

The 1s photoabsorption transitions in Br I and Br II

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Abstract. Relativistic configuration interaction calculations have been performed for the $1s \rightarrow np$ ($n=4-8$) photoabsorption transitions in Br I and Br II and transition energies and transition probabilities have been evaluated. These data are necessary to interpret the experiment photoabsorption spectra. The K edge energy of Br I and Br II have also been computed and compared to the existing values when available.

1. Introduction

In a recent paper, we reported our calculations for the 1s photoabsorption spectra of Kr II and Kr III [1]. The work was a result of collaboration between our research group and the Argonne National Laboratory (ANL) group and has turned out to have good agreement with the experiment.

Most recently, when studying a bromine-containing molecule using high power laser and x-ray sources, the ANL group found some Bromine fragments which manifest themselves as some structures in the photoabsorption spectra across Br K edge. However, it can't be decided if these structures belong to neutral Br, Br II or both. Therefore, the x-ray photoabsorption spectra of both Br I and Br II are necessary to interpret their output.

The ground state configuration of Br I is $4p^5$, the same as that of Kr II. Though the 3d, 4s photoabsorption spectra of Br I have been studied already [2-4], to our knowledge the $1s \rightarrow np$ transitions haven't. Theoretically, dealing with the 1s electron is more challenging than the shallow core electrons (such as 3d and 4s), because the relativistic, QED effects become important and can't be neglected.

In this paper, we report our calculations for the $1s \rightarrow np$ ($n=4-8$) transitions in both Br I and Br II using a relativistic configuration interaction methodology. The K edge energy of Br I and Br II are also obtained and compared with the existing values.

2. Methodology

Since Br I/Br II have identical configurations as Kr II/Kr III and we are studying the same photoexcitation process here for Br I/II, we follow the same methodology we

have used for Kr [1]. Below, we give a brief description of our relativistic configuration interaction (RCI) methodology. A detailed description can be found in [1].

For Br I and Br II, our initial states are of the form $1s^2 2s^2 \dots 4p^n$ and our final states are the 1s hole states of the form $1s 2s^2 \dots 4p^n$ (p'). For brevity, from now on, we'll drop any closed shells in our notation as long as it's appropriate to do so. With a 1s electron missing in the latter, the initial and final states certainly have a considerably different radial basis. We therefore do separate calculations for them so that relaxation effects are automatically included.

The Hamiltonian we use is the Dirac-Breit one. The Breit operator doesn't have large impact on the radial functions, but can significantly impact energy differences and f -values. Its inclusion into the energy matrix often makes the CPU time at least four times longer. Therefore, we usually include it into the Hamiltonian at the final stage of calculation when the radial basis set has been established.

The multi-electron wave functions are linear combinations of Slater determinants and are forced to be eigenstates of J^2 , J_z and parity. We take $4p^n$ as the reference configuration for the initial state and $1s 4p^n$ (p') the reference configurations for the final state. The corresponding reference functions and their one-electron radial functions are solved using the algorithm of Desclaux [5].

With the reference functions known, correlation functions are added to them to generate a first-order (in form) wave function. The correlation functions include configurations obtained by replacing one or two electrons in the reference configuration with other electrons. These "other" electrons could be in subshell(s) unoccupied in the reference configuration and thus have unknown radial functions. In RCI, we choose to use relativistic screened hydrogenic (RSH) functions as radial functions for such subshells, or virtuals (denoted with v). One advantage of RSH function is that it has only one adjustable parameter, Z^* , the effective charge, which provides easy control and avoids variational collapse into the "positron sea". It is determined during the energy variational procedure of RCI.

The RCI procedure produces wave functions and energies for the given state. In the case of states lying in the continuum (final states here), we separate ψ into a localized (bound) part ϕ and a continuum part ψ_{E_i} and employ a Fano-like procedure [6]. The interaction between the parts results in the energy shift in the final state localized energy, E_{loc} , which can be determined [6] by the equation:

$$E - E_{loc} = \sum_{n,i} \frac{|\langle \phi | H | \psi_{ni} \rangle|^2}{E - E_{ni}} + \sum_i P \int dE_i \frac{|\langle \phi | H | \psi_{E_i} \rangle|^2}{E - E_i} \quad (1)$$

Here E is the shifted energy, and ψ_{ni} represents a discrete Rydberg level (e.g. $2p^2 \rightarrow 1s4d$). These Rydberg levels are projected out to approximately satisfy orthogonality constraints [6, 7]. The sum (integral) is over all functions excluded from the localized function, and P indicates the principle value is taken for the integral.

