Inner-Shell Photodetachment of Transition Metal Negative Ions

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INNER-SHELL PHOTODETACHMENT OF TRANSITION METAL NEGATIVE IONS

by

Ileana Dumitriu

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Physics

Western Michigan University
Kalamazoo, Michigan
December 2010
This thesis focuses on the study of inner-shell photodetachment of transition metal negative ions, specifically Fe⁻ and Ru⁻. Experimental investigations have been performed with the aim of gaining new insights into the physics of negative atomic ions and providing valuable absolute cross section data for astrophysics. The experiments were performed using the X-ray radiation from the Advanced Light Source, Lawrence Berkeley National Laboratory, and the merged-beam technique for photoion spectroscopy.

Negative ions are a special class of atomic systems very different from neutral atoms and positive ions. The fundamental physics of the interaction of transition metal negative ions with photons is interesting but difficult to analyze in detail because the angular momentum coupling generates a large number of possible terms resulting from the open $d$ shell.

Our work reports on the first inner-shell photodetachment studies and absolute cross section measurements for Fe⁻ and Ru⁻. In the case of Fe⁻, an important astrophysical abundant element, the inner-shell photodetachment cross section was obtained by measuring the Fe⁺ and Fe²⁺ ion production over the photon energy range of 48-72 eV. The absolute cross sections for the production of Fe⁺ and Fe²⁺ were
measured at four photon energies. Strong shape resonances due to the $3p \rightarrow 3d$ photoexcitation were measured above the $3p$ detachment threshold. The production of Ru$^+$, Ru$^{2+}$, and Ru$^{3+}$ from Ru$^-$ was measured over 30 – 90 eV photon energy range. The absolute photodetachment cross sections of Ru$^-$ ([Kr] 4$d^75s^2$) leading to Ru$^+$, Ru$^{2+}$, and Ru$^{3+}$ ion production were measured at three photon energies. Resonance effects were observed due to interference between transitions of the 4$p$-electrons to the quasi-bound 4$p^54d^85s^2$ states and the 4$d \rightarrow \varepsilon f$ continuum. The role of many-particle effects, intershell interaction, and polarization seems much more significant in Ru$^-$ than in Fe$^-$ photodetachment.
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CHAPTER 1

INTRODUCTION

Negative ions are a special class of atomic systems with properties very different from neutral atoms and positive ions. Negative ions were discovered by Thomson [1] at the beginning of the 20th century and they were neglected until 1939 when Wildt brought up the idea that the main source of opacity in the atmosphere of the Sun at red and IR wavelengths was the absorption by the negative H\textsuperscript{−} ion [2]. It was an amazing finding that a system as fragile as the H\textsuperscript{−} ion could determine such an important condition to life on Earth. Charged particles represent only a small fraction of the total mass of the Earth atmosphere, but they play a crucial role in many geo-physical phenomena such as the variations in the geomagnetic field, lightning and auroras. Communication by radio waves is strongly influenced by the O\textsuperscript{−} and O\textsubscript{2}\textsuperscript{−} negative ions in the Earth’s ionosphere. Being very easy to neutralize, the negative ion beams are exploited in the injection of tokomak plasmas and the accelerator industry. These few examples simply illustrated that the negative ions are not only a curiosity of academic interest, but they play an important role in various branches of physics, ranging from astrophysics, atmospheric and plasma physics to surface physics and accelerator physics [3].

The response of atomic systems to ionizing radiation, the fundamental process of photoionization, is a dominant process in the universe and involves neutral atoms, molecules, and clusters, as well as their ions (positive or negative). The photodetachment process where an electron is emitted by a negative ion upon
absorption of a photon is analogous to the photoionization process in a neutral atom or a positive ion. An atomic negative ion consists of an atom to which an extra electron has been bound. The stability of a negative ion depends on the extent to which the extra electron shares the attractive field of the nucleus with the other electrons. Correlation effects are generally more enhanced in negative ions than in atoms or positive ions [3, 4, 5]. This is a consequence of more efficient screening of the nucleus by the atomic electrons. The interplay of these attractive and repulsive interactions in a weakly bound system such as a negative ion is of fundamental interest and allows us to gain a better understanding of correlated systems such as certain nanostructures and superconducting materials [6].

Many investigations of valence-shell electrons of negative ions have been performed using laser spectroscopy and progress in negative ion physics has been reviewed frequently. In 1976, the book by Massey, “Negative Ions” [7], summarized nearly everything that was known at that time about atomic negative ions. In the 1980s, the atomic structure and spectra of negative ions were described by Bates [8]. Esaulov [9] focused on the collisional aspects, and Buckman and Clark reviewed the negative ion resonances [10]. The binding energies and fine-structure splitting of the ground state in negative ions were also critically reviewed [11]. During the 1990s the development of sophisticated laser techniques combined with very sensitive detection techniques provided new knowledge about the structure and dynamics of negative ions. An extensive and more general review of the properties of negative ions has been given by Andersen in 2004 [3].

Due to the low density of the negative ion beams (< 10^6 cm^-3) [12] and the limited photon flux available from available photon sources it is a challenging to obtain inner-shell information about the structural and dynamical properties of
negative ions. Investigations using lasers provided a lot of information on the structure of negative ions. However, intense laser light necessary for high precision anion spectroscopy is usually limited to photon energies below 15 eV [3] and is difficult to tune over a wide photon energy range. In contrast, synchrotron radiation from undulators is readily tuned over a wide energy range and provides much higher energies. Thus, inner-shell photodetachment of negative ions has become possible providing a unique opportunity for fundamental investigations which explore the dynamics of many-body effects. The first experiments were carried out on Li$^-$ ions by Berrah et al. [13] and Kjeldsen et al. [14] in 2001. The construction of the 3rd generation undulator-based light sources significantly enhanced the experimental possibilities and opened up a new research field. The merged-beam technique which is characterized by co-linearly overlapping beams of photons and ions has proved very successful for studying negative ions. Both charged products of the photodetachment process, the photo-electron and the photo-ion, can be in principle detected. This leads to two principal methods: the photoelectron spectroscopy where the outgoing electron is detected [15] and the photoion yield spectroscopy where the photoion is recorded [15].

The experiments presented in this thesis were performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, using the High Resolution Atomic Molecular and Optical Physics (HRAMO) undulator beamline 10.0.1. with the fixed ion-photon beamline (IPB). The IPB endstation [16] uses the merged-beam technique for photoion spectroscopy, where ions and photons travel collinearly in order to increase the interaction volume between photons and the dilute ion beam. The negative ion beam was produced using a cesium sputter source (SNICS II) [17]. The magnetically mass selected ions were deflected by an
electrostatic deflector and merged collinearly with the counter-propagating photon beam. Inner-shell photodetachment from negative ions followed by Auger decay produced positive ions that were steered out of the primary beam by a de-merger magnet and detected as a function of photon energy.

This thesis focuses on inner-shell photodetachment of transition metal negative ions, specifically Fe\(^-\) and Ru\(^-\). It is known that 90% of matter in the Universe is ionized and transition \(d\) metals are abundant [18], so the interaction of \(d\) metal atoms and ions with radiation is of great importance for astrophysics. Extensive theoretical work has been performed in order to calculate the photoionization cross sections for atoms and ions of astrophysical relevance (see the Opacity [19] or Ferrum [20] Projects). In addition, \(d\) metals and their compounds are of extreme practical importance in metallurgy, magnetism, and data storage systems [21]. The spectra of transition metals are very complex due to the coupling of \(d\) electrons with core holes and strong interaction with the underlying continua [6]. The \(d\) orbital retains, to a high degree, the same characteristics in solids [22], so the atomic and ionic data can be very useful for our understanding of intra- and inter-atomic effects in solids.

The fundamental physics of the interaction of transition metal atoms and ions with photons is interesting but difficult to analyze in detail. Because of angular momentum coupling there is a large number of possible terms resulting from the open \(d\) shell. Thus, for an accurate description of the photoionization process, strong correlations between these terms as well as relativistic effects have to be taken into account [6, 21, 22]. The main features in the spectra of the neutral transition metals are the “giant resonances” which appear in the vicinity of the \(p\) threshold [6]. Comparing the resonances in the transition metal negative ion photodetachment cross
section with the giant resonances in neutral atoms and positive ions could shed some insights into the nature of the resonances and also of the structure of ions.

Iron, lying at the maximum of the nuclear stability curve, is an important astrophysical abundant element [6]. Despite numerous research activities for neutral iron and its positive ions, there are only a few valence-shell photodetachment studies for the iron negative ion. The electron affinity of Fe\(^-\) (0.151(3) eV [23]) has been determined by laser photoelectron spectroscopy. Measurements of partial valence-shell photodetachment cross sections and photoelectron angular distributions of Fe\(^-\) at visible photon wavelengths have also been reported [24]. In this thesis, the inner-shell photodetachment cross section for Fe\(^-\) was obtained by measuring the Fe\(^+\) and Fe\(^{2+}\) ion production over the photon energy range of 48-72 eV. The absolute cross sections for the production of Fe\(^+\) and Fe\(^{2+}\) were measured at four photon energies. Strong shape resonances due to the 3\(p\)\(\rightarrow\)3\(d\) photoexcitation were observed above the 3\(p\) detachment threshold. In addition, simultaneous double-photo-detachment was also observed, resulting in an increased Fe\(^{2+}\) production which obeys a Wannier law.

