ , L ₂ M ₃ , L ₃ M ₂ , L ₃ M ₃	(1s ² 2s ² 2p ⁵ 3s ² 3p ⁵ ... 4p ⁶) ³ D εd	0.0015
	(1s ² 2s ² 2p ⁵ 3s ² 3p ⁵ ... 4p ⁶) ¹ D ₂ εd	0.0344
	(1s ² 2s ² 2p ⁵ 3s ² 3p ⁵ ... 4p ⁶) ³ S ₁ εs	0.0003
	(1s ² 2s ² 2p ⁵ 3s ² 3p ⁵ ... 4p ⁶) ¹ S ₀ εs	0.0063
L ₁ L ₁	(1s ² 2p ⁶ ... 4p ⁶) ¹ S ₀ εs	0.0007
total		0.2557

Table 3. Photoexcitation Transition Energies (in eV) and Transition Probabilities (in 10^{11} s^{-1}) for Kr III

Final State	Transition Energy	A_{ki}		
		Vel. Form	Len. Form	Average
$4p^4 \ ^3P_0 \rightarrow J=1$				
1s $4p^5$ r1	14316.809	46.40	45.94	46.17
1s $4p^5$ r2	14317.654	18.43	18.22	18.33
1s $4p^4$ 5p r2	14341.674	2.98	2.94	2.96
1s $4p^4$ 5p r6	14342.643	30.99	30.65	30.82
1s $4p^4$ 5p r7	14342.752	1.07	1.05	1.06
1s $4p^4$ 5p r9	14343.103	4.15	4.11	4.13
1s $4p^4$ 6p r6	14348.839	8.29	8.22	8.26
1s $4p^4$ 6p r8	14349.158	4.25	4.20	4.22
1s $4p^4$ 7p r6	14351.569	3.25	3.22	3.24
1s $4p^4$ 7p r8	14351.953	2.73	2.70	2.72
1s $4p^4$ (7p+8p)	14352.998	1.38	1.36	1.37
1s $4p^4$ 8p	14353.456	1.69	1.67	1.68
$4p^4 \ ^1S_0 \rightarrow J=1$				
1s $4p^5$ r1	14313.367	18.70	18.51	18.60
1s $4p^5$ r2	14314.212	46.41	45.86	46.14
1s $4p^4$ 5p r13	14343.067	4.84	4.79	4.82
1s $4p^4$ 5p r14	14343.173	33.26	32.92	33.09
1s $4p^4$ 6p r13	1349.345	1.17	1.15	1.16
1s $4p^4$ (6p+7p)	14349.38	11.02	10.92	10.97
$4p^4 \ ^3P_1 \rightarrow J=0$				
1s $4p^5 \ ^3P_0$	14317.612	190.45	188.53	189.49
1s $4p^4$ 5p r1	14341.900	1.81	1.79	1.80
1s $4p^4$ 5p r2	14342.186	22.09	21.81	21.95
1s $4p^4$ 5p r3	14342.311	14.20	14.00	14.10
1s $4p^4$ 6p r2	14348.671	1.30	1.29	1.29
1s $4p^4$ 6p r3	14348.811	11.26	11.10	11.18
1s $4p^4$ 7p r3	14351.631	4.79	4.73	4.76
1s $4p^4$ (7p+8p)	14353.104	1.94	1.91	1.93
$4p^4 \ ^3P_1 \rightarrow J=1$				
1s $4p^5$ r1	14316.904	25.13	24.86	25.00
1s $4p^5$ r2	14317.749	23.48	23.26	23.37
1s $4p^4$ 5p r2	14341.769	2.57	2.54	2.55
1s $4p^4$ 5p r4	14342.339	1.41	1.39	1.40
1s $4p^4$ 5p r5	14342.532	9.13	9.03	9.08
1s $4p^4$ 5p r7	14342.847	18.98	18.76	18.87
1s $4p^4$ 5p r8	14342.907	1.60	1.58	1.59
1s $4p^4$ 5p r9	14343.197	6.32	6.25	6.29

