Photoionization cross sections for the trans-iron element Se$^+$ from 18 to 31 eV

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Abstract
Absolute photoionization cross-section calculations are presented for Se$^+$ using large-scale close-coupling calculations within the Breit–Pauli and Dirac–Coulomb R-matrix approximations. The results from our theoretical work are compared with recent measurements (Esteves 2010 PhD Thesis publication number AAI3404727, University of Reno, NV, USA; Sterling et al 2011 J. Phys. B: At. Mol. Opt. Phys. 44 025701; Esteves et al 2011 Phys. Rev. A 84 013406) made at the advanced light source (ALS) radiation facility in Berkeley, CA, USA. We report on results for the photon energy range 18.0–31.0 eV, which spans the ionization thresholds of the $4s\, ^3S_0^\text{c}/2$ ground state and the low-lying $^2D_{5/2}$ and $^2P_{3/2}$, $^2P_{1/2}$, $^2D_{3/2}$ and $^2D_{5/2}$ metastable states. Metastable fractions are inferred from our present work. Resonance energies and quantum defects of the prominent Rydberg resonances series identified in the spectra are compared for the $4p \rightarrow nd$ transitions with the recent ALS experimental measurements made on this complex trans-iron element.

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, detailed photoionization (PI) cross-section measurements for the trans-iron element Se$^+$, carried out at the advanced light source (ALS) synchrotron radiation facility in Berkeley, CA, were reported in the literature [1–3]. The photon energy studied in the experiments ranged from 18.0 to 31.0 eV and was scanned with a nominal spectral resolution of 28 meV. Measurements were also made at a higher photon energy resolution of 5.5 meV from 17.75 to 21.85 eV spanning the $4s\, ^3S_0^\text{c}/2$ ground-state ionization threshold and the low-lying $^2D_{3/2}$ and $^2D_{5/2}$ metastable states. Metastable fractions are inferred from our present work. Resonance energies and quantum defects of the prominent Rydberg resonances series identified in the spectra are compared for the $4p \rightarrow nd$ transitions with the recent ALS experimental measurements made on this complex trans-iron element.

PI of atomic ions is an important process in determining the ionization balance and hence the abundances of elements in photoionized astrophysical nebulae. It has recently become possible to detect neutron($n$)-capture elements (atomic number $Z > 30$, e.g. Se, Kr, Br, Xe, Rb, Ba and Pb) in a large number of ionized nebulae [7–9]. These elements are produced by slow or rapid $n$-capture nucleosynthesis (the ‘$s$-process’ and ‘$r$-process’, respectively) [8, 10]. Measuring the abundances...
of these elements helps to reveal their dominant production sites in the Universe, as well as details of stellar structure, mixing and nucleosynthesis [11–17, 5]. These astrophysical observations are the motivation to determine the PI and recombination properties of \( n \)-capture elements.

Various \( n \)-capture elements have been detected in the spectra of planetary nebulae (PNe\(^{\pm}\)), the photoionized ejecta of evolved low- and intermediate-mass stars (one to eight solar masses). Planetary Nebula progenitor stars may experience \( s \)-process nucleosynthesis [14, 18], in which case their nebulae will exhibit enhanced abundances of trans-iron elements. The level of \( s \)-process enrichment for individual elements is strongly sensitive to the physical conditions in the stellar interior [14, 16].

The underlying difficulty in studying \( s \)-process enrichment in PNe is due to the large uncertainties (factors of 2–3) of \( n \)-capture element abundances derived from the observational data [2, 5]. There are two main causes for these uncertainties. First, the low cosmic abundances of trans-iron elements, means their emission lines are sufficiently weak that generally only one or two ions of each element can be detected in individual PNe. Second, while robust ionization corrections can be derived from numerical simulations of nebulae [19, 20], this method relies on the availability of accurate atomic data for processes that affect the ionization equilibrium of each element. In photoionized nebulae, these atomic data include PI cross sections and rate coefficients for radiative and dielectronic recombination and charge exchange reactions are unknown for nearly all \( n \)-capture element ions. Uncertainties in the PI and recombination data of \( n \)-capture element ions can result in elemental abundance uncertainties of a factor of 2 or more [7].

The present theoretical investigation is a study to determine the PI and recombination properties of \( n \)-capture element ions, motivated by the astrophysical detection of these species and the importance of their elemental abundances for testing theories of nucleosynthesis and stellar structure. Determining the appropriate atomic data over the range of energies and temperatures encountered in astrophysical environs necessitates a predominantly theoretical approach. Experimental measurements are helpful to validate theoretical studies, particularly in the case of complex heavy ionic systems such as low charge states of trans-iron elements. We note that experimental studies are often limited in the photon energy range studied, energy resolution and to the charge states able to be investigated. In addition, many of the experiments carried out are contaminated by metastable states and require theoretical estimates to help unravel the components in the ion beam.

The prime motivation for choosing Se as the first element for investigation is due to the fact it has been detected in nearly twice as many PNe (70 in total) as any other trans-iron elements [9] in addition to recent experimental measurements becoming available to compare with [1, 2]. Experimental PI studies of other astrophysically observed \( n \)-capture elements have already been conducted by various groups in the cases of select Kr [21–23] and Xe ions [24, 23].