The analysis of ruthenium negative ion is of wide application in the exploitation of marine resources, cosmochemistry and geology [25]. Since neutral ruthenium offers an efficient conversion of solar energy into chemical energy (by photoinduced electron transfer [26]) it is surprising that there exist only few experimental and theoretical data on ruthenium [27, 28, 25] and even less for ruthenium negative ion [29]. This thesis reports an investigation on inner-shell photodetachment of Ru\(^-\). The production of Ru\(^+\), Ru\(^{2+}\), and Ru\(^{3+}\) from Ru\(^-\) was detected over 30 eV – 90 eV photon energy range. The absolute cross sections for the production of Ru\(^+\), Ru\(^{2+}\), and Ru\(^{3+}\) were measured at three photon energies. In the near-threshold region, a Wigner s-wave law, including estimated PCI effects, locates
the $4p_{3/2}$ detachment threshold between 40.10 and 40.27 eV. Resonance effects are observed due to interference between transitions of the $4p$-electrons to the quasi-bound $4p^54d^85s^2$ states and the $4d\rightarrow\varepsilon f$ continuum.

This thesis consists of seven chapters. A general motivation and the present status of inner-shell photodetachment studies for negative ions are given in the first chapter. Chapter two presents a brief introduction to the quantum-mechanical description of atomic systems, with the emphasis on the dominant structures of negative ions. Chapter three provides the fundamental physics concepts: photodetachment, Auger process, post collision interaction, and threshold laws for negative ions. The experimental technique with all details pertaining to the apparatus and data analysis is described in chapter four. Resonance structures and threshold region in the inner-shell photodetachment of Fe$^-$ and Ru$^-$ are investigated in chapters five and six, respectively. Finally, chapter seven contains a summary of the results of this dissertation and provides a source for possible future research in this field.
CHAPTER 2

ATOMIC THEORY

An atomic negative ion is formed when an electron is attached to an atom. With the exception of nitrogen, the noble gases and the mercury group, essentially all elements form negative ions [3]. The major difference between neutral atoms or positive ions and the negative ions is the type of potential which binds the electrons to the system. While in neutral atoms and positive ions electrons are bound in the long-range Coulomb potential (∼1/r), in negative ions electrons are bound in the short-range induced-dipole potential (∼1/r^4) [3].

Neutral atoms have many bound discrete states and most of our knowledge about them is based on investigations of the energy positions of these discrete bound states, extracted from line spectra. Negative ions do not have discrete spectra, due to the lack of the bound states, but they have a continuum above the photodetachment threshold. This continuum contains resonance structure due to excited autodetaching states of the negative ion. The short lifetime of these autodetaching states leads to rather broad resonances, limiting the precision with which the resonance energies can be determined.

In atoms and positive ions the Coulomb potential is strong and can sustain Rydberg series, an infinite number of bound states converging to the ionization limit. In contrast, the short-range potential in a negative ion is weak and does not support a Rydberg series. The binding energy is mainly determined by the strength of the potential. The highest binding energy of the valence electrons in the atoms is about
10 eV which stems for the strength of the Coulomb interaction, compared to 3.5 eV in the case of negative ions [3]. The low value for the binding energy in the negative ions (or electron affinity for the corresponding parent atom) implies that the binding potential for the extra electron is relatively weak, but still allows for a quantum-mechanical description similar to neutral atoms.

In non-relativistic quantum mechanics, a particle is described by a wave function, \( \Psi(r,t) \). If the particle is moving in a potential \( V(r, t) \), the wave function satisfies the non-relativistic time-dependent Schrödinger equation [30]:

\[
\frac{i \hbar}{\partial t} \Psi(r,t) = \{-\frac{\hbar^2}{2m} \nabla^2 + V(r,t)\} \Psi(r,t).
\]

(1.1)

Since the momentum operator is defined by \( p = -i \hbar \nabla \), the term in the brackets is just an expression of the total energy of the atomic system and is called the Hamiltonian:

\[
H = T + V = -\frac{\hbar^2}{2m} \nabla^2 + V
\]

(1.2)

For a static potential, \( V(r, t) = V(r) \), and equation (1.1) admits stationary static solutions

\[
\Psi(r,t) = \Psi_E(r) e^{iEt/\hbar},
\]

(1.3)

where \( \Psi_E(r) \) is a solution for the time independent Schrödinger equation.

\[
H\Psi_E(r) = E\Psi_E(r).
\]

(1.4)

Here \( E \) is an eigenvalue and \( \Psi(r) \) an eigenfunction of the Hamiltonian \( H \).

In a hydrogenic system, the single electron feels a Coulomb attraction \( V(r) = -Ze/r \) from the nucleus of charge \( +Ze \). The equation (1.4) can be solved analytically and the eigenvalues are given by the expression:

\[
E_n(eV) = -R_y Z^2/n^2,
\]

(1.5)

where \( R_y \) is the Rydberg energy and \( n \) is the main quantum number (see Fig.2.1). The Rydberg energy, \( R_y = 1/2 (m_e c^2) \alpha^2 \), where \( m_e c^2 \) is the rest mass energy of the electron (511 keV), \( \alpha \approx 1/137 \) is the fine structure constant, \( m_e \) is the mass of the electron, and
c is the speed of light.

**Figure 2.1.** Bohr’s description of the atom. The electrons can exist in special orbits and jump between orbits by absorbing or emitting photons of energy $h\nu_{a\rightarrow b}=E_b-E_a$.

In the case of a many-electron atom an electron will also feel the presence of the other electrons and the full Hamiltonian now is

$$H = \sum (-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i}) - \sum \frac{e^2}{r_{ij}} \quad i,j = 1,...,N,$$

where $N$ is the number of electrons and $r_{ij} = |r_i - r_j|$ is the distance between the $i^{th}$ and $j^{th}$ electron ($j<i$). Since the changes for one electron will affect the others, through electrostatic interaction, an analytical solution to equation (1.4) can no longer be found (multi-body problem), and different approximate methods must be used.

### 2.1. The independent particle model

In the independent particle model, each electron is approximated to move independently in an effective centrally symmetric potential which represents the attraction of the nucleus and the average effect of the repulsion between the other $(N-1)$ electrons [30]. The effective potential is given by

$$V_{\text{eff}}(r) = -\frac{Ze^2}{r} + S(r)$$

(1.7)
where \( S(r) \) is a model potential representing the screening of the nucleus by the other electrons.

The Hamiltonian (1.6) can be rewritten as

\[
H = \sum \left( -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{eff}}(r_i) \right) + \sum \frac{e^2}{r_{ij}} - \sum (Ze^2/r_i + V_{\text{eff}}(r_i))
\]

(1.8)

where \( H_c \) is the unperturbed part, \( H_{\text{per}} \) is the perturbed part of the Hamiltonian, now much smaller than the mutual repulsion between electrons and can be neglected.

Writing the Schrödinger equation for \( H_c \), this separates into \( N \) one-electron Schrödinger equations:

\[
h_i \Phi_i = E \Phi_i, \quad h_i = \left( -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{eff}}(r_i) \right)
\]

\( i = 1, \ldots, N \) (1.9)

Solutions to this equation can be found and the resulting single-electron wave functions, so-called orbitals, \( \Phi_i \), are described by quantum numbers \( (n, l, m_l) \).

Since the electrons have an intrinsic magnetic moment, the spin \( S \) must also be included in the wave function. The full wave function \( \Psi \) can be expressed as a so-called Slater determinant, which is an antisymmetric product of \( N \) spin-orbitals automatically fulfilling the Pauli Exclusion Principle. A multi-configuration wave function is a superposition of several Slater determinants, \( \Psi = \sum c_i \Psi_i \). Since the electrons are indistinguishable, in accordance with the Pauli principle, only the antisymmetric representations, written for example as Slater determinants, occur for the electrons [30].

The single-electron spin-orbitals are described by the set of quantum numbers \( (n, l, m_l, s, m_s) \) which can take the values:

\[
n = 1, 2, \ldots
\]

\[
l = 0, 1, \ldots, n-1
\]
Pauli Exclusion Principle states that the two electrons in an atom cannot have the same set of quantum numbers. The energy of each electron will be independent of the magnetic quantum numbers $m_l$ and $m_s$ due to the spherical symmetry of the potential, but will not be degenerate in $l$ except for hydrogenic atoms. This is because the screening of the nucleus due to the other electrons will be more pronounced for electrons with large angular momentum, as these are forced out by the centrifugal barrier.

The total energy of an atom will be the sum of energies $E_{m_l,m_s}$ of each electron and therefore will be completely determined by the configuration, the distribution of electrons with respect to $n$ and $l$. This arranges the electrons in shells (electrons with the same $n$) and subshells (electrons with the same $n$ and $l$). Each subshell can hold $2(2l+1)$ electrons with different $m_l$, $m_s$. Using the typical notation where $l = 0, 1, 2, 3, \ldots$ corresponds to the letters $s, p, d, f, \ldots$ the configuration for a carbon atom ($Z = 6$) for example is $1s^22s^22p^2$, where the superscripts denote the number of electrons in the same subshell, i.e. equivalent electrons. In the central field approximation, the configuration of the system will give the total energy of the system.