Final State	Transition Energy	A_{ki}		
		Vel. Form	Len. Form	Average
$4p^4 \ ^3P_1 \rightarrow J=1$ (continued)				
1s $4p^4$ 6p r4	14348.753	3.50	3.46	3.48
1s $4p^4$ 6p r7	14349.033	8.29	8.21	8.25
1s $4p^4$ 6p r9	14349.363	1.62	1.60	1.61
1s $4p^4$ 7p r4	14351.557	1.05	1.03	1.04
1s $4p^4$ 7p r7	14351.751	4.02	3.97	3.99
1s $4p^4$ 7p r9	14352.109	1.06	1.05	1.05
$4p^4 \ ^3P_1 \rightarrow J=2$				
1s $4p^5 \ ^3P_2$	14316.675	48.84	48.30	48.57
1s $4p^4$ 5p r2	14341.638	1.03	1.01	1.02
1s $4p^4$ 5p r3	14341.983	1.52	1.50	1.51
1s $4p^4$ 5p r6	14342.571	32.97	32.59	32.78
1s $4p^4$ 5p r7	14342.656	3.50	3.47	3.48
1s $4p^4$ 5p r8	14343.045	1.43	1.41	1.42
1s $4p^4$ 6p r6	14348.885	6.73	6.67	6.70
1s $4p^4$ 6p r7	14348.909	4.67	4.61	4.64
1s $4p^4$ 6p r8	14349.301	1.80	1.78	1.79
1s $4p^4$ 7p r6	14351.672	1.83	1.82	1.82
1s $4p^4$ 7p r7	14351.687	3.21	3.18	3.20
1s $4p^4$ 7p r8	14352.080	1.26	1.25	1.26
1s $4p^4$ (7p+8p)	14353.182	1.47	1.46	1.46
$4p^4 \ ^3P_2 \rightarrow J=1$				
1s $4p^5$ r1	14317.468	75.75	75.06	75.40
1s $4p^5$ r2	14318.313	13.96	13.82	13.89
1s $4p^4$ 5p r2	14342.333	27.92	27.58	27.75
1s $4p^4$ 5p r3	14342.781	2.05	2.02	2.04
1s $4p^4$ 5p r6	14343.301	1.60	1.58	1.59
1s $4p^4$ 5p r7	14343.411	1.73	1.72	1.73
1s $4p^4$ 5p r8	14343.471	1.10	1.08	1.09
1s $4p^4$ 5p r9	14343.761	2.61	2.59	2.60
1s $4p^4$ 6p r1	14348.636	3.88	3.85	3.87
1s $4p^4$ 6p r2	14348.827	8.52	8.41	8.46
1s $4p^4$ 7p r1	14351.417	2.70	2.66	2.68
1s $4p^4$ 7p r2	14351.670	3.06	3.02	3.04
1s $4p^4$ 8p r1	14352.860	2.23	2.20	2.21
1s $4p^4$ 8p r2	14353.187	1.59	1.56	1.58
$4p^4 \ ^1D_2 \rightarrow J=1$				
1s $4p^5$ r1	14315.653	124.17	122.77	123.47
1s $4p^5$ r2	14316.498	196.30	194.34	195.32
1s $4p^4$ 5p r2	14340.517	1.23	1.22	1.23
1s $4p^4$ 5p r5	14341.281	6.39	6.31	6.35
1s $4p^4$ 5p r8	14341.655	12.85	12.69	12.77