In this paper we present theoretical determinations of the absolute Se\(^{\pm}\) PI cross section near the ground-state ionization threshold and compare our results with recent experimental measurements [1, 2] for this trans-iron ion. We note that the results from our work can be applied to calibrate a broader theoretical effort to determine the PI and recombination properties of \( n \)-capture element ions over a large range of energies and temperatures. Our data would be suitable for incorporation within PI modelling codes such as Cloudy and XSTAR [19, 20], which numerically simulate the thermal and ionization structure of astrophysical nebulae. PI models can be used to derive accurate and robust ionization corrections for trans-iron elements, thereby enabling the accurate determination of their abundances in the Universe. We also intend to explore the properties of other members of this iso-electronic sequence, for example, Br\(^{2+}\) and Rb\(^{3+}\) along with other low-charged Se ions in subsequent publications.

The layout of this paper is as follows. Section 2 presents a brief outline of the theoretical work. Section 3 presents our theoretical PI cross-sections results where comparisons are made with the recent Se\(^{\pm}\) PI experimental measurements [1–3]. Resonance energies and quantum defects for the various dominant Rydberg series (seen in both the experimental and theoretical PI spectra) are tabulated and compared. Finally in section 4 conclusions are drawn from the present investigation.

2. Theory

Relativistic corrections can play an increasingly significant role for atoms with charge \( Z \geq 18 \) [25]. It was shown in recent work on electron-impact excitation of neutral neon (\( Z = 10 \)) that a \( jK \) coupling scheme was required to accurately describe even the low-lying energy target levels [26]. The semi-relativistic Breit–Pauli \( R \)-matrix approach has been successfully applied repeatedly to atomic ions below \( Z = 30 \) for numerous atomic systems by the Iron Project [27]. For atomic ions with \( Z > 30 \), a Dirac–Coulomb approach to electron and photon interactions is ideal, due to the importance of relativistic and correlation effects in accurately modelling these systems.

Computationally, the increased number of relativistic orbitals over the corresponding non-relativistic orbitals can cause a dramatic increase both in the number of integrals required and in the complexity of the angular algebra. We note that in a recent work for the electron-impact excitation of Fe\(^{2+}\) [28] and Fe\(^{5+}\) [29] hundreds of millions of Racah coefficients were calculated for the relativistic treatment of this open-d shell system. To address the future challenge of electron scattering in which hundreds of levels and thousands of scattering channels are to be considered an efficient parallel version [30] of the Dirac atomic \( R \)-matrix codes (DARC) [31–34] suite of codes was developed.

A natural extension of this work was the formation of the numerous bound-free dipole matrix elements required for PI in an equally efficient manner, distributed over an
Parallel DARC dipole codes

- `stg1d_orbs` builds continuum basis
- `pstg1d_ints` integral generation
- `pstg2d_dip` builds Hamiltonian, dipole elements
- `ppto3_dip` Converts DARC to BP matrix order
- `pstg3r_dip` Diagonalises Hamiltonian $\rightarrow$ eigenvectors
- `pstgd_dip` Generates Bound-free Dipole matrix elements
- `pstgbd` Form initial bound states
- `prform` pre-forms all R-matrices
- `pstgdf0damp` Calculate photoionisation cross section

**Figure 1.** Flowchart illustrating the steps necessary to obtain PI cross sections with the parallel DARC. The codes are available at http://connorb.freeshell.org/codes/DARCdipole/.

**Figure 2.** Photoionization of the $^4S_{1/2}$ ground state of the Se$^+$ ion. The cross section from threshold to a photon energy of 30 eV are illustrated. Theoretical results have been obtained from both the DARC and Breit–Pauli approximations with an increasing number of levels included in the close-coupling approximations. The theoretical cross sections have been convoluted with a 28 meV FWHM Gaussian distribution for comparison purposes.

Using this suite of DARC codes detailed PI cross-section calculations for the Se$^+$ ion were performed for the ground state of DARC codes, illustrates the $R$-matrix sequence required to obtain PI cross sections with the parallel DARC. These recent modifications now include the concurrent formation of every dipole matrix, reducing the total time substantially required for the formation of all dipoles to that required by a single dipole. These developments open the frontier to enabling comprehensive pioneering large-scale calculations along iso-nuclear sequences to be performed now within a feasible time frame.

It should be noted that in addition to large-scale relativistic PI calculations, the same dipole matrix elements are the foundation of radiationally damped electron-impact excitation studies required in highly charged ions. With these extensions to the DARC codes one can address the complex problem of trans-iron element single photon ionization. The flowchart in figure 1, with brief annotations beside each module of the suite of DARC codes, illustrates the $R$-matrix sequence required to obtain PI cross sections with the parallel DARC. These recent modifications now include the concurrent formation of every dipole matrix, reducing the total time substantially required for the formation of all dipoles to that required by a single dipole. These developments open the frontier to enabling comprehensive pioneering large-scale calculations along iso-nuclear sequences to be performed now within a feasible time frame.
and all the excited metastable levels associated with the 4s²4p³ configuration. To benchmark our theoretical results we compare them with recent high resolution experimental measurements made at the ALS synchrotron radiation facility [1–3].