A more precise description must include the spin-orbit interaction, a small correction for light atoms. This is a relativistic effect arising from the interaction of the spin of the electron with the magnetic field induced by the electron orbiting around the nucleus, and is described by the Hamiltonian:

$$H_{SO} = \sum (1/2m_i^2c^2) \frac{\partial}{\partial r_i}(V(r_i)) \mathbf{L}_i\mathbf{S}_i.$$ (1.10)
Now the total Hamiltonian can be written as:

$$H = H_c + H_{\text{per}} + H_{\text{SO}}$$  \hspace{1cm} (1.11)

where $H_{\text{SO}}$ corresponds to the spin-orbit term. Two limiting cases appear: first, when the contribution for the relativistic interactions is small compared with the correlation term ($H_c \gg H_{\text{per}} \gg H_{\text{SO}}$) corresponds to LS-coupling; second, when the relativistic interactions exceed the correlation term in magnitude ($H_c \ll H_{\text{per}} \ll H_{\text{SO}}$) corresponds to jj-coupling. For low nuclear charge the $H_{\text{per}}$ dominates over $H_{\text{SO}}$ while for high nuclear charge $H_{\text{SO}}$ dominates over $H_{\text{per}}$.

For LS-coupling, the Hamiltonian commutes with the angular momentum $L = \sum L_i$ and the spin $S = \sum S_i$ and each configuration is split into different energy levels determined by the eigenvalues for $L^2$ and $S^2$, symbolized as $2S+1L$ term. This is called the term splitting. Inclusion of the spin-orbit operator will lead to further splitting of these terms into fine-structure components, which are eigenstates of the total angular momentum operator $J = L + S$, and each eigenstate will be characterized by the symbol $2S+1L_J$. The energy splitting due to inclusions of the perturbations is presented for the carbon atom (see Fig. 2.2).

For heavy atoms, the relativistic interactions may exceed the correlation term in magnitude. In this case, it is inaccurate to assign a particular term, since the magnitude of $L$ and $S$ are not conserved separately and a jj-coupling scheme must be applied. In jj-coupling, a configuration is first split by the spin-orbit interactions into terms with every possible combination of the $j$ values and then by the non-spherical part of the Coulomb interaction into levels. For intermediate nuclear charge values other coupling schemes can be applied [31].
2.2. Continuum states

The Schrödinger equation leads to a set of discrete bound energy levels. If additional energy is supplied, the electron will be completely detached. The wave function of an unbound electron has no boundary conditions; the electron is no longer restrained to assume a particular amount of energy, so it can take any energy above the detachment threshold. The set of unbound states above the electron detachment limit is therefore said to form a continuum of states. For a large extra energy supplied, the residual atom can be excited and an electron is detached simultaneously. A second continuum is then available, see Fig. 2.3.
The autodetaching states are situated above the detachment threshold of the ground state of the parent atom, so it is energetically possible for the system to break apart by ejection of an electron. Autodetaching states influence the photodetachment spectrum of negative ions in the continuous region. When a photon is absorbed by a negative ion it may lead to direct emission of an electron, or excitation of an autodetaching state. The states may decay through various decay mechanisms.

Autodetachment can be described as a transition from a discrete state to an adjacent continuum [33]. The process is induced by the Breit-Pauli Hamiltonian [34, 35]:

\[
H_{PB} = H_{NR} + H_{RS} + H_{J}
\]  

(1.12)
Here $H_{NR}$ and $H_{RS}$ are the $J$ independent non-relativistic and relativistic shift operators and $H_J$ consists of $J$ dependent spin-orbit, spin-spin, and spin-other-orbit operators [30]. In the first approximation, the autodetaching state can be expressed as a sum of a discrete wave function $\Psi_0$ and a continuum wave function $\Psi_{\text{cont}}$ representing the open channel

$$\Psi(E_0) = a\Psi_0 + b\Psi_{\text{cont}}$$

where the $E_0$ is the energy of the state $\Psi_0$, and $|a|^2 + |b|^2 = 1$.

The autodetachment rate is given by Fermi’s Golden Rule [36]

$$R_{\text{autodetachment}} = \left| \langle \Psi_{\text{cont}} | H_{\text{PB}} - E_0 | \Psi_0 \rangle \right|^2$$

The decay of an autodetaching state can be induced by Coulomb repulsion or the relativistic terms in the Hamiltonian. The Coulomb interaction conserves parity $\pi$, the orbital angular momentum $L$, the spin $S$, and the total angular momentum $J$, and consequently the selection rules are: $\Delta \pi = \Delta L = \Delta S = \Delta J = 0$ [36]. Autodetachment induced by the relativistic terms in the Hamiltonian is on the order of a factor of $\alpha^4$ ($\alpha$ is the fine structure constant) slower than Coulomb autodetachment, but the selection rules are less restrictive [36]. If an excited state can decay via Coulomb autodetachment this mechanism will completely dominate, having a much higher decay rate than the relativistically induced decays.

In negative ions, most of the bound excited states are fine structure levels [23]. Only in rare cases (for example, in Pt$^-$ and Ir$^-$ [23]) the excited states are bound, so practically all excited states of negative ions lie above the detachment limit and consequently are autodetaching states. Thus, autodetachment is an important mechanism for the decay of excited states of negative ions.
2.3. Correlation

For atomic systems with more than one electron, the mutual repulsion among the electrons induces correlated motion. Following Amusia [37], the interaction energy $E_{\text{int}}$ is

$$E_{\text{int}} \sim \frac{N_{\text{sh}}}{r_{\text{mean}}}$$  \hspace{1cm} (1.15)

where $N_{\text{sh}}$ is the number of electrons in a shell and $r_{\text{mean}}$ is its mean radius.

The mean kinetic energy for an electron is:

$$E_{\text{kin}} = \frac{p^2}{2m}$$  \hspace{1cm} (1.16)

where $p$ is the momentum and $m$ the mass of the electron.

If the ratio $\eta = \frac{E_{\text{int}}}{E_{\text{kin}}} = \left(\frac{N_{\text{sh}}}{r_{\text{mean}}}/a_0\right)^{1/3}$ is much less than one, the self consistent field dominates [37]. For outer shell electrons in negative ions the mean radius can be much larger than the Bohr radius $a_0$ and the correlation effects dominate.

The correlation energy is defined as

$$E_c = E_{\text{exp}} - E_{\text{HF}} - E_{\text{rel}}$$  \hspace{1cm} (1.17)

where $E_{\text{exp}}$ is the experimental energy value, $E_{\text{HF}}$ is the Hartree-Fock energy, $E_{\text{rel}}$ is the relativistic contribution. The correlation energy increases roughly linearly with the nuclear charge $Z$ and is nearly constant among isoelectronic positive ions, atoms and negative ions [38].

In atoms and positive ions the ground state binding energy is described by the independent particle model and the remaining discrepancy to the correct experimental value is due to the electron correlation (Eq. (1.17)). In contrast, for negative ions, sometimes, not even the stability of the ground state can be predicted by the independent particle model [39]. The electron correlation effects in negative ions are no longer small corrections, but a significant contribution to the binding energy.
Roughly speaking, what is a first order correction for an atom is zero\textsuperscript{th} order for a negative ion. So, negative ions act somehow as a magnifying glass for correlation effects.

2.4. Theoretical approach

A major effort in theoretical atomic physics has been devoted to find different ways of accounting for the deviation of experimental results from the prediction of the independent-particle model. The independent-particle model, as described by the Hartree-Fock method, predicts the energies of excited states in atoms to within a few percent of the exact value. The discrepancy is the correlation energy. The results of such calculations depend significantly on the accuracy of the initial description of the wave function.

The mutual repulsion between valence electrons is more dominating in negative ions than in atoms, so the perturbing part of the total Hamiltonian is enhanced in negative ions. As a consequence, the approximate initial wave functions describe the system in a less accurate way and discrepancy between the calculated and measured energy becomes much larger.

The theoretical models to describe negative ions mainly differ in the way in which the electron-electron interaction is included [15]. Many-electron collective effects such as dynamic polarization effects, intrachannel and interchannel interactions, core-relaxation processes during photoabsorption and electron escape, many-electron excitations (shake-up and shake-off processes) in negative ions are more enhanced than in neutral atoms. Therefore, all the problems related with negative ions turn out to be essentially many-body problems but still the methods developed for neutral atoms may be used [4]. At present, the models successfully
applied to describe photodetachment process of negative ions are: the Configuration Interaction method [41], the multiconfigurational Hartree-Fock (MCHF) [42, 43], R-matrix method [44-48], the Random Phase Approximation with Exchange (RPAE) [41,49-51], and Many-Body Perturbation Theory (MBPT) [37].