According to our experience with Kr, it's sufficient in eqn. (1) to represent the localized function with just the reference function. Continuum solutions are generated

by solving the frozen-core continuum Dirac-Fock radial equation using the code of Perger and coworkers [8, 9].

The reference space for the final state of a given J is large (all $1s \cdots 4p^n p'$ configurations) and thus inclusion of the essential core-valence correlation configurations will make the matrix size easily exceed our current limit of 20k. To get around this, we employ the REDUCE procedure [10, 11] for some correlation configurations (energy errors are likely below 200 cm^{-1}).

With the “first-order” wave functions and transition energies obtained, we calculate the transition probabilities for the electric dipole process using our relativistic f -value code [12], where non-orthogonality between the radial basis of the initial and final states are treated using the methods of King *et al* [13].

3. Calculations

3.1. Br I

The ground state of Br I is $4p^5 \ ^2P_{3/2}$. We performed calculations for $1s^2 4p^5 \rightarrow 1s [4p^6+4p^5 np \ (n=5-8)]$ and obtained the transition energies and transition probabilities.

Our first step was to obtain the transition energies. For this purpose, we did well-correlated RCI calculation for the lowest state, ie $4p^5 \ ^2P_{3/2}$ of the initial state and $1s 4p^6 \ J=1/2$ of the final state, to get an accurate transition energy between them. The relative positions of other levels to the corresponding lowest state for each parity were determined using less-correlated RCI calculations. The combination of the above transition energy and the relative energies give transition energies for any allowed electric dipole transition.

In the two well-correlated calculations, we included the energetically differentially important correlations from single and double replacement of np , $4p$, and $4s$ electrons, double replacement of one $1s$ electron and one L-shell electron and double replacement of $1s$ electron (only allowed in the initial state). For both states, 5 sets of RSH functions (symmetry $l \leq 4$) were employed. In addition to the above correlation replacements, there are also other replacements that have small contributions but were not included in our wave functions. These include double replacement of one $1s$ electron and one M-shell electron, as well as one M-shell electron and one $4p$ electron. Since we didn't expect their inclusion into the wave function to produce noticeable second-order effects, we evaluated their contribution to the transition energy using small separate calculations.

As stated, our radial spaces were truncated at $l=4$, yet the correlation energy of replacing two $4p$ electrons was not diminishingly small at $l=4$. We estimated the size of the truncated correlation energy of this effect by extrapolating, just as we did for Kr II, and added these estimates to the transition energy.

The Breit effect was included as stated in section 2. Using the MCDF code by Desclaux [14], the combined effect of retardation and QED effects was found to decrease the transition energy by $\sim 8.3 \text{ eV}$.

The Auger shift in the $1s\ 4p^6$ state has also been taken into account. We made the reasonable assumption that the important open channels in Br I are the same as in Kr II [1, 15]. To test this, we calculated the shift caused by the dominant channel $2p^2 \rightarrow 1s\epsilon d$ for Br I using eqn. (1). The value was the same as that for Kr II, ie 0.1550 eV.

For the relative level positions within the initial $4p^5$ state, we used NIST's data [16] which is $3685.2\ \text{cm}^{-1}$. Our RCI calculations for the two levels, which produce the wave functions for the transition probability purpose, give an energy difference of $3630.2\ \text{cm}^{-1}$ without the Breit effect, $3561.6\ \text{cm}^{-1}$ with the Breit effect.

When positioning the even parity levels, we had no observed reference for energy. We made sure all reference configurations were correlated equivalently within each J state, and that all the J states were correlated similarly. Due to the current limit on the size of matrix, we included only replacements of np , $4p$ and $4s$ electrons in the wave function. Small ($\leq 100\ \text{cm}^{-1}$) energy splittings between adjacent levels of the same configuration were found in each J state.