In R-matrix theory, all PI cross-section calculations require the generation of atomic orbitals based primarily on the atomic structure of the residual ion. The present theoretical work for the PI of the Se^{+} ion employs relativistic atomic orbitals generated for the residual Se^{2+} ion, which were calculated using the extended-optimal-level (EOL) procedure within the GRASP structure code [36, 37, 25]. We explored various structure and scattering models of increasing complexity with the R-matrix approach in order to investigate an optimum model for determining the total PI cross sections.

PI cross-section calculations for this complex trans-iron system began by including only levels from the 4s²4p², 4s²4p³ and 4p⁴ configurations which gave rise to 20 Jπ levels. We found this model to be inadequate to represent the complex experimental spectrum and it was necessary to extend the theoretical model. Our first approach was to supplement the configurations of this 20-level model with addition levels

![DARC: 336-state, 28 meV FWHM](image)

**Figure 3.** Theoretical PI cross sections (336-level close-coupling DARC calculations) for the 4s²4p³ ground state, 2D_o^{3/2}, 2D_o^{5/2}, 2P_o^{1/2} and 2P_o^{3/2} metastable states arising from the 4s²4p³ configuration are illustrated (top five panels). The theoretical results were convoluted with a Gaussian of 28 meV FWHM to simulate the photon energy resolution of the experimental measurements (bottom panel) taken at the ALS synchrotron radiation facility.

| Level | Configuration | Term \( ^L_J \) | Energy | Energy | Energy | Energy | Δ(%) |
|-------|---------------|----------------|--------|--------|--------|--------|-------|
|       |               |                | NIST   | GRASP  | Breit–Pauli | AUTO |       |
| 1     | 4s²4p²        | 3P₀           | 0.000 000 | 0.000 000 | 0.000 000 | 0.000 00 | 0.00 | 0.0 |
| 2     | 4s²4p²        | 3P₁           | 0.015 870 | 0.015 061 | 0.014 19  | 0.015 80 | 5.1  |
| 3     | 4s²4p²        | 3P₂           | 0.035 880 | 0.035 409 | 0.033 47  | 0.036 20 | 1.3  |
| 4     | 4s²4p³        | 1D₂           | 0.118 760 | 0.140 979 | 0.138 35  | 0.143 70 | 18.7 |
| 5     | 4s²4p³        | 1S₀           | 0.259 070 | 0.285 184 | 0.271 16  | 0.259 50 | 10.1 |
| 6     | 4s²4p³        | 3S₁           | 0.579 910 | 0.566 575 | 0.553 04  | –       | 2.3  |
| 7     | 4s²4p³        | 3D₁           | 0.830 080 | 0.853 381 | 0.814 98  | 0.830 80 | 2.8  |
| 8     | 4s²4p³        | 3D₂           | 0.844 950 | 0.854 258 | 0.815 43  | 0.845 00 | 1.1  |
| 9     | 4s²4p³        | 3D₃           | 0.879 810 | 0.859 092 | 0.819 09  | 0.879 80 | 2.3  |
| 10    | 4s²4p³        | 3P₀           | 0.970 335 | 0.991 048 | 0.944 28  | 0.967 50 | 2.1  |
| 11    | 4s²4p³        | 3P₁           | 0.970 636 | 0.994 054 | 0.946 14  | 0.965 40 | 2.4  |
| 12    | 4s²4p³        | 3P₂           | 0.971 329 | 0.992 406 | 0.946 16  | 0.967 60 | 2.2  |

\[ a^{2} \sum_{J} \ \text{EOL} \]

\[ b \text{ GRASP, absolute percentage difference relative to NIST values.} \]

\[ c \text{ Esteves PhD thesis [1].} \]

\[ d \text{ Breit–Pauli.} \]

\[ e \text{ Sterling and Witthoeft [4].} \]
Figure 4. Comparison of ALS PI cross-section measurements from 18 to 22 eV taken at 28 meV (shaded area) with the 336-state close-coupling DARC calculations. The theoretical cross sections (solid black line) for each of the five initial states have been convoluted with a 28 meV FWHM Gaussian and a weighting of the states (see text for details) to simulate the measurements. The absolute measurements (solid black circles) have been obtained with a larger energy step. The error bars give the total uncertainty of the experimental data.

Figure 5. Comparison of ALS PI cross-section measurements from 18 to 21.8 eV taken at 5.5 meV (shaded area) with the 336-state close-coupling DARC calculations. The theoretical cross sections (solid black line) for each of the five initial states have been convoluted with a 5.5 meV FWHM Gaussian and a weighting of the states (see text for details) to simulate the measurements. The absolute measurements (solid black circles) have been obtained with a larger energy step. The error bars give the total uncertainty of the experimental data.
Figure 6. Comparison of ALS PI cross-section measurements from 21 to 31 eV taken at 28 meV (shaded area) with the 336-state close-coupling DARC calculations. The theoretical cross sections (solid black line) for each of the five initial states have been convoluted with a 28 meV FWHM Gaussian and a weighting of the states (see text for details) to simulate the measurements. The absolute measurements (solid black circles) have been obtained with a larger energy step. The error bars give the total uncertainty of the experimental data.