In the Configuration Interaction (CI) approach the correlated initial and final state wave functions $\Psi_i$ and $\Psi_f$ are expanded into a complete set of un-correlated basis functions with the same symmetry properties. For example, the ground state of Li is

$$\Psi_{corr} = a_1\Psi(1s^2\,^1S_0) + a_2\Psi(1s2s\,^1S_0) + a_3\Psi(2s^2\,^1S_0) + a_4\Psi(2p^2\,^1S_0) + \ldots \quad (1.18)$$

where the absolute square of the mixing coefficients, $a_n$, represent the weights of the corresponding state. Such an expansion requires an infinite number of basis functions which is not possible for practical purposes. The quality of CI calculations therefore depends on the number and type (usually Hartree-Fock one-electron wave functions) of basis function used [41]. The basis function is kept fixed in the calculation.

In the multiconfigurational Hartree-Fock (MCHF) approach the radial functions of the single electron orbitals are optimized variationally in addition to the coefficients entering the configuration expansion of the total wave function [30]. The MCHF method is very useful for calculating the electronic structure and the energy spectrum. A very important aspect in this method is to choose those configurations that give the main contribution to the total wave function. The MCHF method has been applied to study photodetachment of He$^-$ [42] and Ca$^-$ [43].

The R-matrix method proved to be very valuable in calculating a large number of photoionization cross sections for positive ions within the Opacity project [19]. The R-matrix theory separates configuration space into two regions, an inner region, where the wavefunction of an atom is expanded in a limited set of
eigenfunctions of a modified Schrödinger equation, and an outer region, where only one electron is allowed to move, and thus only single detachment processes are considered. The R-matrix method is very effective in describing the total and partial cross sections and the doubly excited resonances associated with higher thresholds [4]. With several modifications, the R-matrix method was successfully used to describe the photodetachment of He⁻[44], Li⁻[45], B⁻[46], C⁻[47], and Ca⁻[48].

Both Many-Body Perturbation Theory (MBPT) and the Random Phase Approximation with Exchange (RPAE) describe the dynamical collective response of an atomic system to a weak external field. MBPT is able to take into account two and three-electron excitations in the intermediate states simultaneously and provide a simpler extension to open-shell systems [37]. On the other hand, the RPAE [41, 49-51] method describes better the intra- and interchannel interactions [52]. As a part of interelectron interaction, the interchannel interaction leads to autoionization, decay of vacancies, and creation of satellites [40]. When an electron is photoexcited, it collides or interacts with an electron from another subshell. The interaction causes the second electron to be ionized, and the first electron falls back into its original location. The states formed due to the interchannel interaction are more complex than a simple one-electron excitation and lead to strong modifications of the partial photoionization cross section. The intrachannel interaction has the same form except that the photoexcited electron collides or interacts with an electron in the same subshell. The second electron absorbs all the energy and the first electron is de-excited back to its original location. Due to the intrachannel interaction, the cross section maxima are broader and pushed to higher photon energies.

Doubly excited states, where two electrons are simultaneously excited, can also be modeled using the independent-particle approach. The non-radial interaction
between two electrons becomes very important with an increased distance from the nucleus [53], thus the difference between calculated and measured values can be large for doubly excited states. A linear combination of different configurations allows the determination of the energies of low lying doubly excited states, but the physical interpretation is unclear since the assignment of individual quantum numbers to the electron is no longer possible. The method becomes inapplicable in the case of high lying doubly excited states and a new set of quantum numbers is needed in order to describe more accurately the double excitation in atomic systems. Several approaches have been used to formulate theories that describe double excitation in atoms in a more accurate way than the independent-particle model [54, 55]. One of them, based on hyperspherical coordinates [56, 57] provides a good conceptual picture of double electron excitation to interpret the experimental data for H\(^-\) [58, 59] and He\(^-\) [60, 61, 62, 63].

Many-body effects play an important role in inner-shell photodetachment of negative ions. To understand the inner-shell photodetachment process better and to test the present theoretical methods, it is necessary to compare the results of the calculations with the experimentally measured values. Therefore, one can only hope to get quantitative agreement by using models that include all possible correlations. The use of synchrotron radiation for inner-shell photodetachment studies is still a very young field, and there is no doubt that future experiments will bring valuable insight into the structural and dynamical properties of negative ions, testing also the theoretical methods. In particular, inner-shell photoelectron spectroscopy will allow for differential measurements of partial cross sections and electron angular distributions.
CHAPTER 3

PHYSICAL BACKGROUND

An atomic negative ion consists of an atom to which an extra electron has been bound. The photodetachment process in a negative ion is analogous to the photoionization process in a neutral atom or a positive ion. The photodetachment process where an electron is emitted by a negative ion upon absorption of a photon gives important information about the structure of negative ions. While the photoionization of neutral atoms and positive ions is governed by the long-range Coulomb interaction ($\sim 1/r$), the photodetachment of negative ions is governed by the short-range induced-dipole potential ($\sim 1/r^4$) [3]. Thus negative ions differ fundamentally from neutral atoms or positive ions.

3.1. The attachment of the extra electron

Like any physical system, atoms minimize their energy as much as possible and, as a consequence, most atoms are normally in their ground state. The size of the atomic nucleus is typically five orders of magnitude smaller than the electronic cloud. Therefore a good approximation states that the nucleus is a point-like charge with no geometrical extension. An atomic negative ion is formed when an extra electron is attached to a neutral atom. It may be surprising that an atom with a total charge of zero can attract an additional electron by electric forces, but still the negative ions are stable atomic systems [3].
To first order, the extra electron feels no Coulomb attraction to the neutral atom since the positive charge in the nucleus is totally screened by the core electrons. As an electron approaches a neutral atom, the field from the electron will perturb the electron cloud of the atom by pushing the electrons away from the incoming extra electron, see Fig. 3.1. The extra electron can share the attractive force from the nucleus with the other electrons by rearrangement of their positions. Since the center of the electron cloud is displaced to the far side of the nucleus, the resulting induced electric dipole will be attractive.

![Figure 3.1. Schematic of the attachment of an extra electron.](image)

Classically, the potential produced by a dipole at large distances $r$ from its center is given by $\Phi \sim \frac{P \cdot r}{2r^3}$, where $P$ is the dipole moment [64]. The induced dipole moment depends on the perturbing electric field $E$, and obeys $P \sim \alpha E$ for a uniform electric field. The dipole polarizability $\alpha$ is a measure of the ability of the system to polarize. When the distance to the approaching electron is much larger than the dimension of the atom, the electric field of the electron varies little over the atom and can therefore be regarded as constant. At the nucleus, the field created by the approaching electron is then given by $|E| \sim \frac{r}{r^3}$. Thus the outermost electron in a
negative ion, when it is far from the nucleus, experiences the attractive asymptotic potential given by:

\[ \Phi \sim \frac{\alpha}{r^4} \]  

(1.19)

One of the main features of this short-range potential is the lack of an infinite series of Rydberg states for the negative ions contrasting with the long-range Coulomb potential in a neutral atom that is capable of supporting an infinite spectrum of bound states that converge to the ionization limit, as illustrated in Fig. 3.2. The weakness of the short-range potential is also reflected in the binding energies of negative ions, or electron affinities (EA) of the parent atoms, which are usually an order of magnitude smaller than the ionization energies of neutral atoms [3]. For example, the electron affinity of H is only 0.75 eV while its ionization energy is 13.6 eV.

\[ \text{Energy} \]

\[ \begin{array}{c}
\text{Negative Ion} \\
\text{Neutral Atom}
\end{array} \]

**Figure 3.2.** Energy level diagram of the negative ion and correspondent neutral atom.

When the approaching electron penetrates the electron cloud surrounding the nucleus, the response of the atom can no longer be described as a classical dipole. Hence, a description of the system at small distances requires a quantum-mechanical
treatment which takes into account the reduced screening of the nucleus and the correlated motion of the electrons. The reduced screening results in an increased attraction of the electron situated at the smaller distance to the nucleus. Correlation between the motion of the electrons, resulting from their mutual electrostatic repulsion, increases the mean distance between the electrons and can lead also to a reduction of the total energy. The size of the energy reduction due to the reduced screening and the electrons correlated motion strongly depends on the shell structure of the atom. Typically, atoms with closed shells are less likely to form negative ions since the extra electron has to be attached to an unfilled shell with a larger mean radius. Furthermore, this newcomer electron will feel a more effective screening of the core by the other electrons, which are reluctant to rearrange themselves. As a consequence, the noble gas atoms having close shell structure are believed not to be able to form stable negative ions. This is in contrast to the halogen elements whose atoms have a single vacancy in the outermost shell. As a result, the halogens form stable negative ions having the highest binding energies of all negative ions [23].

Since the description of a negative ion as a single electron moving in the potential of a classical dipole is inadequate, the calculations of binding energies, fine structures or excitation energies of negative ions must be based on a full quantum–mechanical description. For example, the alkali earth metals negative ions are bound with only tens of meV, which is $10^{-7}$ of the total electronic energy, so very high precision has to be attained in the calculation of the total energy in order to obtain a good value for the electron affinity [3]. Note that the motion of the electron far away
from the nucleus is quite well described by $\Phi \sim a/r^4$ potential. However the quantum-mechanical nature of the system is hidden in the size of the dipole polarizability.

### 3.2. Photodetachment process

The stability of a negative ion depends on the extent to which the extra electron shares the attractive field of the nucleus with the other electrons. Essentially all information on the structure and dynamics of negative ions is coming from experiments designed to ionize the system in a controlled manner [6]. Negative ions are ionized in the photodetachment process when one or more electrons are ejected following the absorption of a photon.