Though there is a total of 122 electric dipole transitions, many of them are weak and should make a negligible contribution to the x-ray absorption spectra. So in table 1, we list only those strong ones ($A_{ki} \geq 10^{10}\ \text{s}^{-1}$) which contribute to the major features in the spectra. The excited states are not pure LS coupling, so we use 'rn' to denote different levels from the same configuration, with the bottom level being r1. For levels that are mixture of more than one configuration, we give the large components with the first one being the dominant configuration. Those lying above such levels are given their dominant configuration(s) only and without the 'rn' labelling. We follow the same scheme in the table for Br II (table 2). As in Kr II, $4p^4\ vp$ in the initial state and $1s\ 4p^5\ vp$ in the final state are important FOTOS [17] contributors to f -values. We have correlated them with all the large replacements. It can be seen from table 1 that absorption from $1s\ 4p^6$ and $1s\ 4p^5\ 5p$ will dominate the spectrum, while absorption from the $7p$ and $8p$ Rydberg states will have a very small contribution.

3.2. Br II

The ground state of Br II is $4p^4\ ^3P_2$. Calculations were performed for $1s^2\ 4p^4 \rightarrow 1s\ [4p^5 + 4p^4\ np\ (n=5-8)]$ and transition energies and transition probabilities obtained. For the final states, we calculated all the levels of each given J except for $J=1$, where only the lowest 50 levels were extracted from the RCI energy matrix. This is because higher in the spectrum, the transition probabilities to these levels are small (usually at least 3 orders of magnitude smaller than the strongest one) and thus of minor experimental interest.

As before, we calculated first the transition energy between the two lowest states ($4p^4\ ^3P_2$ in the initial state and $1s\ 4p^5\ J=2$ in the final state) using two well-correlated RCI runs. Then we found relative positions of other levels for each parity state.

The relative energy levels of the initial $4p^4$ state have been established previously [18] and agree very well with those in NIST database [16]. We used the NIST values for

the energy levels of $4p^4$.

When creating one-electron radial functions for the final state, some small improvements were made. As has happened in Kr III, the MCDF calculations to obtain 7p and 8p radial functions in the $J=0$ final state failed. To solve the problem, we used the 4 largest eigenvectors (out of 6), instead of using radials from a different J state. This has led to good self-consistency. The 5p, 7p and 8p radials in the $J=1$ state were obtained in a similarly way, while in Kr III, they were created by restricting the subgroup of $(1s 4p^4)$ to be $J=3/2$. This resulted in lower total energy and better self-consistency of the reference function at the DF stage.

As before, we included only replacements of 4s, 4p and np electrons when constructing the wave functions for the transition probability. According to our experience with Kr III, the partial Breit treatment [1] was employed to save CPU time. Intermediate calculations show that $4p^3 vp$ in the initial state and $1s 4p^4 vp$ in the final state are the dominant contributors to transition probabilities. These two configurations dominate some higher levels nearby. Our analysis tables also show that in the decreasing order of importance, $4s 4p^4 vd$, $4p^2 vp^2$ and $4p^3 vf$ in the initial state are other big contributors in some transitions. The correlation configuration $1s 4p^3 5p^2$ in the final state is a large contributor in the $J=0 \rightarrow J=1$ transition. All the above configurations as well as $1s 4p^3 5p np$ ($n=6-8$) (replacement of 4p with 5p in other reference configurations) have been correlated with the large replacements. The changes caused by correlating the $4p \rightarrow 5p$ replacement in transition probabilities of the largest order of magnitude are tiny, but in several transitions that are one order of magnitude smaller, there are big changes with the largest one being 34%. The sum of nearby f -values is nearly conserved (difference is 0.19%), so we are redistributing the individual f -values over these levels. For the final state, we had to use REDUCE for many correlation configurations in order to accommodate the above second-order effects.

A total of 490 E1 transitions were evaluated, but for the same reason as before, we only list those big ones ($A_{ki} \geq 10^{11} s^{-1}$) in table 2. Again, the large contributions will be exclusively from $1s 4p^5$ and $1s 4p^4 5p$. Absorption from 7p and 8p will have a even smaller contribution than in Br I. It can be easily seen from both table 1 and table 2 that the agreement between the two gauges of transition probabilities is very good, though this doesn't guarantee that our wave functions are almost exact.

3.3. K edge Energy for Br I and Br II

Our calculated K edge energies, the individual contributions and available experimental and other theoretical results are listed in table 3. The K edge energy was obtained by finding the energy difference between the lowest state of the 1s hole state and that of the closed core state directly. Since only the occupation number of the 1s subshell differs, the bulk of correlation is from replacement involving the 1s electron. We have included double replacement of two 1s electrons (in the closed core states only), one 1s and one

L-shell electron in the wave function. We did separate calculations to estimate the size of replacement of one 1s and one M-shell electron. We also made the assumption that the Auger shift in the 1s hole states of Br is the same as that in Kr, which is 0.256 eV.