Figure 7. Eigenphase sum $\delta$ and its derivative $\delta'$ (for each $2J^\pi$ symmetry contributing to the PI cross section $\sigma$ for the $4s^2 4p^3 3P_{1/2}$ initial state) as a function of photon energy in the region below the $^1D_2$ and $^1S_0$ excited state thresholds of the residual Se$^{2+}$ ion for (a) $2J = 1^e$ symmetry, (b) $2J = 3^g$ symmetry and (c) PI cross section $\sigma$ for the $^3P_{1/2}$ metastable state convoluted with a Gaussian of 28 meV FWHM (solid black line). The prominent Rydberg resonances series in the PI cross section have been identified (open and solid triangles) as members of two different Rydberg autoionizing series converging to the $^1D_2$ and $^1S_0$ excited states of the residual Se$^{2+}$ ion indicated by thick vertical lines.
from several 3d-hole configurations, 3d⁉4s²4p³, 3d⁉4s⁴p⁴ and 3d⁉4p⁵. This increased the number of levels in our close coupling expansion to 126 yielding improved agreement with experiment. Further extensive theoretical models were then investigated with the inclusion of levels from configurations involving a 4d orbital in our close coupling expansion rather than levels from the 3d hole configurations. The first of these models included all 246 levels arising from the eight configurations: 4s²4p³, 4s⁴p⁴, 4s²4p⁵d, 4s⁴d³, 4p⁷d², 4s⁴p⁷d⁴ and 4p⁷d⁴ were included in the close-coupling expansion. The second model investigated was when this 246-level model was augmented with levels from an additional 4s⁴p⁴d³ configuration, giving rise to a total of 336 levels.

The final model augmented this 336-level model with the 4s²4p⁵s, 4s²4p⁵p and 4s²4p⁵d configurations which gave rise to a total of 362 levels. Table 1 shows a sample comparison of our results for the lowest 12 levels of the residual Se²⁺ (Se III) ion with the available experimental and theoretical work. However, these comparisons with experiment are slightly misleading as the energy levels of the DARC R-matrix calculation are shifted to experimental values prior to the matrix diagonalization. Since converged results are obtained within the 336-level model we used this approximation to determine all the remaining PI cross sections for the metastable states with the DARC codes.

PI cross-section calculations were performed in the Dirac–Coulomb and Breit–Pauli approximation with the various models. The advantage of the DARC calculation over the Breit–Pauli result is marginal for the PI of outer shell electrons. However, it does provide the repeatability of the result using completely independent structure codes and for the most part independent collisional codes to provide the cross section.

Considering the ionization potential between the ground state of Se II and that of Se III is approximately 1.6 Ryd and according to NIST tables the 4s²4p⁴d, 4s²4p⁵ℓ levels are over 1 Ryd above the Se III ground state. This gives a photon energy of greater than 36 eV to photexcite to either the 4d²4p⁴d or the 4s²4p⁵s levels. Therefore, their influence on the ground-state PI cross section within the energy range presented in this paper, is solely in terms of changes in structure through CI mixing.

Figure 2 shows that the inclusion of the additional 5s, 5p and 5d orbitals in the basis set has a minimal effect on the total PI cross section for the 4S¹/₂ ground state over the energy range investigated and for energies less than 31 eV. However, these comparisons with experiment are slightly misleading as the energy levels of the DARC R-matrix calculation are shifted to experimental values prior to the matrix diagonalization. Since converged results are obtained within the 336-level model we used this approximation to determine all the remaining PI cross sections for the metastable states with the DARC codes.

The R-matrix boundary radius of 8 Bohr radii was sufficient to envelop the radial extent of all the atomic orbitals of the residual Se²⁺ ion. A basis of 16 continuum orbitals was sufficient to span the incident experimental photon energy range of up to 32 eV. The 336-state model produced a maximum of 1758 coupled channels in our scattering work with Hamiltonian matrices of dimension of the order of 28 300 by 28 300 in size. Due to dipole selection rules, for total ground-state PI we need only consider the three bound-free
The resonance energy $\epsilon$ converging to the $1S_0$ threshold is not observed in the PI cross sections. As members of a Rydberg autoionizing series converging to the $1D_2$ threshold of the residual Se$^+$ ion, the weak resonance series converging to the $1S_0$ threshold is not observed in the PI cross sections.

Figure 9. Eigenphase sum $\delta$ and its derivative $\delta'$ (for each $2J^o$ symmetry contributing to the PI cross section $\sigma$ for the $4s^24p^3 \, ^3D_{5/2}$ initial state) as a function of photon energy in the region below the $1D_2$ and $1S_0$ excited state thresholds the residual Se$^+$ as a function of appropriate width (FWHM of 28 and 5.5 meV respectively) and weighted accordingly in order to simulate the energy resolution of the measurements performed at the ALS synchrotron radiation facility.