The simplest photodetachment process involves the detachment of a single electron following the absorption of a single photon.

$$A^- + \text{photon} \rightarrow A^0 + \text{electron}$$

When the free negative ion in state $i$ interacts with a photon having energy $h\nu$, an electron with kinetic energy $E_{\text{kin}}$ is emitted as shown in Fig. 3.3

$$E_{\text{kin}} = h\nu - E_{\text{bin}}$$

The neutral atom in the state $j$, together with the outgoing electron, form the final state $f$. $E_{\text{bin}}$ is the energy difference between the negative ion ground state $i$ and the final neutral state $j$, and this is the binding energy of the electron in the negative ion (or the electron affinity EA of the parent neutral atom).

Since we know the energy of the photon absorbed in the photodetachment process, by measuring the kinetic energy of the electron we can calculate the binding energy of the electron in the negative ion. When the detached electron is detected, the technique is called photoelectron spectroscopy.
Most experimental determinations of negative ion binding energies are based on laser threshold photodetachment spectroscopy. The outer-shell electrons are far away from the nucleus, and the nucleus is strongly screened by the other electrons, so the binding energy for an outer-shell electron is very small. The energy from a laser is enough to detach the outer-shell electron. Progress on the knowledge of binding energies in negative ions is still a growing field as evidenced by the review reports [11] following the 1985 review article by Hotop and Linenberger [23]. However, the stable negative ion states of many elements still are poorly known.

Over the last ten years, intense sources of VUV and soft X-ray photons have become available at the 3rd generation synchrotron-radiation facilities. These synchrotrons contain magnetic insertion devices (undulators) which produce an exceptionally bright photon beam. The available flux is high enough to measure high statistics photo-ion yields that result from overlapping such a photon beam with the target-ion beam (the merged-beam technique). The yield can be translated into an absolute cross section, because the target-ion density can be measured directly. Consequently, the measurement of absolute cross sections has been a fairly intense activity in recent years, with a number of different groups working at
In case of photon-ion merged-beam experimental set-up, the total cross section $\sigma$ may be calculated using the expression

$$\sigma = \frac{q \cdot v \cdot R}{I \cdot \Phi} \cdot F$$

(1.20)

where $I$ is the measured target-ion current, $v$ is the negative ion velocity, $q$ is the negative ion charge, $R$ is the measured signal rate, $\Phi$ is the photon flux, and $F$ is the form factor, which is a measure of the quality of the overlap of the ion beam with the photon beam.

Absolute photodetachment cross sections are important as applied data in astrophysics and plasma physics. Extensive theoretical work has been performed in order to calculate the photoionization cross section for atoms and ions of astrophysical relevance (see Opacity Project [19] or Ferrum [20]). Experimental cross section data allow benchmarking of the calculation in many cases and thereby stimulate further development of theoretical models. The enhanced correlation effects in negative ions make them particularly suitable as objects for testing the theoretical methods.

### 3.2.1. Photodetachment cross section

Photodetachment is the process whereby a negative ion interacts with electromagnetic radiation resulting in the formation of a free electron and an atom. When the photon energy is larger than the binding energy of the atomic system, the final state is an unbound continuum state.

Branscomb et al. studied for the first time the photodetachment process [65, 66, 67]. The cross section ($\sigma$) expresses the strength of a photoabsorption process into a continuum. The cross section can be imagined as the area around a negative ion
through which a photon must pass in order to induce the photodetachment process. The cross section can be calculated as the ratio of the transition probability \( P(\omega) \) and the photon flux \( I \), \( \sigma(\omega) = \frac{P(\omega)}{I} \), and is a quantity which depends only on properties of the atomic system itself [33].

Photodetachment cross sections for negative ions are typically of the order of 1 – 100 M barn [67, 3] (1 barn = \( 10^{-24} \) cm\(^2\)). Often the cross section for photodetachment is much smaller than the geometrical size of a negative ion, so only a small fraction of the photons passing through the geometrical boundaries of an ion actually induces the photodetachment process.

The photodetachment cross section depends on the photon energy. Typically the total cross section for negative ions is zero at energies below threshold, it then increases above threshold, reaches a maximum and then falls again at larger photon energies as shown in Fig. 3.4.

![Figure 3.4](image.png)

**Figure 3.4.** Typical photodetachment cross section for negative ions.

For large photon energy it is possible to both detach one electron and simultaneously excite the residual atom. In this case several decay channels are
available and each of them is characterized by the excited state of the residual atom, as illustrated in Fig. 3.5.

Figure 3.5. Schematic picture of energy levels in a negative ion and the corresponding atom.

Each separate channel has a specific partial cross section dependence associated with it and the shape of the partial cross section varies from channel to channel. For each partial cross section a specific state of the residual atom, a certain orbital angular momentum of the outgoing electron and the coupling of these two angular momenta have to be specified. The partial cross section for photodetachment ($d\sigma$) can be described according to Fermi’s Golden Rule [30]

$$d\sigma = 4\pi^2 \alpha a_0^2 \hbar^2 |M_{if}|^2 d\Omega$$

(1.21)

where $\alpha \approx 1/137$ is the fine structure constant, $a_0 = 5.29 \times 10^{-9}$ cm is the Bohr radius,
\( \nu \) is the photon energy in Rydbergs (1 Ry = 13.6 eV), and |\( M_{if} \)| is the transition matrix element. In the dipole approximation, the transition matrix element is given by the expression

\[
|M_{if}|^2 = |\langle f | \Sigma D_{\mu} | i \rangle|^2. \tag{1.22}
\]

Here \( \Sigma D_{\mu} \) is the dipole operator of an N-electron system.

The total cross section for photodetachment is defined as the sum of all partial cross sections, \( \sigma = \int d\sigma \) [30], and exhibits the same general behavior for all negative ions. In the total cross section, no further distinction can be made regarding the final residual atom state. At large photon energies, the cross section is small due to the small overlap between the rapidly oscillating wave function of the detached electron and the more localized initial wave function leading to a small dipole matrix element in equation (1.28). At the lowest threshold, the shape of the cross section depends on the density of the final states and on the centrifugal barrier that the outgoing electron has to overcome. The overall behavior of the cross section can become modified in the vicinity of excited state thresholds where resonance structure may arise.

### 3.2.2. Resonance structure

Apart from the overall smooth variations of the photodetachment cross sections, in some cases sharper structures may occur. Some of them are resonances due to the autodetaching states of the negative ion, others are Wigner cusps located at the threshold of s-wave detachment channels. Among the resonances, it is possible to distinguish Feshbach resonances, due to negative ion states below the atomic parent state, and shape resonance, due to the negative ion states bound by the centrifugal barrier above the atomic parent state [68, 9]. The characteristics of these resonances are summarized in Table 3.1. In the simplest analysis the resonance structures are
assumed to be isolated, i.e. well separated in energy from threshold region and other resonance states.

Table 3.1. Characteristics for Shape and Feshbach resonance.

<table>
<thead>
<tr>
<th>Resonance Initial Condition</th>
<th>Shape</th>
<th>Feshbach</th>
</tr>
</thead>
<tbody>
<tr>
<td>The centrifugal force experienced by the detached electron creates a barrier in the negative ion potential.</td>
<td>An excited state which is bound with respect to an excited state of the parent ion.</td>
<td></td>
</tr>
<tr>
<td>Decay Mechanism</td>
<td>Tunneling</td>
<td>Simultaneous de-excitation of one electron and ejection of another electron.</td>
</tr>
<tr>
<td>Lifetime</td>
<td>$10^{-13} – 10^{-14}$ s</td>
<td>$10^{-11} – 10^{-12}$ s</td>
</tr>
<tr>
<td>Appearance in the cross-section</td>
<td>Broad structure</td>
<td>Narrow structure</td>
</tr>
</tbody>
</table>

When a photon is absorbed by a negative ion it may either lead to the direct emission of an electron or, at certain energies, to the excitation of an autodetaching excited state of the negative ions. The autodetaching states are situated above the detachment threshold of the ground state of the parent atom, so it is energetically possible for the system to break apart by ejection of an electron. The lifetimes of these states, as a result of the different decay mechanisms, varies by many orders of magnitude, between $10^{-13}$ s and $10^{-4}$ s [10]. Except for the rare cases of very long-lived states, the excitation of an autodetaching state is observed in an indirect manner. Experimentally, for example, this may be an induced resonance structure in the photodetachment cross section. In this case, the autodetaching state only acts as an unobserved intermediate state connecting the initial state (negative ion) and the final state (neutral atom and a free electron).

There are now two different routes from the initial bound state to the final
continuum state, either by direct emission of an electron (direct channel) or the resonant process which proceeds via autodetaching state (indirect channel), as shown in the Fig. 3.6.

**Figure 3.6.** The photodetachment channels of a negative ion. The black/solid line represents the direct channel. The dashed/green line represents the indirect channel.

The non-radiative process of electron emission (~ $10^{-14}$ s) is a much faster process than the radiative decay (~ $10^{-8}$ s). As a consequence, the formation and the decay of the excited state can therefore no longer be treated separately. Resonance structure in the photodetachment process is mathematically best described using scattering theory [69], which is more suitable for describing autodetachment since it deals directly with scattering amplitudes and transition probabilities rather than with excitation and subsequent decay of an excited state.

