Inner-shell Excitations of Krypton 3d and Argon 2p Investigated by Electron Impact with High Resolution

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(Dated: October 22, 2004)

Abstract

The inner-shell excitation spectra of krypton 3d and argon 2p electrons at 0° and 4° scattering angles were measured by a fast-electron energy-loss spectrometer (EELS) at an incident energy of 2.5 keV with an energy resolution better than 80 meV (FWHM). Some new optically forbidden transitions were observed and the natural widths of the optically allowed and forbidden transitions were analyzed. It shows that the natural widths of transitions excited from the same inner-orbital are nearly equal, no matter they are optically allowed or optically forbidden or different members of Rydberg series. We also proposed the possibility to measure resonant auger process of optically forbidden excited intermediate states.

PACS numbers: 34.80.Dp, 31.15.Ar, 32.70.Fw, 32.80.Dz

Keywords: Krypton, Argon, Inner-shell excitation, Nature width, and Optically allowed and forbidden

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I. INTRODUCTION

The atomic inner-shell excitations were investigated by different methods, such as electron impact, photoabsorption, and etc.. King and co-workers [1, 2] carried out pioneer studies on the energy level and linewidth of inner-shell excitations of rare gases by electron-energy-loss spectroscopy. The structures near the Xe \(N_{4,5}\), Kr \(M_{4,5}\) and Ar \(L_{2,3}\) edges were measured. From their data King et al [1] inferred that there was an anomalous tendency for the linewidth \(\Gamma\) to increase with the principle quantum number \(n\) along a Rydberg series. Their results have served a long time as a reference, e.g., they have been applied when testing the performance of new monochromators [3–5]. More accurate experiments by photoabsorption method based on advanced synchrotron radiation were carried out by Masui et al [6], Quaresima et al [4], Sairanen et al [7], Prince et al [8] and Jurvansuu et al [9]. Till now inconsistency still exists in these literatures for both the linewidth and its variation tendency with the principle quantum number \(n\). Therefore corresponding explanations are various. In the present work, we set out to extend the study of energy level and linewidth from optically allowed to optically forbidden excited states.

In the energy range of inner shell excitations, the chief advantage of electron impact method is that the energy resolution \(\Delta E\) is independent of the incident energy and the excitation energy \(E\). This is unlike the situation in photon excitation where \(\Delta E\) is approximately proportional to either \(E^2\) or \(E\) (depending on the range of wavelength and technique employed). Thus the higher the excitation energy the more advantageous is electron impact excitation. Furthermore, electron impact excitation has the advantage that optically forbidden transitions can be observed.

In the present measurements, a resolution from 50 meV to 80 meV was achieved corresponding to different experimental conditions. Hence it is possible to measure these linewidths, and to deduce the lifetimes of these resonant states. The present incident energy is 2.5 keV, which is much higher than the excitation energies interested. The spectrum measured at 0° scattering angle approximates to the photoabsorption spectrum since the momentum transfer is very small [10]. In addition, for the fast-electron impact, the spin-forbidden excitation is much less important than the spin-allowed ones even when the spectrometer works in the condition with a larger momentum transfer [11]. Thus, only singlet-to-singlet transition can be observed from the rare gas ground state \(^1S_0\). Therefore,
we are able to obtain the widths of \( \text{Kr}(^1S_0 \rightarrow 3d_{5/2}^1s \text{ and } ^1S_0 \rightarrow 3d_{3/2}^1s) \). To identify the optically forbidden transitions, energy-loss spectra were measured at both 0° and 4° scattering angles.

The presently used spectrometer and experimental method were introduced in Sec. II. Then, we presented the measured spectra and the obtained linewidth in Sec. III with detailed discussion. Based on the experimental results and previous resonant auger literatures, a new proposal was put forward to investigate the resonant auger effect of optically forbidden excited states. Finally, in Sec. IV, we draw the conclusion.