3. Results and discussion

Figure 2 shows the convergence of the PI results obtained from the Breit–Pauli and Dirac–Coulomb (DARC) approximations for the $4s^24p^3 \, ^4S_{5/2}$ ground state using an $n = 4$ basis. The theoretical PI cross-section results are illustrated for the $4s^24p^3 \, ^4S_{5/2}$ ground state of this complex trans-iron element with an increasing number of levels retained in the close-coupling expansion. As illustrated in figure 2, the 336-level model (for the $4s^24p^3 \, ^4S_{5/2}$ ground state using an $n = 4$ basis). The theoretical PI cross-section results are illustrated for the $4s^24p^3 \, ^4S_{5/2}$ ground state of this complex trans-iron element with an increasing number of levels retained in the close-coupling approximation. At this level of approximation it ensures consistency in our theoretical work. Using this 336-level model we obtained the PI cross sections for all the remaining metastable levels associated with the $4s^24p^3$ configuration within the Dirac–Coulomb (DARC) approximation. The theoretical PI cross-section results for the individual levels arising from the $4s^24p^3$ configuration within the Dirac–Coulomb (DARC) approximation.
The eigenphase sum $\delta$ and its derivative $\delta'$ (for each $2J^e$ symmetry contributing to the PI cross section $\sigma$ for the $4s^24p^32D^0_{5/2}$ initial state) as a function of photon energy in the region below the $^1D_2$ and $^1S_0$ excited state thresholds of the residual Se$^+$ observed in the PI cross sections. The weak resonance series converging to the $^1S_0$ threshold is not of $28$ meV FWHM (solid black line). The prominent Rydberg resonances series in the PI cross section have been identified (solid triangles) as members of a Rydberg autoionizing series converging to the $^1D_2$. To determine the fractions of metastable ions present in the experimental ion beam PI cross-section calculations were performed using the Dirac–Coulomb $R$-matrix method for both the $^4S_{5/2}$ ground state and the excited metastable states ($^2D_{3/2}^1$, $^2D_{5/2}^1$, $^2P_{1/2}^1$ and $^2P_{3/2}^1$) associated with the $4s^24p^3$ configuration. The individual fractions were estimated by first scaling the highest-lying metastable state to the absolute experimental cross section. Each subsequent state was then scaled such that the sum of the theoretical cross sections matched the experiment as closely as possible, with all four metastable states together with the ground-state fractions ultimately constrained to sum to unity. Using this technique the various fractions were determined and it was found that a non-statistical distribution of the ground and metastable states gave best agreement with experiment by weighting the contribution of the $^4S_{3/2}$, $^2D_{5/2}^1$, $^2D_{3/2}^1$, $^2P_{1/2}^1$ and $^2P_{3/2}^1$ states by $0.52$, $0.13$, $0.19$, $0.03$ and $0.13$ respectively.

As noted previously, PI cross-section calculations have been made recently on this complex ion using AUTOSTRUCTURE [4] within the MCBP distorted-wave approximation for a wider range of energies and for higher charged states of the ion. Using this distorted-wave approximation the authors find that the direct PI cross sections for these Se ions differ by 30–50% when compared to the available ALS experimental measurements. It was concluded from that study on Se ions [4] (by visual comparison) that best agreement with experiment was obtained by weighting the contribution of the ground configuration states ($^4S_{3/2}$, $^2D_{5/2}^1$, $^2D_{3/2}^1$, $^2P_{1/2}^1$, $^2P_{3/2}^1$) by $0.53$, $0.15$, $0.05$, $0.11$, $0.16$ respectively. Therefore a non-statistical distribution of the PI cross sections in both theoretical approaches is seen to provide the best agreement with experiment.

Furthermore the Fano profile in the PI cross section near 23.0 eV is not reproduced by the AUTOSTRUCTURE calculations [4] ($R$-matrix techniques are necessary to reproduce resonance interference effects), and the lack of this interference causes the discrepancy in the direct cross section in this energy region. The calculated and experimental Se$^+$ direct cross sections agree to within 30–50% over the range of experimental energies, except above 30 eV, where the experimental measurements are more uncertain since only a single absolute measurement was made above 27 eV (compared to absolute measurements at lower energies, where independent estimates were performed two to three times for each energy). Therefore, they report uncertainties in the experiment of over 50% in the high-energy region. As $R$-matrix techniques are necessary to reproduce resonance interference
effective quantum numbers (\(v = n - \mu\)) and the linewidth \(\Gamma\) (meV) versus photon energy (eV) for the \(4s^24p^2(^1D_2)nd\) resonances lying below the \(^1D_2\) threshold of the residual Se\(^{2+}\) ion. Experimental data (open red squares, ALS \([1, 2]\)) and theoretical estimates (solid blue triangles, QB); (a) effective quantum numbers \((v)\) for the \(4s^24p^2(^1D_2)nd\) series originating from the initial Se\(^{2+}(^2D_{5/2})\) state; (b) effective quantum numbers \((v)\) for the \(4s^24p^2(^1D_2)nd\) series originating from the initial Se\(^{2+}(^2D_{5/2})\) state; (c) \(4s^24p^2(^1D_2)nd\), resonance linewidths \((\Gamma)\) originating from the initial Se\(^{2+}(^2D_{5/2})\) state and (d) \(4s^24p^2(^1D_2)nd\), resonance linewidths \((\Gamma)\) originating from the initial Se\(^{2+}(^2D_{5/2})\) state.

Figure 11. Effective quantum number \(v = n - \mu\) and the linewidth \(\Gamma\) (meV) versus photon energy (eV) for the \(4s^24p^2(^1D_2)nd\) resonances lying below the \(^1D_2\) threshold of the residual Se\(^{2+}\) ion. Experimental data (open red squares, ALS \([1, 2]\)) and theoretical estimates (solid blue triangles, QB); (a) effective quantum numbers \((v)\) for the \(4s^24p^2(^1D_2)nd\) series originating from the initial Se\(^{2+}(^2D_{5/2})\) state; (b) effective quantum numbers \((v)\) for the \(4s^24p^2(^1D_2)nd\) series originating from the initial Se\(^{2+}(^2D_{5/2})\) state; (c) \(4s^24p^2(^1D_2)nd\), resonance linewidths \((\Gamma)\) originating from the initial Se\(^{2+}(^2D_{5/2})\) state and (d) \(4s^24p^2(^1D_2)nd\), resonance linewidths \((\Gamma)\) originating from the initial Se\(^{2+}(^2D_{5/2})\) state.