Figure 3.7 illustrates the interaction of a photon ‘projectile’ and a negative ion from which an electron is detached in the photodetachment process. The negative ion scatters the incoming electromagnetic plane wave and gives rise to a radial outgoing
wave and an attenuated plane wave. The radial outgoing wave is related to the probability distribution of the detached electron for a negative ion. Therefore, the photodetachment cross section can be calculated using the scattering theory, and more than that the cross section in the vicinity of autodetaching state can be obtained.

Figure 3.7. Elastic scattering before (a) and after (b) the scattering event.

The classical description of a shape resonance in scattering theory depicts the projectile tunneling through a potential barrier, remaining confined within the barrier for the lifetime of the resonance, and tunneling out again [10]. The mechanism for a Feshbach resonance involves the capture of the projectile via deposition of its energy into some internal degree of freedom of the target, and its release when it reacquires enough energy to escape [10]. Using scattering theory [69] the cross section for photodetachment can be written as

\[
\sigma = \sigma_0 + \frac{B(\Gamma/2) + A(\Delta E)^2}{(\Delta E)^2 + (\Gamma/2)^2}
\]

where \(\Delta E\) is the energy detuning from the resonance, and \(\Gamma\) is the width of the resonance; \(\sigma_0\) is the non-resonant background; and \(A\) and \(B\) are parameters related to the
amplitude and asymmetry of the resonance.

The general expression for the photodetachment cross section in the vicinity of the autodetaching state embedded in one continuum has been also derived by Fano [59] giving the more frequently used parametric form

\[ \sigma = \sigma_b(E) + \sigma_a(\varepsilon + q)^2/(\varepsilon^2 + 1) \]  

Here, \( \sigma_b(E) \) is the background due to the non-resonant (direct) process; \( \sigma_a \) is the resonant part of the total cross section; \( q \) is the Fano asymmetry parameter, \( \Gamma \) is the width of the resonance and \( \varepsilon \) is the reduced energy

\[ \varepsilon = (E - E_0)/(\Gamma/2) \]  

where \( E \) is the photon energy and \( E_0 \) is the resonance position.

The asymmetry parameter \( q \) carries detailed information about the relative strength of the direct and indirect channels for photodetachment. The \( q \) parameter influences the shape of the resonance; if \( q=0 \), the strength of the two routes is approximately the same, whereas for large \( q \), one dominates over the other and the shape of the Fano profile becomes nearly Lorentzian, as shown in Fig. 3.8.

![Figure 3.8. Schematic of symmetric Fano profiles.](image)
The autodetaching states in negative ions are generally bound with respect to the atomic parent states in the same way as negative ion ground states are bound with respect to the atomic ground states. A Feshbach resonance is due to an isolated state of a negative ion embedded in one continuum as shown in Fig. 3.9. The isolated state $\varepsilon$ in the channel 2 would be stable without the continuum channel 1 to which it can decay by autodetachment. More complicated systems with more than one level embedded in one continuum lead to a much richer and complex continuum structure.

**Figure 3.9.** Two channel level scheme.

Feshbach resonances correspond to states which are bound with respect to an excited state of the parent ion, but decay to a lower lying state of the atom by simultaneous de-excitation of one electron and ejection of another. The lifetime of the states is generally relatively long ($10^{-11} - 10^{-12}$ s) [3]. As a consequence, the Feshbach resonances are narrow structures in the photodetachment cross section [10, 68, 9].
Feshbach resonances give rise to characteristic asymmetric structures in the photodetachment cross section known as Fano profiles described by the equation (1.24) and shown in Fig. 3.8.

A shape resonance can occur in attractive potentials with a centrifugal barrier. The attractive polarization potential, see equation (1.27), with a repulsive centrifugal term has a maximum \( V_{\text{max}} = (l+1/2)^{4/8} \alpha \) (a.u) [70], where \( \alpha \) is the atomic dipole polarisability, and \( l \) is the angular momentum of the photoelectron. Any shape resonance must be situated below \( V_{\text{max}} \). Friedrich [71] performed a model calculation for a potential

\[
V_{\text{shape}} = -V_0 e^{-r^2} + l(l+1)/2r^2 \text{ (a.u.)}. \tag{1.26}
\]

This calculation confirmed that the width of the shape resonance is usually about equal to the excess energy above the parent state.

Shape resonances are situated just above the ground or an excited state of the parent atoms. In this case, the centrifugal force experienced by the detached electron (for \( l > 0 \)) creates a barrier in the negative ion potential. The primary decay mechanism of these states is tunneling through the barrier into their atomic parent states making their lifetime fairly short, \( 10^{-13} - 10^{-14} \) s [3]. As a consequence, the shape resonances are broad structures in the photodetachment cross section [10, 68].

Since they are often located very close to a threshold, the corresponding Wigner threshold behavior is severely altered by their presence, as pointed out by Peterson et al [72]. If the shape resonance is associated with an excited state of the neutral atom, it may also decay by deexcitation of the atom and emission of an electron. This process clearly shows that no strict distinction can be made between the Feshbach and shape resonances.

In the simplest analysis the resonance states are assumed to be isolated, i.e.,
well separated in energy from the threshold region and other resonance states. In some cases, resonances close to thresholds can be described by modified threshold laws [72, 73, 74].

### 3.3. Auger process

In atoms and ions the electrons are bound in orbitals with specific energy. The electrons can “jump” between the orbitals $a$ and $b$ by absorbing or emitting photons of energy $h\nu_{a\rightarrow b} = E_b - E_a$, where $E_a$ and $E_b$ are the energy levels for the final and initial state, respectively. If a photon with energy $h\nu$ is absorbed by an electron in an atom, the electron may be excited to a higher energy level and the process is called photoexcitation, as shown in Fig. 3.10. The binding energy of an electron is the minimum energy required to release the electron from its orbital. If the energy of an absorbed photon is higher than the binding energy, the electron will be emitted with a kinetic energy and the process is called photoionization [33], shown in Fig. 3.10.

![Figure 3.10](image.png)

**Figure 3.10.** Schematic representation of the photoexcitation and photoionization processes. The filled circles represent the electrons and the empty circles represent the vacancy left by the excited or emitted electron.
The energy is conserved in this process, so the kinetic energy of the emitted electron, \( E_{\text{kin}} = \hbar \nu - E_b \), is the difference between the photon energy \( \hbar \nu \) and the electron binding energy \( E_b \). The above formula is just a modified version of the photoelectric formula, discovered in 1905 by Albert Einstein when he explained the photoelectric effect [75].

In both processes, photoexcitation and photoionization, a hole or vacancy is left in the atom or ion and one or more electrons could be excited. In the language of the independent particle model, singly excited states correspond to one electron occupying an excited orbital, and doubly excited states correspond to two electrons occupying excited orbitals [30]. All of the doubly excited states lie above the ionization threshold and are therefore discrete states embedded in the continuum. These states correspond to two-electron excitation: firstly, a core electron is excited; secondly, an outer electron occupies an excited state in the electron-core potential. Due to the interaction between this discrete state and the nearby continuum states (so-called channel coupling), the excited core electron can impart its excitation energy \( (E_2 - E_1) \) to the outer electron. Thus, the outer electron attains the energy above the continuum threshold and can be ejected without absorption or emission of electromagnetic radiation (photons). This process is called autoionization [76].

The transition rate for the autoionization [36] is given by the Fermi Golden Rule

\[
P_{\text{autoionizing}} = \frac{2\pi}{\hbar} \left| \langle \Psi_{(E)}(E) \mid V_{12} \mid \Psi_\alpha \rangle \right| ^2 \rho_f(E)
\]

where \( \rho_f(E) \) is the density of the final states corresponding to the continuum wave function \( \Psi_{(E)}(E) \), and \( E \) is the kinetic energy of the free electron specified by energy conservation; the potential \( V_{12} \) encompasses all contributions which couple the channels; \( \Psi_\alpha \) is the wave function of the doubly excited state \( |\alpha> \).
The doubly excited states which are unstable against ionization are called autoionizing states and appear in the cross section as Feshbach resonances [5]. There are various kinds of autoionizing states:

A. The state corresponds to the excitation of two electrons when for each electron the energy of the excitation has the same order of magnitude and the total excitation energy exceeds the ionization potential of the atom. As an example, an autoionizing state of a heliumlike atom: if \( Z >> 1 \), the excitation energy is \( 3Z^2/4 \) which exceeds the ionization potential \( Z^2/2 \) of the atom.

B. The state is realized when the sum of the excitation energy of a valence electron and the atom core exceeds the ionization potential of the atom. For example, the excitation energy from the ground state of \( \text{Kr}^+ (4p^5 \ 2p_{3/2}) \) to the lowest excited state of this ion \( \text{Kr}^+ (4p^5 \ 2p_{1/2}) \) is 0.666 eV. If an excited state of a Kr atom is formed such that its atomic core is found in the upper state \( 2p_{1/2} \) and the ionization potential of the excited electron is lower than 0.666 eV, this state is an autoionizing state. This autoionizing state can decay with transition of the ion in the \( 2p_{3/2} \) state which leads to the release of the excited electron.

