Isoelectronic study of triply excited Li-like states

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Abstract
Absolute doubly differential cross sections (DDCSs) for the production and Auger decay of the intra-shell 2s2p2 2D triply excited state formed in collisions of He-like ions (Z = 5–9) with H2 were determined experimentally, using zero-degree Auger projectile electron spectroscopy. The 2D state was directly produced by 180° resonant scattering of the quasi-free H2 electrons from the 1s2s 3S metastable state of the ion. Resonant energies and DDCSs calculated using the R-matrix approach within the electron scattering model were found to be in good overall agreement with experiment.

(Some figures in this article are in colour only in the electronic version)
triply excited states were found to be in good overall agreement with \( R \)-matrix calculations [3–7]. Supplementary approaches include multi-configuration Dirac–Fock calculations [8], the truncated diagonalization method [9], \( 1/Z \) expansion [10], and the highly accurate saddle-point and complex-rotation methods [11, 12]. Motivated by these results, a deeper understanding of triply excited states has been sought, including the visualization of their angular and radial correlations [13, 14], as well as new classification schemes [9] based on approximate quantum numbers and new selection rules [14].

While the Li investigations have already attained a satisfactory understanding for neutral triply excited states, there exist just a few theoretical studies [9, 10, 14, 15], and no experimental results, for higher members of the Li-like sequence. Theoretically, similar features can be expected for higher-lying members, based on simple scaling laws. For instance, in a single-configuration approximation, where all initial and final electrons are described by hydrogenic orbitals with the same effective charge \( Z^* \), properties such as the partial and total autoionization widths are constant throughout the series, as found by Safronova and Bruch [10] for the Li-like series. Higher-order \( Z \)-dependent configuration interaction effects, however, may strongly influence the energies and widths of triply excited states and their associated Rydberg series [9]. Experiments for \( Z > 3 \) would provide further insight into their isoelectronic behaviour, but this is not presently feasible using conventional photoionization methods due to the inherent low luminosity of crossed or merged ion–photon beam experiments. Recently, triply excited states of \( F^{6+} \) have been populated by triple-electron capture [16].

In this letter, we present the first measurements along the Li-like isoelectronic sequence for the production and subsequent Auger decay of triply excited states. The \( 2s2p^2\,^2D \) state with \( Z = 5–9 \) was populated by \( 180^\circ \) quasi-free resonant electron scattering (RES) from the \( 1s2s\,^3S \) metastable state of He-like ions [17]. For a He-like ion \( A^{q+} \), where the charge state \( q = Z − 2 \), the following channels were investigated:

\[
e^{-} + A^{q+} (1s2s\,^3S) \rightarrow A^{(q−1)+} (2s2p^2\,^2D) \tag{1}
\]

(elastic channel): \( \rightarrow A^{q+} (1s2s\,^3S) + e^{-} (\varepsilon d) \tag{2} \)

\( (^1S \) inelastic channel): \( \rightarrow A^{q+} (1s2s\,^1S) + e^{-} (\varepsilon d) \tag{3} \)

\( (^3P \) inelastic channel): \( \rightarrow A^{q+} (1s2p\,^3P) + e^{-} (\varepsilon p, f) \tag{4} \)

A typical energy level diagram is shown in figure 1. Absolute doubly differential cross sections (DDCSs—in both electron energy and solid angle) for RES into the above channels were determined experimentally by detecting the ejected Auger electron with high resolution at zero degrees with respect to the ion beam direction. \( R \)-matrix calculations are also presented and compared to the data.

Quasi-free electron–ion differential scattering measurements exploit the \( \sim 10^8 \) higher luminosity available in collisions between \textit{lightly bound} target electrons and energetic highly charged ions than with merged or crossed electron–ion beams. In the ion rest frame, the quasi-free \( H_2 \) electrons scatter from the ions as free particles with a momentum distribution given by their Compton profile. This approach, refined over the last decade [18–20] by substantially reducing undesirable target-nucleus–ion contributions using favourable collision conditions and low-\( Z \) targets [18, 20], has evolved into what is known as the electron scattering model (ESM) [19]. Recently, DDCS measurements of elastic RES from H-like [20] and He-like boron ions [17, 20], otherwise too tedious to perform by conventional electron–ion crossed beam experiments [21], were found to be in excellent agreement with \( R \)-matrix results over the broad energy range of 140–200 eV, having many resonances, providing renewed and definitive proof for the validity of the ESM. Here, we apply our expertise in RES with He-like ions [20] to study the population and decay dynamics of the \( ^2D^e \) state as a function of \( Z \).
Figure 1. Boron energy level diagram: RES from B^{3+} (1s^2) leads to B^{2+} (1s2lnl') doubly excited states, and that from B^{3+} (1s2s 3S) leads to B^{2+} (2s2p^2 nl''') triply excited states, of which the 2s2p^2 2P state is most strongly populated. The quasi-free electron ‘beam’ spectral profile in 4.0 MeV B^{3+} collisions with H_2 (shaded areas) has a mean energy of 184 eV above each of the initial states, with a broad FWHM of 112 eV, overlapping many resonances.