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effects we have carried out these calculations in the present investigation.

In figure 4, the rich resonance structure observed in the experimental spectra is generally well represented in the metastable region by theory. This is still apparent when the theoretical work is compared with the experimental measurements taken at an even higher resolution \([3]\). Figure 5 shows the ALS experimental measurements taken at a higher resolution of 5.5 meV (from 18 to 21.8 eV) together with the theoretical results convoluted with a Gaussian of the same FWHM to simulate the experimental resolution and non-statistically weighted as before. Here again there is good agreement between the experimental and theoretical results.

In the energy region 21–31 eV (figure 6) the theoretical results are larger than experiment. The solid line corresponds to the sum of the ground and metastable state fractions of the theoretical calculations. As indicated in the ALS experimental studies for Se\(^{2+}\) \([1, 2]\), contamination from higher order radiation produced by the undulator beamline may be a possible cause for uncertainties. Previous experiments on Xe\(^{2+}\) \([42]\) estimated a lower fraction of 2% at around 40 eV. The measurements on Se\(^{2+}\) \([1, 2]\) are between these two photon energies and it was concluded in that work \([1, 2]\) the maximum contamination is no greater than 4%. At lower photon energies, the contamination of higher order radiation is expected to be larger, but not by more than a factor of 2–3 compared to the contamination at 40 eV. It was concluded from the Se\(^{2+}\) ALS measurements \([1, 2]\) that the experimental uncertainties on the absolute measurements made are estimated to be 30% including the possible contamination of the photon beam by higher order radiation.

Earlier studies on the PI spectrum of O\(^{+}\) at the ALS synchrotron radiation facility \([43]\) were used to identify the resonance structure due to the metastable states \([1, 2]\). This is apparent when the spectra of O\(^{+}\) and Se\(^{2+}\) are compared, the resemblance is remarkable but not totally unexpected. These respective ions have an np\(^o\) configuration (\(n = 2\) for O\(^{+}\) and \(n = 4\) for Se\(^{2+}\)) in their outermost shell giving rise in each case to the same term designation for the \(^4S_{3/2}\) ground state and the \(^2D_{5/2,2/2,3/2}\) and \(^2P_{1/2,3/2}\) metastable states. In the case of O\(^{+}\), the region of the spectrum covering the energy range from the \(^2P_{1/2,3/2}\) threshold to the \(^4S_{3/2}\) threshold consisted of very strong resonances due to 2p \(\rightarrow\) nd electron excitations of the metastable ions as well as weak resonances due to 2p \(\rightarrow\) ns transitions. Similarly, the Se\(^{2+}\) spectra, shows the corresponding 4p \(\rightarrow\) nd transitions but the 4p \(\rightarrow\) ns series appear to be too weak to be observed.

At energies below 21.2 eV there are prominent Rydberg resonance features resulting from PI of the initial metastable Se\(^{2+}\) states in the experimental and theoretical cross sections, as is seen in figure 3. Multiple overlapping Rydberg resonance series in the spectra are also clearly visible converging to the \(4s^24p^2\ ^1D_2\) and \(4s^24p^2\ ^3S_0\) thresholds respectively of the residual Se\(^{2+}\) ion. The presence of interfering resonances disrupt the regular Rydberg pattern of resonances, as can be seen in the spectra for the \(^2P_{1/2}\) and \(^2P_{3/2}\) metastable states, respectively figures 7 and 8.
state of Se [1, 2]. From the ALS measurements [1, 2] it was shown that
results (obtained for the dominant resonance features in the
narrow resonances. For this trans-iron element our theoretical
excellent method for locating and determining the properties of
properties of the

Table 2. Principal quantum number (n), resonance energies E (eV) and quantum defect (μ) from experimental measurements of Se+ [1, 2] compared with present theoretical estimates from the QB method. The Rydberg series originating from the 2Po 1/2 metastable state of Se+ due to 4p → nd transitions is tabulated. The uncertainties in the experimental energies are stated to be ±0.010 eV or less. The series limits are taken from the NIST [38] tabulations and from Esteves and co-workers [1, 2].