Our calculated K edge energy for Br I is 13483.67 eV. This is in very good agreement with another theoretical value of 13483.86 eV [19]. However, as shown in table 3, when comparing to experimental values, our value is about 9~13 eV too large. Recall that for Kr II, our calculated K edge energy was only 0.94 eV larger than experiment [1] and that we have used similar methodology here for Br I, so this large discrepancy is really confusing and it would be interesting to find out the reason(s). First of all, we believe such a large energy shouldn't come from missing correlation effects. Then we wonder if inadequate treatment of the QED effects may account for some portion of the discrepancy. We have been using Desclaux's code [14] for the QED corrections. To test its adequacy, we compared this method with the more thorough ones of Drake *et al* [20] for the ionization potential of Kr^{34+} . The two methods agreed quite well with Desclaux's method giving ~ 11.097 eV and Drake's method giving ~ 11.164 eV. This may indicate the QED corrections we included should be adequate and therefore the bulk of the difference in K edge energy may not lie with QED.

As we searched in literature, we began to think the discrepancy may be due to the chemical state effect. In Kr's case, since it's a monoatomic gas, both theory and experiment are readily available for the Kr atom and their difference is small. Br is quite different as naturally it exists as a diatomic molecule, or other compound and in various states (solid, gas). Some earlier work [21, 22] gave evidence of the dependence of the K edge energy on chemical state. For example, the experimental work by Hanawalt [21] showed the K edge energy in Br compounds is smaller than that in Br_2 molecule, by as much as 6.9 ± 2.3 eV depending on the state of the compound. Later calculations by Martin *et al* [23] showed the K edge energy in Br_2 molecule is about 0.9 eV smaller than that in Br atom. Combining these together, it seems the K edge energy of some Br compounds could be ~ 10 eV smaller than that of Br atom. At this point it's essential to know in which chemical state the K edge energy of Br in [19] were measured. Those values are rescaled data of Bearden *et al*'s [24]. Though Bearden *et al* mentioned [24] that the chemical state of the absorber is important in absorption edge measurement, they didn't make it clear in which chemical state the edge energy of Br was obtained [24, 25]. Based on the above statements and considering what we deal with in our calculation is isolated Br atom and the experiment might work with Br compound, it seems our disagreement with experiment is expected.

As to the absolute value of the edge energy, there is also favorable though indirect evidence that our value is reasonable. Nahon *et al* [2] measured the $3d \rightarrow np$ ($n > 5$) photoexcitation spectrum for atomic Br. They estimated the first 3d ionization energy to be 76.5 eV. If we take this as the $3d_{5/2}$ or M_5 edge energy of atomic Br and make the assumption that the x-ray fluorescence energies are not affected by the chemical environment, we could combine this M_5 edge energy with the KL_3 , L_3M_5 energy in table V of [19] and thus obtain an estimate for the K edge energy based on experiment:

K edge energy = $KL_3+L_3M_5+M_5= 11924.36 + 1480.46 + 76.5 = 13481.3$ (eV)
 Alternately, the combination of the experiment $KN_{2,3}$ energy (13469.60(43) eV) [19] with the 4p ionization energy of Br I (~ 11.81 eV) [16] gives a similar estimated experimental K edge energy of 13481.41 eV for Br. As can be seen, both of these estimates are much smaller than the experimental values in [19] but very close to our calculated energy of 13483.67 eV.

While the above analysis tend to favor theoretical values for K edge energy, the most recent work by D'Angelo *et al* [26] on gaseous HBr seems to support the experimental values in [19]. It's long been assumed that HBr is a close approximation to the Br atom and the X-ray absorption spectrum of gaseous HBr is essentially the same as that of the Br atom alone [27]. As part of their experiment, D'Angelo *et al* measured the x-ray absorption spectra of gaseous HBr near K edge. Then they deconvoluted the spectrum as a sum of an arctangent and a Lorentzian function and thus estimated the transition into the continuum state occurs at 13473 eV for HBr. This value is obviously very close to other experimental K edge energies for Br [19].