Measurements were performed at the 7 MV EN tandem Van de Graaff accelerator facility of the J R Macdonald Laboratory of Kansas State University, which provided the He-like ions. Details of the experimental set-up and procedures have already been given in [17, 20, 22, 23]. For each Z, the elastic 3S channel and the unresolved inelastic 1S + 3P scattering channels were identified. R-matrix RES calculations performed for the 1s2l' 2l' resonances [20] were used to both energy calibrate the spectra and to accurately determine the projectile collision energy. This procedure introduced an absolute uncertainty of 2 eV, but a relative uncertainty of only 0.3–0.9 eV. The absolute electron detection efficiency was determined to within 20% by normalizing the 4.0 MeV B^{3+} + H_2 electron DDCS to the theoretical elastic electron scattering continuum [20]. The metastable fraction, f_{3S}, measured in situ [22, 23] with a ~30% error, gave rise to an overall absolute DDCS uncertainty of 35%.

Details of our R-matrix (based on the Belfast suite of inner-region codes [24] and the University College London suite of outer-region codes [25]) ESM approach have already been given for calculations of RES from the B^{3+} (1s^2) ground state [20]. Calculations of RES from the 1s2s 3S metastable state are similar, but more tedious, as they involve more final decay channels. Here, we included all 1snl (n = 1–3) and 2s2l' final states. Present atomic structure calculations and those from [10] show that the rate for the Auger decay to the 1s2p 1P state,
as well as to other possible 1s3l final states, is at least three orders of magnitude smaller, and therefore unobservable. Furthermore, the T-matrices for excitation from the 1s2s 3S state require the inclusion of partial waves with up to \( L_{\text{max}} = 40 \), rather than just \( L_{\text{max}} = 9 \) needed to describe excitation from the 1s2 \([20]\), primarily due to the increased spatial extent of the 2s electron. In figure 2, we show our results for \( \text{C}^4+ \) ions having \( f_{3s} = 12\% \). The ESM (see equation (2) of \([20]\)) was used to convert the R-matrix single-differential cross sections (SDCSs) to DDCSs, which were then convoluted with the spectrometer resolution (figures 2 (bottom) and 3).

Since our experimental technique is not widely known, we discuss it in comparison to the recent two-colour photoexcitation technique (2CPT) used to obtain triply excited even-parity states of Li (including the \( ^2D^\circ \) studied here) \([5]\), with which it has much in common. The two experiments use a two-component target mixture of ground and pre-excited states in approximately the same ratios. Both target components contribute to the observed electron decay channels. In the 2CPT, however, only triply excited states are populated and the resulting photoelectrons are well separated in energy. In our case, the 1s2lnl' doubly excited resonances (curves a, b, c, ...) are seen to sweep through the triply excited 2s2p2 \( ^2D \) lines (shaded areas) as \( Z \) is increased (see figures 2 and 3). For carbon, the \( 1S \) decay channel is seen to lie directly under one of the doubly excited Auger decay lines and therefore cannot be separated. For fluorine, all the doubly excited lines are energetically higher, above 640 eV. This interesting \( Z \)-behaviour results from the accidental binding-energy matching of the different Auger channels involved.

In both measurements the excitation mechanisms are highly selective. In the 2CPT, the dipole selection rules allow only even or odd parity triply excited states to be populated from the pre-excited odd parity or even parity initial state, respectively. The synchrotron’s high spectral resolution ensures unprecedented excitation selectivity as a function of photon energy. In our case, the selectivity is provided through RES and high-resolution electron spectroscopy on the exit channel. The much broader spectral profile of our quasi-free electron ‘beam’ (e.g. see figure 1), determined by the H2 Compton profile, is actually advantageous \([20, 26]\), since all resonances within the broad profile are excited simultaneously, thus avoiding the need for time consuming energy scanning. Except for line blending, an Auger electron energy resolution of 0.25% was sufficient to resolve and identify most of the low-lying triply excited decay channels \([16]\).