| Initial Se+ state | Initial Se+ state | Initial Se+ state |
|-------------------|-------------------|-------------------|
| 4s^24p^1(3P_y/2) | 4s^24p^1(3P_y/2) | 4s^24p^1(3P_y/2) |
| Rydberg series    | Rydberg series    | Rydberg series    |
| 4s^24p^1(1D_2) nd| 4s^24p^1(1D_2) nd| 4s^24p^1(1D_2) nd|
| n    | E (eV) | μ      | n    | E (eV) | μ      | n    | E (eV) | μ      |
|------|-------|--------|------|-------|--------|------|-------|--------|
| 6    | 18.256 | 0.14   | 6    | 18.268 | 0.14   | 6    | 18.350 | 0.24   |
| 7    | 18.684 | 0.15   | 7    | 18.697 | 0.14   | 6    | 20.118 | 0.23   |
| 8    | 18.957 | 0.16   | 8    | 18.972 | 0.14   | 7    | 20.556 | 0.22   |
| 9    | 19.149 | 0.16   | 9    | 19.160 | 0.14   | 8    | 20.851 | 0.22   |
| 10   | 19.280 | 0.16   | 10   | 19.296 | 0.12   | 9    | 21.044 | 0.22   |
| 11   | 19.379 | 0.15   | 11   | 19.395 | 0.10   | 10   | 21.081 | 0.22   |
| 12   | 19.455 | 0.14   | 12   | 19.455 | 0.14   | 11   | 21.283 | 0.22   |
| ∞    | 19.842a |        | ∞    | 19.853 ±0.05b |      | ∞    | 21.751a |        |

a NIST tabulations [38].
b Esteves PhD thesis [1].

To obtain the resonance parameters a theoretical analysis with a modification to the widely used eigenphase derivative (QB) technique (for j j-coupling) that determines resonance parameters in electron collisions with atomic and molecular systems [39–41] was used. This technique exploits the properties of the R-matrix in multi-channel scattering and is an excellent method for locating and determining the properties of narrow resonances. For this trans-ion element our theoretical results (obtained for the dominant resonance features in the PI spectra) are compared with the recent ALS measurements [1, 2]. From the ALS measurements [1, 2] it was shown that the ^2P_y/2 and ^2P_o/2 initial metastable states of the Se+ ion both produce two dominant Rydberg resonance series. Our results for these resonances are illustrated in figures 7 and 8. The 4s^24p^1(1D_2) nd series converging to the ^1D_2 series limit is indicated with solid triangles and the 4s^24p^1(1S_o) nd series converging to the ^1S_0 limit by the open triangles. Furthermore, two additional autoionizing Rydberg series were identified associated with the ^2D_o/2 and ^2D_y/2 metastable states, our theoretical results are shown by the solid triangles in figures 9 and 10.

The relationship between the principal quantum number n, the effective quantum number ν and the quantum defect μ for an ion of effective charge Z is given by ν = n − μ where the resonance position ϵ_r can be determined from Rydberg’s formula

ε_r = ϵ_∞ − Z^2/ν^2,

and ϵ_∞ is the resonance series limit [44]. Tables 2–5 lists the principal quantum number n, resonance energy ε, and quantum defect μ of the first few members obtained from our work for each of the prominent Rydberg series originating from the 2Po 1/2 and 2Po 3/2 metastable states. The experimental results of Esteves and co-workers [1, 2] are included in tables 2–5 for comparison purposes where it is seen our theoretical work is in satisfactory agreement with experiment for the resonance energies and quantum defects. Measurements taken at the ALS

Table 3. Principal quantum number (n), resonance energies E (eV) and quantum defect (μ) from experimental measurements of Se+ [1, 2] compared with present theoretical estimates from the QB method. The Rydberg series originating from the 2Po 1/2 metastable state of Se+ due to 4p → nd transitions is tabulated. The uncertainties of the experimental energies are stated to be ±0.010 eV. The series limits are taken from the NIST [38] tabulations and from Esteves and co-workers [1, 2].

| Initial Se+ state | Initial Se+ state | Initial Se+ state |
|-------------------|-------------------|-------------------|
| 4s^24p^1(3P_y/2) | 4s^24p^1(3P_y/2) | 4s^24p^1(3P_y/2) |
| Rydberg series    | Rydberg series    | Rydberg series    |
| 4s^24p^1(1D_2) nd| 4s^24p^1(1D_2) nd| 4s^24p^1(1D_2) nd|
| n    | E (eV) | μ      | n    | E (eV) | μ      | n    | E (eV) | μ      |
|------|-------|--------|------|-------|--------|------|-------|--------|
| 6    | 18.345 | 0.17   | 6    | 18.354 | 0.17   | 6    | 18.354 | 0.17   |
| 7    | 18.786 | 0.16   | 7    | 18.788 | 0.16   | 7    | 18.788 | 0.16   |
| 8    | 19.062 | 0.16   | 8    | 19.070 | 0.16   | 8    | 19.070 | 0.16   |
| 9    | 19.251 | 0.16   | 9    | 19.262 | 0.14   | 9    | 19.262 | 0.14   |
| 10   | 19.280 | 0.16   | 10   | 19.298 | 0.12   | 10   | 19.298 | 0.12   |
| 11   | 19.485 | 0.16   | 11   | 19.498 | 0.16   | 11   | 19.498 | 0.16   |
| 12   | 19.506 | 0.15   | 12   | 19.515 | 0.15   | 12   | 19.515 | 0.15   |
| ∞    | 19.842a |        | ∞    | 19.853 ±0.05b |      | ∞    | 19.853 ±0.05b |      |

a NIST tabulations [38].
b Esteves PhD thesis [1].
The Rydberg series originating from the 2Do state of Se$^+$ due to 4p$\rightarrow$nd transitions is tabulated. The uncertainties in the experimental energies are stated to be ±0.010 eV. The series limits are taken from the NIST [38] tabulations and from Esteves and co-workers [1, 2].