Our calculated K edge energy of Br II is 13496.20 eV. There aren't any existing results to compare with, but this number is consistent with our calculated K edge energy of Br I . Specifically, given

$$\text{Br II K edge} = E(1s 4p^4) - E(4p^4) = 13496.20 \text{ eV}$$

$$\text{Br I K edge} = E(1s 4p^5) - E(4p^5) = 13483.67 \text{ eV},$$

subtracting these two equations and noticing $E(4p^4)-E(4p^5)$ is the 4p ionization potential (IP) of Br I, which is ~ 11.81 eV, one gets

$$E(1s 4p^4) - E(1s 4p^5) = 24.34 \text{ eV}$$

According to the 'Z+1 approximation', this difference should be about the same as the 4p IP of Kr II (~ 24.36 eV) [16], and it is.

4. Conclusion

We have done relativistic configuration interaction calculations for the $1s \rightarrow np$ ($n \geq 4$) transitions for Br I and Br II and obtained transition energies and transition probabilities for a total of 612 electric dipole transitions. With these results and given the relative population of different initial states, the theoretical $1s \rightarrow np$ absorption profile can be obtained and compared to experiment to classify the strong features. We have also calculated the K edge energy for Br I and Br II and found good agreement with the existing theoretical value for the former, but comparison of it with experiment is complicated by the ambiguity in chemical binding. The large discrepancy between theoretical and experimental K edge energy for Br I still needs to be resolved.

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Table 1. 1s photoexcitation transition energies (in eV) and transition probabilities (in 10^{10} s^{-1}) for Br I.

Final State	Transition Energy	A_{ki}		
		Coulomb Gauge	Babuskin Gauge	Average
$4p^5 \ ^2P_{3/2} \rightarrow J=1/2$				
1s $4p^6$	13469.681	1195.8	1183.5	1189.6
1s $4p^5 \ 5p \ r1$	13481.118	75.9	75.4	75.6
1s $4p^5 \ 5p \ r6$	13482.012	13.2	13.1	13.1
1s $4p^5 \ 6p \ r1$	13482.450	8.4	8.3	8.3
1s $4p^5 \ 6p \ r2$	13482.558	7.8	7.7	7.7
1s $4p^5 \ 6p \ r3$	13482.612	1.2	1.2	1.2
1s $4p^5 \ 7p \ r1$	13482.912	3.5	3.5	3.5
1s $4p^5 \ 7p \ r2$	13483.045	4.1	4.0	4.1
1s $4p^5 \ 8p+6p$	13483.131	1.7	1.6	1.6
1s $4p^5 \ 6p$	13483.201	1.4	1.3	1.3
1s $4p^5 \ 8p$	13483.291	1.9	1.9	1.9
1s $4p^5 \ 7p$	13483.655	1.6	1.6	1.6
$4p^5 \ ^2P_{3/2} \rightarrow J=3/2$				
1s $4p^5 \ 5p \ r2$	13481.192	31.2	30.6	30.9
1s $4p^5 \ 5p \ r3$	13481.306	32.4	31.9	32.1
1s $4p^5 \ 5p \ r4$	13481.360	17.2	16.9	17.1
1s $4p^5 \ 5p \ r7$	13481.928	1.5	1.5	1.5
1s $4p^5 \ 6p \ r2$	13482.409	15.6	15.3	15.5
1s $4p^5 \ 6p \ r3$	13482.556	7.9	7.7	7.8
1s $4p^5 \ 6p \ r4$	13482.573	4.1	4.0	4.0
1s $4p^5 \ 7p \ r2$	13482.879	8.4	8.2	8.3
1s $4p^5 \ 7p \ r3$	13483.037	3.6	3.5	3.6
1s $4p^5 \ 8p$	13483.111	5.5	5.4	5.4
1s $4p^5 \ 8p$	13483.276	1.9	1.8	1.9
1s $4p^5 \ 8p$	13483.281	1.2	1.2	1.2
$4p^5 \ ^2P_{3/2} \rightarrow J=5/2$				
1s $4p^5 \ 5p \ r1$	13481.120	36.3	35.9	36.1
1s $4p^5 \ 5p \ r2$	13481.188	28.5	28.3	28.4
1s $4p^5 \ 5p \ r3$	13481.311	20.9	20.8	20.8
1s $4p^5 \ 5p \ r4$	13481.893	1.2	1.2	1.2
1s $4p^5 \ 6p \ r1$	13482.384	11.9	11.8	11.9
1s $4p^5 \ 6p \ r2$	13482.407	5.2	5.2	5.2
1s $4p^5 \ 6p \ r3$	13482.557	9.1	9.0	9.0
1s $4p^5 \ 7p \ r1$	13482.866	5.4	5.4	5.4
1s $4p^5 \ 7p \ r2$	13482.876	2.1	2.1	2.1
1s $4p^5 \ 7p \ r3$	13483.038	4.2	4.2	4.2
1s $4p^5 \ 8p \ r1$	13483.102	2.9	2.9	2.9
1s $4p^5 \ 8p \ r2$	13483.108	1.1	1.0	1.0
1s $4p^5 \ 8p \ r3$	13483.274	2.1	2.1	2.1