C. The state is a bound state situated above the continuum limit, but the radiative decay is prohibited by conservation of quantum numbers. Example of such state is \( \text{He}^- (1s2s2p \ ^4P) \) situated lower than the metastable state \( \text{He} (1s2s \ ^3S) \). So, the only channel of decay corresponds to formation of the He atom in the ground state: \( \text{He}^- (1s2s2p \ ^4P) \rightarrow \text{He} (1s \ ^21S) + e^- \), where the spin of the initial state is 3/2 and the spin for the final state is 1/2. From the spin conservation law it follows that the transition proceeds due only to a weak relativistic interaction. Hence the lifetime of this autoionizing state is larger by several orders of magnitude compared to the other autoionizing states.
In 1925, Pierre Auger [77] used a Wilson cloud chamber to study the ionization of atoms under the action of X-rays. He observed tracks of V-form which was evidence of the release of two electrons from one atom. When the energy of the incident photon is high enough (>15 eV) [3], it causes emission of at least two electrons, a photoelectron from the initial ionizing event and an Auger electron from the decay of the original ion formed.

\[ \text{A}^{-} + \text{photon} \rightarrow \text{A}^{0*} + e_{\text{photoelectron}} \]

\[ \downarrow \]

\[ \text{A}^{+} + e_{\text{Auger electron}} \]

After a photon is absorbed by the atom, an electron is emitted leaving an atom with an electron vacancy in an inner-shell. One electron from an outer-shell fills the inner-shell vacancy and another electron is emitted from the same or another outer-shell. This process is illustrated in Fig. 3.11 and is called the Auger process [77].

![Figure 3.11. Schematic of Auger decay process.](image)

According to the contemporary representations, the Auger process is an example of the decay of an autoionising state [36]. The excess energy is consumed on the removal of one or several electrons from outer-shells. The process of filling an
inner-vacancy can be sequential or simultaneous, and several shells can take part in this process, with several electrons being released. For example, a double Auger decay (sequential or simultaneous) leads to high charged states, see Fig. 3.12.

![Sequential and Simultaneous Double Auger Decay](image)

**Figure 3.12.** (top panel) Sequential double Auger decay process. 
(lower panel) Simultaneous double Auger decay process.

In negative ions, most of the bound excited states are fine structure levels [23]. For ones where the electronic configuration is different from the ground state, we call them excited states. Only in rare cases (for example, in Pt$^-$ and Ir$^-$ [23]) the excited states are bound, so practically all excited states of negative ions lie above the detachment limit and consequently are autodetaching states. Autodetaching states influence the photodetachment spectrum of negative ions in the continuous region.

Autodetachment is described as a transition from a discrete state to an adjacent continuum. In the first order approximation of perturbation theory, the
continuum wave function $\Psi_\varepsilon$ in the absence of the autodetaching state is normalized in the standard way [36]

$$<\Psi_\varepsilon \mid H \mid \Psi_\varepsilon> = \varepsilon \delta(\varepsilon - \varepsilon') \quad (1.28)$$

where $H$ is the Hamiltonian, and $\varepsilon$ is the energy of a given state of the continuous spectrum.

The autodetaching state in the absence of the interaction with the continuum can be described as a discrete state with energy $\varepsilon_a$ and wave function $\Psi_a$ [36]

$$<\Psi_a \mid H \mid \Psi_a> = \varepsilon_a. \quad (1.29)$$

In the first order approximation, interaction of the autoionizing state and the adjacent continuum states are determined by the matrix element

$$<\Psi_\varepsilon \mid H \mid \Psi_a> = V_\varepsilon. \quad (1.30)$$

The width of the autodetaching state is $\Gamma = 2\pi |V_\varepsilon|^2$ [36].

Taking into account the interaction between the autodetaching state and the continuum, in first order approximation, the wave function $\Phi_a$ and the energy $\varepsilon_a$ of the autodetaching state become:

$$\Phi_a = \Psi_a + \int dE \Psi_E V_E/ (\varepsilon - E); \quad \varepsilon_a = \varepsilon_a + \int |V_E|^2 dE/ (\varepsilon - E) \quad (1.31)$$

Under the above conditions, the continuum wave function is given by the formula

$$\Psi_\varepsilon = (V_\varepsilon \Phi_a + [\varepsilon - \varepsilon_a(\varepsilon)] \Psi_\varepsilon)/[(\varepsilon - \varepsilon_a)^2 + \pi^2 |V_\varepsilon|^4]^{1/2}. \quad (1.32)$$

The wave function $\Psi_\varepsilon$ includes the interference of the continuum states and the autodetaching states.

In order to compare the cross section in the absence ($\sigma_0$) and presence ($\sigma$) of an autodetaching state, we introduce the Fano parameter

$$q = <\Psi_0 \mid D \mid \Phi_a> / \pi V_\varepsilon <\Psi_0 \mid D \mid \Psi_\varepsilon> \quad (1.33)$$

where $\Psi_0$ is the wave function of the initial state and $D$ is the dipole moment.
operator. Therefore the ratio of the cross sections in the presence and absence of the autodetaching state becomes

$$\frac{\sigma}{\sigma_0} = \left| \frac{\langle \Psi_0 | D | \Psi_e \rangle}{\langle \Psi_0 | D | \Psi_a \rangle} \right|^2 = \frac{(q + \zeta)^2}{1 + \zeta^2} \tag{1.34}$$

where $$\zeta = (\varepsilon - \varepsilon_a(\varepsilon)) \pi \left| V_{\varepsilon} \right|^2 = \frac{\varepsilon - \varepsilon_a(\varepsilon)}{\Gamma/2}.$$

If the related autodetaching state and the continuum states have the same symmetry they interact and the cross section is given by the relation

$$\sigma = \sigma_0 \left[ 1 + \frac{q^2 - 1 + 2q\zeta}{1 + \zeta^2} \right]. \tag{1.35}$$

If a part of the continuum states correspond to different symmetry they do not interact with the autodetaching state. The cross section in the absence of the autodetaching state has the form $$\sigma_c = \sigma_0 + \sigma_1$$, where $$\sigma_1$$ corresponds to the non-interacting part of the continuum states.

The result of the Auger decay is a positive ion which can be more easily detected with present technology compared to a neutral atom. In the experiments described in this thesis, the positive ions, produced by the photodetachment process followed by the subsequent Auger decay, were measured as a function of photon energy.

### 3.4. Threshold laws

Of general interest in many areas of physics are “threshold laws” describing the energy dependence of a reaction yield near a threshold. Threshold laws are independent of the specifics of the reaction and the reaction products [3, 78] and can yield insight into the dynamics of the process under study.

In 1948, Wigner derived the expression for the near-threshold cross section behavior of reactions with two final products [79]. In the case of negative ions, the final photodetachment state includes a neutral and a charged particle, and the near-
threshold cross section is given by $\sigma \sim (h\nu - \varepsilon_t)^l + 1/2$, where $h\nu$ is the photon energy, $\varepsilon_t$ is the threshold energy, and $l$ is the photoelectron angular momentum. The selection rule $\Delta l = \pm 1$, with $s$-, $p$-, or $d$- wave ($l = 0, 1, or 2$) therefore determine the shape of the near-threshold cross section. In 1953, Wannier studied the ionization process with three final products: two electrons and a positive ion [80]. The result is known as the Wannier law: $\sigma \sim (h\nu - \varepsilon_t)^n$, where $h\nu$ is the photon energy, $\varepsilon_t$ is the threshold energy and $n$ is the Wannier coefficient. The Wigner and Wannier laws hold “near” threshold, but there is no theoretical guideline either for their range or accuracy.

### 3.4.1. Wigner law

We are interested here in the Wigner law that applies to photodetachment. The final state of the photodetachment process includes one neutral particle (the atom) and one charged particle (the electron). This is not actually covered by Wigner’s original formulation [79], since there is an induced-dipole interaction between the electron and the neutral atom. So, in order to derive the threshold law for negative ion photodetachment we used the following assumptions:

1. The neutral core does not interact with the outgoing electron. For atomic negative ions, it is sufficient to assume in the derivation that the interaction potential between the photoelectron and the neutral core decreases faster than the centrifugal potential at large electron-atom separations $r$.

2. The energy of the photoelectron is small, so it is possible to consider only the lowest order of $k$ in the expansion of the wave function. Here $k = p/h$ is the wave number of the exiting electron and $p$ is the momentum of the electron. This implies also that the detachment cross section is dominated by only one angular momentum channel, which is the case for an $s$-electron, where the $l = 1$ channel is the only one
available.

In general two-electron angular momentum channels are available \( l = |l_0 \pm 1| \) where \( l_0 \) is the angular momentum of the bound electron to be detached. Previous valence studies [78] have shown that at sufficiently low photon energies the centrifugal barrier effectively suppresses the higher angular momentum channels.