II. SPECTROMETER AND EXPERIMENTAL METHOD

An angular-resolved high-resolution fast-electron energy-loss spectrometer was used in the present work. Detail of this spectrometer was described in [12–14]. Briefly, it consists of an electron gun, a hemispherical electrostatic monochromator made of aluminium, a rotatable energy analyser of the same type, an interaction chamber, a number of cylindrical electrostatic lenses and a one-dimension position sensitive detector for gathering the analysed electrons. All of these components are enclosed in four separate vacuum chambers made of stainless steel. In the present experimental measurements, this spectrometer was operated at an incident electron energy of 2.5 keV. The energy resolution has a slight variation according to different energy region and scattering angle. As verified in the following, the energy resolutions are 60 meV (FWHM) for krypton 3\( d \) excitation and 50 meV for argon 2\( p \) excitation at 0° scattering angle, while are 80 meV for krypton 3\( d \) excitation and 73 meV for argon 2\( p \) excitation respectively at 4°. The sample of krypton (or argon) gas was introduced into the gas cell in the centre of the interaction chamber with the gas pressure of \( 1 \times 10^{-2} \) Pa. The measured spectra were the sum of many repetitive scans and the energy scale was calibrated to 3\( d_{5/2}^1s \) (91.200 eV) for krypton and to 2\( p_{3/2}^1s \) (244.390 eV) for argon [1].

The measured spectrum, in fact, is the result of the physically real spectrum convoluted by the instrumental function. It is well known that the profile of the absorption line is Lorentzian. Here, we ignore the interaction between the discrete and continuum states because the excited states decay most probably by auger electron emission, i.e. resonant auger effect [15]. Otherwise, the resonant profile should be more asymmetric as investigated by Fano [16]. Considering our instrumental function, a Gaussian approximately, we obtained
that the measured resonant profile is a Voigtian. So the instrumental and natural width can be achieved with the method deduced by Lee [17]. For example, after the energy calibration of the measured spectrum of Kr 3d excitation at 0° scattering angle (see Fig.1), a least-square fitting procedure was used to fit the resonance 3d_{5/2}5p consequently resulting in the measured width $W$ of 133±2 meV. Using the previously observed natural width $\Gamma$ of 83±1 meV for this resonance [7], we then found the instrumental width $R$ (the energy resolution) is 60±3 meV by the following relation [17].

$$\Gamma = W - 1.12R^2/W + 0.12R^3/W^2.$$ \hfill (1)

Analogously, the energy resolutions in other experimental conditions can be obtained which help us further achieve the natural widths of the other resonances.

### III. RESULTS AND DISCUSSION

![Kr spectrum](image)

FIG. 1: The measured spectrum of Kr 3d excitation at 0° scattering angle.

**A. The features in the observed spectra**

In Fig.1, multiplied by the known Bethe-Born conversion factor [18] of the spectrometer, the electron-energy-loss spectrum of Kr 3d excitation measured at 0° was converted to
optical oscillator strength density (OOSD) spectrum. We have reported the OOSD in a previous measurement [19] with slight worse statistics and a shorter energy range. Compared with the work by Sairanen et al [7], there are two weak features arising at about 89.7 eV and 92.0 eV besides the photoabsorption resonances. These features come from optically forbidden transitions because of the limited angle resolution. The similar phenomenon was reported in literatures [12, 19–21]. The resonance $3d_{5/2}^{-1} 4d$ at 91.990 eV was observed in the experiment by King et al [1], and its strength relative to the resonance $3d_{5/2}^{-1} 5p$ is larger than the presently corresponding relative strength. This is understandable when one notices the differences of the incident energies [the present, 2.5 keV, is higher than that in Ref. [1], 1.5 keV]. Contrastively, the other feature at 89.7 eV has never been observed before. According to the following analysis of the spectrum measured at 4° as shown in Fig.2, we determined that this feature should be the optically forbidden transition $3d_{5/2}^{-1} 5s$. There are also more optically forbidden transitions compared with Fig.1. After the least-square fitting procedure, we obtained the energy levels of $3d_{5/2}^{-1} 5s$ and $3d_{3/2}^{-1} 5s$, 89.639(10) eV and 90.892(15) eV, respectively. Using the equivalent-core model [1, 22, 23], we assign the Rydberg series $3d_{5/2}^{-1} ns$, $3d_{3/2}^{-1} ns$, $3d_{5/2}^{-1} nd$, and $3d_{3/2}^{-1} nd$ as shown in Fig.2.