Final State	Transition Energy	A_{ki}		
		Coulomb Gauge	Babuskin Gauge	Average
$4p^5 \ ^2P_{1/2} \rightarrow J=1/2$				
1s $4p^6$	13469.224	622.1	615.0	618.5
1s $4p^5 \ 5p \ r1$	13480.661	1.0	1.0	1.0
1s $4p^5 \ 5p \ r2$	13480.842	4.1	4.0	4.0
1s $4p^5 \ 5p \ r3$	13480.986	2.5	2.5	2.5
1s $4p^5 \ 5p \ r4$	13481.347	20.9	20.7	20.8
1s $4p^5 \ 5p \ r5$	13481.424	50.1	49.8	50.0
1s $4p^5 \ 5p \ r6$	13481.555	8.4	8.4	8.4
1s $4p^5 \ 6p \ r1$	13481.994	1.8	1.8	1.8
1s $4p^5 \ 7p \ r2$	13482.588	1.3	1.3	1.3
1s $4p^5 \ 6p+7p$	13482.636	3.2	3.1	3.1
1s $4p^5 \ 6p$	13482.701	18.4	18.2	18.3
1s $4p^5 \ 7p$	13483.118	1.9	1.9	1.9
1s $4p^5 \ 7p$	13483.181	7.7	7.6	7.6
1s $4p^5 \ 8p$	13483.356	1.0	1.0	1.0
1s $4p^5 \ 8p$	13483.420	3.6	3.6	3.6
$4p^5 \ ^2P_{1/2} \rightarrow J=3/2$				
1s $4p^5 \ 5p \ r4$	13480.903	2.4	2.3	2.3
1s $4p^5 \ 5p \ r5$	13481.375	17.1	16.8	17.0
1s $4p^5 \ 5p \ r6$	13481.402	44.9	44.3	44.6
1s $4p^5 \ 5p \ r7$	13481.471	24.2	23.8	24.0
1s $4p^5 \ 6p+7p$	13482.613	6.3	6.2	6.3
1s $4p^5 \ 8p+6p$	13482.647	1.2	1.2	1.2
1s $4p^5 \ 6p$	13482.675	13.2	13.0	13.1
1s $4p^5 \ 6p$	13482.699	6.8	6.7	6.8
1s $4p^5 \ 7p$	13483.094	3.4	3.3	3.7
1s $4p^5 \ 7p$	13483.160	5.7	5.6	5.6
1s $4p^5 \ 7p$	13483.170	5.5	5.3	5.4
1s $4p^5 \ 8p$	13483.329	2.0	2.0	2.0
1s $4p^5 \ 8p$	13483.399	3.0	3.0	2.9
1s $4p^5 \ 8p$	13483.404	2.4	2.4	2.4

Table 2. 1s photoexcitation transition energies (in eV) and transition probabilities (in 10^{11} s^{-1}) for Br II.