| n | $E$ (eV) | $\mu$ | n | $E$ (eV) | $\mu$ |
|---|---|---|---|---|---|
| 5 | 19.469 | 0.23 | 5 | 19.468 | 0.17 |
| 6 | 20.227 | 0.22 | 6 | 20.202 | 0.17 |
| 7 | 20.673 | 0.22 | 7 | 20.637 | 0.17 |
| 8 | 20.958 | 0.22 | 8 | 20.922 | 0.15 |
| 9 | 21.151 | 0.22 | 9 | 21.116 | 0.11 |
| 10 | 21.288 | 0.22 | 10 | 21.238 | 0.20 |
| 11 | 21.389 | 0.22 | – | – | – |
| 12 | 21.465 | 0.22 | – | – | – |
| ∞ | 21.857$^a$ | ∞ | 21.805 ± 0.05$^b$ |

$^a$ NIST tabulations [38].
$^b$ Esteves PhD thesis [1].

Table 6. Principal quantum number ($n$), resonance energies $E$ (eV) and quantum defect ($\mu$) from experimental measurements of Se$^+$ [1, 2] compared with present theoretical estimates from the QB method. The Rydberg series originating from the $^3D_{3/2}$ metastable state of Se$^+$ due to 4p$\rightarrow$nd transitions is tabulated. The uncertainties in the experimental energies are stated to be ±0.010 eV. The series limits are taken from the NIST [38] tabulations and from Esteves and co-workers [1, 2].

| n | $E$ (eV) | $\mu$ | n | $E$ (eV) | $\mu$ |
|---|---|---|---|---|---|
| 6 | 19.573 | 0.17 | 6 | 19.572 | 0.18 |
| 7 | 20.009 | 0.16 | 7 | 20.009 | 0.17 |
| 8 | 20.287 | 0.16 | 8 | 20.289 | 0.17 |
| 9 | 20.476 | 0.16 | 9 | 20.479 | 0.16 |
| 10 | 20.610 | 0.16 | 10 | 20.613 | 0.17 |
| 11 | 20.710 | 0.16 | 11 | 20.713 | 0.16 |
| 12 | 20.784 | 0.16 | 12 | 20.788 | 0.16 |
| ∞ | 21.172$^a$ | ∞ | 21.176 ± 0.025$^b$ |

$^a$ NIST tabulations [38].
$^b$ Esteves PhD thesis [1].

Table 7. Principal quantum number ($n$), resonance energies $E$ (eV) and quantum defect ($\mu$) from experimental measurements of Se$^+$ [1, 2] compared with present theoretical estimates from the QB method. The Rydberg series originating from the $^3D_{5/2}$ metastable state of Se$^+$ due to 4p$\rightarrow$nd transitions is tabulated. The uncertainties in the experimental energies are stated to be ±0.010 eV. The series limits are taken from the NIST [38] tabulations and the work of Esteves and co-workers [1, 2].

| n | $E$ (eV) | $\mu$ | n | $E$ (eV) | $\mu$ |
|---|---|---|---|---|---|
| 5 | 19.469 | 0.23 | 5 | 19.468 | 0.17 |
| 6 | 20.227 | 0.22 | 6 | 20.202 | 0.17 |
| 7 | 20.673 | 0.22 | 7 | 20.637 | 0.17 |
| 8 | 20.958 | 0.22 | 8 | 20.922 | 0.15 |
| 9 | 21.151 | 0.22 | 9 | 21.116 | 0.11 |
| 10 | 21.288 | 0.22 | 10 | 21.238 | 0.20 |
| 11 | 21.389 | 0.22 | – | – | – |
| 12 | 21.465 | 0.22 | – | – | – |
| ∞ | 21.857$^a$ | ∞ | 21.805 ± 0.05$^b$ |

$^a$ NIST tabulations [38].
$^b$ Esteves PhD thesis [1].

4. Conclusions

State-of-the-art theoretical methods were used to investigate the photoionization (PI) of Se$^+$ ions in the energy region of the ground-state ionization threshold (18–31 eV). Given the complexity of this trans-iron element, overall, satisfactory agreement is found between theoretical and experimental results both on the photon-energy scale and on the absolute PI cross-section scale. The PI cross section exhibits a wealth of resonances. Prominent members of the Rydberg series are analysed and compared with experiment. Resonance positions and quantum defects for the 4s$^2$4p$^2$(1D$_2$) nd series converging to their respective series limits are presented. The metastable state content of the Se$^+$ ion beam has been determined along with prominent autoionizing Rydberg resonances series seen in the experimental PI cross sections. A clear pattern of Rydberg resonance series is seen in the spectra of the PI cross sections disrupted by interloping resonances.

We point out that the strength of the present study is in the convergence between two different state-of-the-art theoretical methods and the comparison with available experimental data.
Such detailed comparisons, between theory and experiment, strengthens the validity of our results for use in astrophysical applications.

The PI cross sections from the present study are suitable to be included into state-of-the-art PI modelling codes Cloudy and XSTAR [19, 20] that are used to numerically simulate the thermal and ionization structure of ionized astrophysical nebulae. In combination with our determinations of the PI properties of other low-charge Se ions (to be addressed in subsequent publications), this will enable the abundance of Se to be accurately determined in astrophysical nebulae. Such detailed comparisons, between theory and experiment, strengthens the validity of our results for use in astrophysics.

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