In table 1, Auger transition energies and total widths \( \Gamma' \) from this work are given, and compared to recent calculations (see footnote 4). These were determined by a Lorentzian fit of the form \( \Gamma' / [(E - E_r)^2 + (\Gamma/2)^2] \) to the trace of Smith’s time delay matrix \([27]\), \( Q = iS dS^\dagger/\partial E_r \), where \( S \) is the scattering matrix and \( E_r \) the excitation energy. Fano \( q \)-parameters were not fitted, since they are only physically meaningful for total cross sections. Experimental widths could not be accurately extracted, due to the much larger spectrometer resolution (~0.5–1.5 eV). Instead, the theoretical DDCSs are directly compared with experiment in figures 2 and 3 and are seen to be in good overall agreement in both line shape and absolute cross section, even though the peak energies are consistently offset by 0.5–1.5 eV. Similar but smaller offsets (~0.1–0.3 eV) have been reported in photo-ionization \([4]\). In our case, these offsets reflect small inaccuracies in the ionic target 1s2l energies used, having a total uncertainty of ~0.2 eV. We also note that the strong interference between the Rutherford and short range scattering potential amplitudes, while permissible in the elastic channel, is forbidden in the inelastic channels \([28]\). Finally, even though the RES SDCSs seem to drop sharply with increasing \( Z \), this is just a reflection of their underlying inverse dependence on \( E_r \), which is strongly \( Z \)-dependent. Multiplying the energy-integrated SDCSs by \( E_r \) factors out most of this.

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4 More extensive results will be given in a follow-up article.
Letter to the Editor

Figure 2. Top, R-matrix calculations for 180° RES from the C\textsuperscript{4+} (1s2s \textsuperscript{3}S) metastable state leading to the formation of the triply excited C\textsuperscript{4+} (2s2p\textsuperscript{2} \textsuperscript{2}D) state. Both elastic (decay back to the C\textsuperscript{4+} (1s2s \textsuperscript{3}S) state) and inelastic (decay to the C\textsuperscript{4+} (1s2s \textsuperscript{1}S and \textsuperscript{3}P states) RES channels are shown. Middle, the same as the top, but for RES from the C\textsuperscript{4+} (1s\textsuperscript{2} 1S) ground state leading to C\textsuperscript{3+} (1s\textsuperscript{2} lnl\textsuperscript{′}) doubly excited resonances (a, b, c, . . .) lying on top of the non-resonant continuum. Bottom, data (open circles): zero-degree electron spectra for 6.58 MeV C\textsuperscript{4+} (1s\textsuperscript{2} 1S, 1s2s \textsuperscript{3}S) collisions with H\textsubscript{2}. Error bars are due to statistics only. Theory: the above calculations were added together weighted by the respective population fraction in the ground state (gs) and metastable state (ms) according to the recipe \(\frac{d\sigma}{d\Omega} = (1 - f_{3S})\frac{d\sigma}{d\Omega}^{gs} + f_{3S}\frac{d\sigma}{d\Omega}^{ms}\), and were then converted to DDCSs (ESM model [20]), and convoluted with the electron spectrometer resolution. Lines: 1s2lnl\textsuperscript{′} transition groups correspond to (a, b, c, . . .) resonances (middle). Shaded areas: triply excited \(2\text{D}^\text{\textsuperscript{+}}\) Auger decay channels (top). The non-resonant continuum has been subtracted.

Z-dependence effect, leading to just a mild increase of this product with increasing Z. In figure 4, we plot the observed Z-dependence for the SDCSs (left scale) and the theoretical total widths \(\Gamma\) (right scale).

In conclusion, we report on the first experimental isoelectronic sequence investigation of the properties of a triply excited state for ions having \(Z = 5–9\). This was accomplished by the
Figure 3. As in figure 2 (bottom), but for collisions of B^{3+}, N^{5+}, O^{6+} and F^{7+} mixed state (1s^2 1S, 1s2s 3S) beams with H_2.
determination of absolute DDCSs for 180° quasi-free RES from a metastable ionic state, thus allowing for the population of the 2s2p^2 2D triply excited resonance and the observation of its associated Auger decay channels with high resolution. *R*-matrix calculations performed within
the ESM model are in good overall absolute agreement. Total widths and energy-integrated RES SDCS times $E_r$ for the $^2$D$^e$ resonance were found to increase mildly with $Z$. When free-electron lasers become available within the next decade [29], photo-ionization investigations of Li-like triply excited states with $Z > 3$ may become possible. Until then, however, only charged-particle collisional techniques can be expected to provide any insight to the study of triply excited states with $Z > 3$.

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