Final State	Transition Energy	A_{ki}		
		Coulomb Gauge	Babuskin Gauge	Average
$4p^4 \ ^3P_2 \rightarrow J=1$				
1s $4p^5$	13472.107	45.5	44.8	45.4
1s $4p^5$	13472.721	11.0	10.9	11.0
1s $4p^4 \ 5p \ r2$	13488.925	17.2	17.0	17.1
1s $4p^4 \ 5p \ r7$	13489.695	1.1	1.0	1.0
1s $4p^4 \ 6p \ r1$	13492.343	2.4	2.4	2.4
1s $4p^4 \ 6p \ r2$	13492.516	4.0	4.0	4.0
1s $4p^4 \ 7p \ r1$	13493.761	1.7	1.7	1.7
1s $4p^4 \ 7p \ r2$	13494.044	1.1	1.1	1.1
$4p^4 \ ^1D_2 \rightarrow J=1$				
1s $4p^5$	13470.608	96.3	95.8	96.1
1s $4p^5$	13471.222	141.3	139.9	140.6
1s $4p^4 \ 5p \ r5$	13487.931	2.1	2.0	2.0
1s $4p^4 \ 5p \ r7$	13488.197	2.1	2.1	2.1
1s $4p^4 \ 5p \ r8$	13488.291	5.0	4.9	4.9
1s $4p^4 \ 5p \ r9$	13488.451	2.0	2.0	2.0
1s $4p^4 \ 5p \ r10$	13489.302	4.3	4.2	4.3
1s $4p^4 \ 5p \ r11$	13489.502	1.5	1.5	1.5
1s $4p^4 \ 6p$	13491.884	1.1	1.1	1.1
1s $4p^4 \ 6p+7p$	13492.774	1.5	1.4	1.5
1s $4p^4 \ 6p+7p$	13492.795	2.6	2.6	2.6
1s $4p^4 \ 7p$	13494.254	1.6	1.6	1.6
$4p^4 \ ^3P_2 \rightarrow J=2$				
1s $4p^5$	13471.936	101.7	100.7	101.2
1s $4p^4 \ 5p \ r2$	13488.780	19.9	19.7	19.8
1s $4p^4 \ 6p \ r2$	13492.335	4.5	4.5	4.5
1s $4p^4 \ 6p \ r3$	13492.484	1.7	1.6	1.6
1s $4p^4 \ 7p \ r2$	13493.733	1.7	1.7	1.7
$4p^4 \ ^1D_2 \rightarrow J=2$				
1s $4p^5$	13470.437	2.6	2.6	2.6
1s $4p^4 \ 5p \ r11$	13489.483	8.2	8.1	8.1
1s $4p^4 \ 5p \ r12$	13489.554	13.8	13.7	13.8
1s $4p^4 \ 6p$	13492.811	4.3	4.3	4.3
1s $4p^4 \ 6p+7p$	13492.884	3.8	3.8	3.8
1s $4p^4 \ 7p$	13494.237	1.7	1.7	1.7
1s $4p^4 \ 7p$	13494.291	2.0	1.9	1.9
1s $4p^4 \ 8p$	13494.959	1.0	1.0	1.0
1s $4p^4 \ 8p$	13495.033	1.1	1.1	1.1

Final State	Transition Energy	A_{ki}		
		Coulomb Gauge	Babuskin Gauge	Average
$4p^4 \ ^3P_2 \rightarrow J=3$				
1s $4p^4$ 5p r2	13488.789	11.7	11.6	11.6
1s $4p^4$ 5p r3	13489.008	11.1	11.0	11.1
1s $4p^4$ 5p r4	13489.406	1.4	1.4	1.4
1s $4p^4$ 6p r2	13492.233	4.8	4.7	4.7
1s $4p^4$ 6p r3	13492.497	3.0	2.9	2.9
1s $4p^4$ 7p r2	13493.679	2.4	2.4	2.4
1s $4p^4$ 7p r3	13493.962	1.3	1.3	1.3
1s $4p^4$ 8p r2	13494.433	1.3	1.3	1.3
$4p^4 \ ^1D_2 \rightarrow J=3$				
1s $4p^4$ 5p r5	13489.126	9.0	8.9	8.9
1s $4p^4$ 5p r6	13489.250	15.6	15.5	15.6
1s $4p^4$ 6p r5	13492.679	3.6	3.6	3.6
1s $4p^4$ 6p r6	13492.757	4.5	4.5	4.5
1s $4p^4$ 7p r5	13494.160	1.8	1.8	1.8
1s $4p^4$ 7p r6	13494.210	1.1	1.0	1.1
1s $4p^4$ 7p r7	13494.244	1.0	1.0	1.0
1s $4p^4$ 8p r5	13494.926	1.1	1.1	1.1
$4p^4 \ ^3P_1 \rightarrow J=0$				
1s $4p^5$	13472.228	135.0	133.6	134.3
1s $4p^4$ 5p r1	13488.630	1.2	1.2	1.2
1s $4p^4$ 5p r2	13488.819	13.6	13.4	13.5
1s $4p^4$ 5p r3	13488.887	5.6	5.6	5.6
1s $4p^4$ 5p r5	13490.530	1.2	1.2	1.2
1s $4p^4$ 6p r2	13492.400	2.5	2.4	2.4
1s $4p^4$ 6p r3	13492.454	3.2	3.2	3.2
1s $4p^4$ 6p+7p	13493.875	1.2	1.1	1.2
$4p^4 \ ^3P_1 \rightarrow J=1$				
1s $4p^5$	13471.718	20.6	20.5	20.5
1s $4p^5$	13472.332	15.0	14.8	14.9
1s $4p^4$ 5p r2	13488.536	1.1	1.1	1.1
1s $4p^4$ 5p r4	13488.969	1.9	1.9	1.9
1s $4p^4$ 5p r5	13489.041	5.1	5.1	5.1
1s $4p^4$ 5p r7	13489.307	11.9	11.8	11.8
1s $4p^4$ 5p r9	13489.561	2.8	2.7	2.8
1s $4p^4$ 6p r4	13492.482	1.5	1.5	1.5
1s $4p^4$ 5p+6p	13492.602	1.3	1.3	1.3
1s $4p^4$ 6p+5p	13492.731	2.3	2.3	2.3
1s $4p^4$ 7p+8p	13494.120	1.5	1.5	1.5
$4p^4 \ ^3P_1 \rightarrow J=2$				
1s $4p^5$	13471.547	34.8	34.4	34.6
1s $4p^4$ 5p r3	13488.612	1.4	1.4	1.4
1s $4p^4$ 5p r5	13488.937	2.0	2.0	2.0
1s $4p^4$ 5p r6	13489.052	18.1	17.9	18.0
1s $4p^4$ 5p r8	13489.406	1.1	1.1	1.1
1s $4p^4$ 6p	13492.517	5.2	5.1	5.1