Final State	Transition Energy	A_{ki}		
		Vel. Form	Len. Form	Average
$4p^4 \ ^1D_2 \rightarrow J=1$ (continued)				
1s $4p^4$ 5p r10	14342.917	6.39	6.32	6.36
1s $4p^4$ 5p r12	14343.319	2.59	2.56	2.57
1s $4p^4$ 6p r9	14348.111	1.56	1.55	1.55
1s $4p^4$ 6p r10	14349.095	7.04	6.97	7.01
1s $4p^4$ 6p r11	14349.150	1.90	1.88	1.89
1s $4p^4$ (7p+8p)	14351.892	2.43	2.40	2.42
1s $4p^4$ (7p+8p)	14351.976	1.36	1.34	1.35
$4p^4 \ ^3P_2 \rightarrow J=2$				
1s $4p^5 \ ^3P_2$	14317.239	142.39	140.97	141.68
1s $4p^4$ 5p r1	14341.797	1.22	1.20	1.21
1s $4p^4$ 5p r2	14342.202	35.24	34.80	35.02
1s $4p^4$ 5p r6	14343.135	1.19	1.18	1.18
1s $4p^4$ 6p r2	14348.685	9.94	9.87	9.90
1s $4p^4$ 6p r3	14348.863	2.16	2.12	2.14
1s $4p^4$ 7p r2	14351.443	2.95	2.95	2.95
1s $4p^4$ 7p r3	14351.688	2.22	2.19	2.21
1s $4p^4$ 8p r2	14352.890	1.72	1.72	1.72
1s $4p^4$ 8p r3	14353.204	1.29	1.27	1.28
$4p^4 \ ^1D_2 \rightarrow J=2$				
1s $4p^5 \ ^3P_2$	14315.424	4.86	4.79	4.82
1s $4p^4$ 5p r10	14342.741	1.27	1.27	1.27
1s $4p^4$ 5p r11	14343.104	12.49	12.35	12.42
1s $4p^4$ 5p r12	14343.205	26.07	25.82	25.95
1s $4p^4$ 6p r11	14349.217	7.20	7.15	7.18
1s $4p^4$ 6p r12	14349.303	7.17	7.13	7.15
1s $4p^4$ (7p+8p)	14351.949	1.48	1.47	1.48
1s $4p^4$ (7p+8p)	14351.972	1.88	1.87	1.87
1s $4p^4$ 7p	14352.043	2.97	2.96	2.97
1s $4p^4$ 8p	14353.422	1.83	1.83	1.83
1s $4p^4$ 8p	14353.522	1.76	1.76	1.76
$4p^4 \ ^3P_2 \rightarrow J=3$				
1s $4p^4$ 5p r2	14342.154	19.05	18.81	18.93
1s $4p^4$ 5p r3	14342.439	21.90	21.63	21.77
1s $4p^4$ 5p r4	14342.975	1.54	1.52	1.53
1s $4p^4$ 6p r2	14348.436	8.70	8.58	8.64
1s $4p^4$ 6p r3	14348.772	6.13	6.05	6.09
1s $4p^4$ 7p r2	14351.214	4.56	4.50	4.53
1s $4p^4$ 7p r3	14351.573	2.86	2.82	2.84
1s $4p^4$ 8p r2	14352.702	2.83	2.79	2.81
1s $4p^4$ 8p r3	14353.073	1.68	1.66	1.67

Final State	Transition Energy	A_{ki}		
		Vel. Form	Len. Form	Average
$4p^4 \ ^1D_2 \rightarrow J=3$				
1s $4p^4$ 5p r5	14342.445	15.12	14.91	15.01
1s $4p^4$ 5p r6	14342.652	28.03	27.67	27.85
1s $4p^4$ 6p r5	14348.888	6.39	6.30	6.35
1s $4p^4$ 6p r6	14349.015	9.22	9.10	9.16
1s $4p^4$ 7p r5	14351.720	3.44	3.39	3.42
1s $4p^4$ 7p r6	14351.806	2.87	2.84	2.86
1s $4p^4$ 7p r7	14351.852	1.50	1.48	1.49
1s $4p^4$ 8p r5	14353.232	2.08	2.05	2.07
1s $4p^4$ 8p r7	14353.343	1.58	1.56	1.57

Table 4. 1s ionization energy of Kr I, Kr II and Kr III (unit: eV).

Ionized state	Kr I	Kr II	Kr III
	1s ... 4p ⁶ ² S _{1/2}	1s ... 4p ⁵ ³ P ₂	1s ... 4p ⁴ ⁴ P _{5/2}
Coulomb Dirac-Fock	14360.144*	14372.115	14386.869
Coulomb corr	-	1.274	1.298
Magnetic	-23.699	-23.709	-23.706
Retardation	1.563	1.647	1.642
QED	-10.703	-10.787	-10.787
Magnetic Breit corr	0.566	0.557	0.578
Auger shift	0.256	0.256	0.256
Total ionization energy	14328.127	14341.353	14356.150
Other theoretical energy ^a	14328.07	-	-
Experiment energy	14327.19 (13) ^b	14340±1 ^c	-

* Because of the way the K edge energy is calculated (see the text), we are not able to separate the Coulomb correlation energy from the Coulomb Dirac-Fock energy. So this number includes both Coulomb Dirac-Fock energy and full Coulomb correlation energy.

^a From reference [36].

^b From reference [38].

^c From reference [39].