![Kr 3d excitation spectrum at 4° scattering angle](image)

**FIG. 2:** The measured spectrum of Kr 3d excitation at 4° scattering angle.

One may ask why there is no transitions of $3d \rightarrow nf$ in the spectrum measured at either 0° or 4°. In principle, those transitions are optically allowed which should be distinct both at 0° or 4°. In order to clarify this ambiguity, we appealed for the aid of wavefunctions
obtained by a Dirac-Slater (DS) approach based on a self-consistent-field calculation and the independent particle approximation [24–26]. Based on the Fermi’s Golden rule, the transition strength is proportional to the square of the transition matrix element, i.e., the
transition-operator-weighted overlap integral between the initial state $\Psi_i$ and the final state $\Psi_f$, $|\langle \Psi_f | T | \Psi_i \rangle|^2$. Assuming single configuration-interaction approximation is valid, the transition matrix element is reduced to the transition-operator-weighted overlap integral between the initial orbital and the final orbital, e.g., $|\langle \phi_{nf} | T | \phi_{3d} \rangle|^2$ for the present case. The large components of $3d_{3/2}$, $5p_{1/2}$, $5p_{3/2}$ and $4f_{5/2}$ wavefunctions are shown in Fig. 3(a), and those of $3d_{5/2}$, $5p_{3/2}$, $4f_{5/2}$ and $4f_{7/2}$ wavefunctions are shown in Fig. 3(b). The small components of the wavefunctions are not concerned here because of neglectable amplitude. It can be seen that the wavefunction of $3d$ is very localized compared with that of $4f$ (which is very dispersed) and there is bare overlap between them. On the contrary, the overlap between the wavefunctions of $3d$ and $5p$ is considerable. This is why the Rydberg series of $3d^{-1}np$ is dominated while the series of $3d^{-1}nf$ is invisible.

![Figure 4](image_url)

**FIG. 4**: The measured spectrum of Ar $2p$ excitation at $0^\circ$ scattering angle.

The electron-energy-loss spectrum of Ar $2p$ excitation measured at $0^\circ$ scattering angle is depicted in Fig. 4. After least-square fitting of the resonance $2p_{3/2}^{-1}4s$ whose natural width is $114 \pm 2$ meV [7], we obtained the energy resolution $50 \pm 4$ meV with the measured width $134 \pm 2$ meV. The present spectrum is comparable with those measured by Domke et al [3], Quaresima et al [4], Sairanen et al [7], and Zangrando et al [5] although most of these literatures stated an energy resolution better than $30$ meV. It is interesting that the present continuum is flat at both $0^\circ$ and $4^\circ$, while the continuum rises sharply in the experiments carried by Domke et al [3], Sairanen et al [7], and Zangrando et al [5], but descends in the
FIG. 5: The measured spectrum of Ar 2p excitation at 4° scattering angle.

experiment by [4]. We suspect that this may come from the variation of the photon flux with the photon energy and the beam lifetime in the measurement with synchrotron radiation, which makes it harder to deduce the relative strengths of the different resonances.

Similarly to the features in Kr 3d excitation, the optically forbidden transition 2p_{3/2} 4p arises at 245.956 eV. But when we measured the energy-loss spectrum at 4° (as shown in Fig.5), the variation of the resonances is not remarkable as the case for Kr. However, the feature at 247.364 eV can be identified as the optically forbidden transition 3p_{3/2} 5p. Then the spectrum was assigned as shown in Fig.5 according to the calculation by the equivalent-core model. In Fig.4, the resonance 2p_{1/2} nd is very asymmetric. Nakamura et al [22] pointed out that this might come from the autoionization of 2p_{1/2} (n + 2)s which should lead to an asymmetric Fano profile [16], while Sairanen et al [7] suggested that the asymmetry was partly due to background and partly due to excitations to the 2p_{1/2} (n + 2)s states that should lie near the 2p_{1/2} nd states. We can not say which explanation is better based on the presently experimental evidences. But we would like to suggest an experiment to clarify this problem. If the asymmetry comes from autoionization, there must be autoionized electrons whose kinetic energy is discrete in the range of 0 → 2.1 eV. So, the autoionization process can be identified by the measurement of the photoelectron yield spectrum with the kinetic energies in a window of 0 → 2.1 eV. If the asymmetry arises from the second interpretation,
there should be no distinct structures in the spectrum.