Final State	Transition Energy	A_{ki}		
		Coulomb Gauge	Babuskin Gauge	Average
$4p^4 \ ^3P_1 \rightarrow J=2(\text{cont'd})$				
1s $4p^4$ 6p	13492.845	1.2	1.2	1.2
1s $4p^4$ 7p+6p	13493.974	1.8	1.8	1.8
1s $4p^4$ 8p	13494.724	1.0	1.0	1.0
$4p^4 \ ^3P_0 \rightarrow J=1$				
1s $4p^5$	13471.631	32.0	31.7	31.8
1s $4p^5$	13472.245	17.0	17.0	17.0
1s $4p^4$ 5p r2	13488.450	1.1	1.1	1.1
1s $4p^4$ 5p r6	13489.127	14.3	14.2	14.3
1s $4p^4$ 5p r7	13489.220	1.5	1.4	1.4
1s $4p^4$ 5p r8	13489.314	1.9	1.9	1.9
1s $4p^4$ 5p r9	13489.475	2.6	2.5	2.5
1s $4p^4$ 6p	13492.464	1.2	1.2	1.2
1s $4p^4$ 5p+6p	13492.515	1.9	1.8	1.9
1s $4p^4$ 6p	13492.815	3.3	3.3	3.3
1s $4p^4$ 7p	13494.288	1.5	1.5	1.5
$4p^4 \ ^1S_0 \rightarrow J=1$				
1s $4p^5$	13468.652	13.4	13.3	13.4
1s $4p^5$	13469.266	36.1	35.9	36.0
1s $4p^4$ 5p+6p	13489.464	1.0	1.0	1.0
1s $4p^4$ 5p+6p	13489.535	9.6	9.5	9.5
1s $4p^4$ 5p+6p	13489.595	7.9	7.8	7.8
1s $4p^4$ 6p+5p	13489.665	1.4	1.4	1.4

Table 3. K edge energy and individual contributions of Br I, Br II (unit: eV).

Ionized state	Br I	Br II
	$1s\ 4p^5\ J=2$	$1s\ 4p^4\ J=5/2$
Coulomb Dirac-Fock	13511.558	13523.997
Coulomb corr	1.210	1.340
Magnetic	-21.624	-21.623
Retardation	1.484	1.480
QED	-9.816	-9.816
Magnetic Breit corr	0.604	0.564
Auger shift	0.256	0.256
Total ionization energy	13483.671	13496.199
Other theoretical energy ^a	13483.86(19)	-
Experiment energy ^a	13470.5(22)	-
	13474.10(65)	-

^a From reference [19]. Numbers in parentheses are one standard deviation uncertainties of the quoted value referred to the last figures of the quoted value.