B. Natural widths for the resonances

The natural widths for Kr 3d excitations are listed in Tab.I. The widths obtained at 0° and 4° scattering angles are consistent in the present measurement. Considering the previous experimental results [1, 7], we can see that the widths approximately keep constant along a Rydberg series within experimental error. Besides the optically allowed excitations, we obtained for the first time the natural widths of 3d_{5/2}5s and 3d_{3/2}5s, which are optically forbidden transitions. And it is interesting that these two natural widths are close to those of optically allowed excitations.

Because the resonant auger effect is the main decay route for the present excitation energy [15], the lifetime of the resonance is equivalent to the lifetime of the core hole approximately. Normally, the excited electron does not participate in the decay process. It automatically cascades into the discrete or continuum orbitals of the final ionic states from the intermediate state, the so-called spectator model [15]. So the total decay rate of the core hole may be affected little by the excited spectator electrons staying in different Rydberg orbitals, although the strengths of the final states are redistributed according to different excitation energies (i.e., different initial states). Therefore, the natural widths of different excited states are identical approximately in spite of optically allowed or forbidden excitation as long as these states have the same core hole.

Similarly to the results for Kr, the natural widths for Ar 2p excitations are listed in Tab.II. There is no width for optically forbidden transitions because it is hard to obtain the accurate width by least-square fitting on the spectrum shown in Fig.5. It can be seen that the presently obtained widths at 0° and 4° are consistent within the experimental error for each state. The present results are also comparable to the previous works [1, 7, 8].

C. A proposal for resonant auger (RA) effect investigation based on electron impact

The resonance auger effect is important for the investigation of intermediate-state coherence and electron correlation [15]. Based on the above investigation of inner shell excitations,
we are enlightened to propose a scheme to study the resonant auger effect with the high-resolution electron-impact excitation. As shown in Fig. 6, an electron energy analyser with resolution $\leq 100$ meV is employed to detect the auger electrons. This energy analyser should have high efficiency, and can collect electrons with a large solid angle. This will make the experiment easier despite of the very low signal count rate. With the coincidence of the scattering electron and the auger electron, the auger electron spectrum can be obtained for a special excited state. The energy resolution of the present high-resolution fast-electron energy-loss spectrometer is about 60 meV for the scattering electron, which is narrower than the natural widths. This will helpful to select the excitation energy accurately. When we detect the scattering electrons at $0^\circ$, the present auger electron spectrum is identical to that obtained by photon excitation. Furthermore, we can measure the resonant auger effect of the optically forbidden excited states by detecting the scattering electrons at non-zero degree, e.g., $\theta$ as shown in Fig. 6.

FIG. 6: The scheme to investigate resonant auger effect based on high-resolution electron-impact excitation.
IV. CONCLUSION

With the electron energy-loss spectrometer, we measured the spectra of Kr $3d$ (Fig.1 and 2) and Ar $2p$ (Fig.4 and 5) inner shell excitations. The natural widths of Kr$(^1S_0 \rightarrow 3d_{5/2}^{-1}5s$ and $^1S_0 \rightarrow 3d_{3/2}^{-1}5s$) excitations were obtained for the first time (shown in Tab.I). We think that the resonant auger effect makes the excitations have the close natural width regardless of the optically allowed, optically forbidden excitations or the principle quantum number $n$. The electron-impact based scheme was proposed to investigate the resonant auger effect of inner shell excitations, especially for the optically forbidden excited initial state. This scheme is probably realized with the present techniques.

Acknowledgments

Supports by National Nature Science Fund of China (10134010,10474089) are gratefully acknowledged.


TABLE I: Natural widths of Kr-3d excitations (the numbers in parentheses are standard errors with the unit of meV)

| State  | Level (eV)
|--------|------------
| 3d$^{-1}_{5/2}$ | 5s 90.892(15)$^\dagger$ /84(15) 
|         | 5p 92.425(2) 76(9)/87(12) 83(2) 
|         | 6p 93.809(4) 78(10)/ 98(12) 84(3) 
|         | 7p 94.319(8) 76(11)/ 77(3) 
|         | 8p 94.567(19) 70(5) 
|         | 9p 70(8) 
|         | 10p 68(8) 
| 5d     | 94.037(30) 
| core hole | 95.038(10) 88(4) 

| State  | Level (eV)$^a$ | Natural Width (meV) 
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>present 0°/4°</td>
<td>King Sairanen Jurvansuu</td>
</tr>
<tr>
<td>3d$^{-1}_{5/2}$</td>
<td>5s 89.639(10)$^\dagger$ /88(8)</td>
</tr>
<tr>
<td>5p</td>
<td>91.200(10) 83/83$^b$ 83(4) 83(1)</td>
</tr>
<tr>
<td>6p</td>
<td>92.560(2) 89(8)/81(10) 79(2)</td>
</tr>
<tr>
<td>7p</td>
<td>93.063(4) 78(10)/ 79(2)</td>
</tr>
<tr>
<td>8p</td>
<td>93.301(20) 76(3)</td>
</tr>
<tr>
<td>9p</td>
<td>78(5)</td>
</tr>
<tr>
<td>10p</td>
<td>75(8)</td>
</tr>
<tr>
<td>4d</td>
<td>91.990(20)</td>
</tr>
</tbody>
</table>

$^a$ The energy levels are taken from Ref. [1].

$^b$ For calibration, taken from Ref. [7].

$^\dagger$ The presently observed values.

The data of other groups are from, King et al [1], Sairanen et al [7], Jurvansuu et al [9], respectively.
TABLE II: Natural widths of Ar-2p excitations (the numbers in parentheses are standard errors with the unit of meV).

<table>
<thead>
<tr>
<th>State level (eV)</th>
<th>Natural Width (meV)</th>
<th>present $0^\circ/4^\circ$</th>
<th>King</th>
<th>Sairanen</th>
<th>Prince</th>
<th>Jurvansuu</th>
</tr>
</thead>
<tbody>
<tr>
<td>2p$_{3/2}^{-1}$</td>
<td>$4s$ 244.390(10)</td>
<td>114/114$^b$</td>
<td>121(6)</td>
<td>114(2)</td>
<td>111(3)</td>
<td></td>
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<tr>
<td></td>
<td>$4p$ 245.956(9)</td>
<td></td>
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<td></td>
<td>$5p$ 247.364(15)</td>
<td></td>
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<tr>
<td>3d 246.927(1)</td>
<td>124(8)/120(10)</td>
<td>126(11) 125(3) 112(4)</td>
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<tr>
<td>4d 247.669(4)</td>
<td>131(12)/125(15)</td>
<td>142(16) 129(5) 116(5)</td>
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<tr>
<td>5d 248.026(5)</td>
<td>133(10)</td>
<td></td>
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<tr>
<td>6d 248.211(15)$^\dagger$</td>
<td></td>
<td>139(10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>core hole</td>
<td>248.628(4)</td>
<td>118(4)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2p$_{1/2}^{-1}$</td>
<td>$4s$ 246.514(4)</td>
<td>111(10)/106(12)</td>
<td>109(3)</td>
<td>111(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$3d$ 249.074(3)</td>
<td>116(13)/108(15)</td>
<td>115(5)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>$4d$ 249.819(4)</td>
<td>118(15)/</td>
<td>117(10)</td>
<td></td>
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<tr>
<td></td>
<td>$5d$ 250.171(12)</td>
<td>112(10)</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>$6d$ 250.371(20)$^\dagger$</td>
<td></td>
<td>133(10)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>core hole</td>
<td>250.776(1)</td>
<td>118(4)</td>
<td></td>
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</tbody>
</table>

$^a$ The energy levels are taken from Ref. [1].

$^b$ For calibration, taken from Ref. [7].

$^\dagger$ The presently observed values.

The data of other groups are from, King et al [1], Sairanen et al [7], Prince et al [8], Jurvansuu et al [9], respectively.