The system containing the free electron and the residual atom after photodetachment is described by an effective potential \( V_{\text{eff}}(r) \) expressed as [81]

\[
V_{\text{eff}}(r) = V(r) + l(l + 1) \frac{\hbar^2}{2\mu r^2}. \tag{1.36}
\]

Here \( V(r) \) is the potential due to an atomic neutral core and the second term is the centrifugal potential; \( l \) is the angular momentum for the outgoing electron; \( \mu \) is the reduced mass and \( r \) is the distance between the electron and the core of the residual atomic system. The potential \( V(r) \sim 1/r^4 \) decreases faster than \( 1/r^2 \) which makes the centrifugal part dominant in Eq. (1.36).

The detachment rate from an initial bound negative ion state \( |\Psi_i> \) to a final continuum state \( |\Psi_f> \) is given by Fermi’s Golden Rule [30]

\[
R_d = \frac{2\pi}{\hbar}|<\Psi_i|D|\Psi_f>|^2 \rho_f \tag{1.37}
\]

where \( D \) is the dipole operator for photoabsorption process and \( \rho_f \) is the density of final states.

In a box of volume \( V \), the number of free electron states available to an electron with energy less than \( \varepsilon \) is

\[
N(\varepsilon) = \frac{(2V/3\pi^2)(2m\varepsilon/\hbar^2)^{3/2}}{2}. \tag{1.38}
\]

The density of states is then \( dN/N = 3/2 \text{ de}/\varepsilon \) [40]. Considering the detached electron as a free electron and the wave functions volume normalized, the density of states is \( \rho_f \text{ de} \sim \varepsilon^{1/2}\text{de} \), where \( \varepsilon = \hbar \nu - \varepsilon_t \) is the excess energy carried off by the detached electron; \( \hbar \nu \) is the photon energy and \( \varepsilon_t \) is the threshold energy. Assuming that the
detached electron does not interact with the residual neutral atomic core, the final state can be expressed in a partial wave expansion, where only the lowest order angular momentum channel \( l \) will contribute to the detachment cross section (\( \varepsilon \) and \( k \) small)

\[
|\Psi_f> \sim k^l \sim \varepsilon^{l/2}. \tag{1.39}
\]

The photodetachment cross section \( \sigma_d \) is proportional to the rate given by Eq. (1.37)

\[
\sigma_d \sim \varepsilon^{l+1/2}. \tag{1.40}
\]

Equation (1.40) is called the Wigner law, where \( l = |l_0 \pm 1| \), \( l_0 \) is the angular momentum of the bound electron to be detached, and \( l \) is the angular momentum of the photoelectron.

The Wigner law is in fact the first term in an expansion of the cross section about the threshold energy [55]. If the energy of the photoelectron \( \varepsilon \) is large, then a more general form of the threshold law is

\[
\sigma_d = A_0 \varepsilon^{l+1/2}(1 + A_1 \varepsilon + A_2 \varepsilon^2 + \ldots). \tag{1.41}
\]

Here, the first term in the expansion is the Wigner law, with undetermined amplitude \( A_0 \). The constants \( A_n \) (\( n = 0, 1, \ldots \)) could be obtained by analysis, such as the zero core contribution approximation (ZCC) [81] or by fitting to the experimental data over a large region in energy. At large photon energies above the threshold, the higher order terms in the expansion, become significant.

The Wigner law can also be expressed in terms of the energy of the incoming photon

\[
\sigma(h\nu) = \begin{cases} 0, & h\nu < \varepsilon_t \\ \sigma_0(h\nu - \varepsilon_t)^{l+1/2}, & h\nu > \varepsilon_t \end{cases} \tag{1.42}
\]

where the \( h\nu \) is the incoming photon energy, \( \varepsilon_t \) is the threshold energy, \( l \) is the angular momentum of the photoelectron, and \( \sigma_0 \) is a constant.
The selection rule describing the change in parity for one-photon dipole transitions, $\Delta l = l - l_0 = \pm 1$, therefore determines the shape of the near-threshold cross section. If, for example, an $s$-electron ($l_0 = 0$) is detached, the outgoing wave will have a $p$-wave ($l = 1$) dependence. If a $p$-electron ($l_0 = 1$) is detached, it will result an $s$-wave ($l = 0$) and a $d$-wave ($l = 2$), as shown in Fig. 3.13.

The Wigner law holds “near” threshold, but there is no theoretical guideline for either its range or validity. In order to extend the range of the Wigner law we can use two theories: the short-range potential correction [82] and the leading-term correction [81].

![Graph showing wave types (s-wave, p-wave, d-wave) as a function of photon energy (eV)](image)

**Figure 3.13. s, p, d-wave.**

The theories explore two extreme situations, that of a large or small polarizability. In the derivation of the Wigner threshold law it was assumed that the ejected electron does not interact with the residual neutral core. In fact, the photoelectron being at a small distance from the atom induces an electric dipole moment in the electron cloud of the atom.

The induced dipole potential falls off as $r^{-4}$ with large electron-atom separation $r$. The electron interacts with the neutral atom via this induced dipole
potential, therefore an additional term must appear in the threshold law expansion in order to correctly account for the short-range interactions. The modification of the Wigner law caused by this interaction has been calculated by O’Malley [82] to be

\[ \sigma_{OM}(\varepsilon) = k^{2l+1} \left[ 1 - 4\alpha k^2 \ln(k/(2l+3)(2l+1)(2l+1)) + O(k^2) \right] \]  

(1.43)

where \( k = \sqrt{2\varepsilon} \) and \( \alpha \) is the dipole polarizability of the neutral atom. The O’Malley correction is independent of the threshold energy and only depends on the photoelectron energy \( \varepsilon \). Farley has proposed an analytic model called zero core contribution model (ZCC) [81] to calculate the photodetachment cross section near the threshold, given the core radius and the electron affinity. The Farley correction depends on the relative energy above the threshold. When the threshold energy is large, the polarization term should be more significant, while for weakly bound ions the leading correction should be dominant. Despite the fact that these correction terms have good qualitative agreement with observation, they seem not to be accurate enough.

The Wigner threshold law has been verified in countless valence-shell detachment experiments [3, 78]. Recent work in He\(^-\) (1s), S\(^-\) (2p) [83], Pt\(^-\) (4f) [84], Fe\(^-\) (3p) [120], and Ru\(^-\) (4p) [175] has shown that it is also valid in inner-shell detachment, and \( p-, s-, \) and \( d- \) wave detachment laws were observed, respectively.

### 3.4.2. Wannier law

In 1953, Wannier [80] made the prediction about the variation of the double photoionization cross section with energy in a critical zone where electron correlation effects dominate. Since then much effort has gone into testing the Wannier law and its range of validity [85]. Below we explore the Wannier law in the context of negative ions.
In inner-shell photo-double-detachment, two electrons emerge from a positively charged ion core. There have been several investigations of double photodetachment cross sections for negative ions since the early eighties, such as H⁻ [86], He⁻ [83, 87, 88, 89], Li⁻ [89, 14], K⁻ [90], Na⁻ [91], Cl⁻ [92], and F⁻ [93].

The near-threshold total cross section for this double electron escape process, the so-called Wannier law, has the form [80, 94, 95, 96]

\[
\sigma_{\text{total}}(h\nu) = \begin{cases} 
0 & , \quad h\nu < \varepsilon_t \\
\sigma_0 (h\nu-\varepsilon_t)^m & , \quad h\nu > \varepsilon_t
\end{cases} 
\]

where \(\sigma_0\) is the total cross section at the threshold energy, \(h\nu\) is the photon energy, and \(\varepsilon_t\) is the threshold energy. For the case of photo-double-ionization, shown in Fig. 3.14, \(m\) is predicted to be 1.056 [97] and the difference from unity is due to the electron correlation effects.

**Figure 3.14.** Wannier law for the case of photo-double-photodetachment from Fe⁻. The black open diamonds are the extracted photo-double detachment cross section and the solid red line represents the Wannier law fits of the extracted experimental data.
In photo-double-detachment a single incident photon produces two photoelectrons that escape from a positively charged ion core. This is a three body problem in which there are interactions between the core and each electron, as well as between the two electrons.

In the direct (or simultaneous) double photodetachment process the two electrons are simultaneously detached from the negative ion and the reaction is:

\[ h\nu + A^- (i) \rightarrow A^+(j) + 2e^- \]

The initial state (i) is the ground state of \( A^- \) and the intermediate state (j) is an excited state of the \( A^+ \) ion that can decay to either the ground state or an excited final state (f) of the \( A^{2+} \) ion. Our group has measured the double photodetachment cross section in case of the He\(^-\) [83] negative ion.

The indirect (or sequential) double photodetachment process is a two-step process involving the formation of an intermediate core-excited state of the A atom which rapidly decays into the two-electron detachment continua, resulting in \( A^+ \) ions. The reaction can be written as:

\[ h\nu + A^- (i) \rightarrow A^*(j) + e^- \]

(1) \( A^*(j) \rightarrow A^{++}(f) + e^- \)

(2) \( A^*(j) \rightarrow A^{++}(f) + e^- \rightarrow A^{2+*}(f) + e^- + e^- \)

(3) \( A^*(j) \rightarrow A^{2+*}(f) + 2e^- \)

The initial state (i) is the ground state of the negative ion \( A^- \), the intermediate state (j) is a core excited state of an A atom, the final state (f) is the ground or excited state of the \( A^+ \) or \( A^{2+} \) ion. This process has been investigated in numerous negative ions [3, 6].
Usually the cross section for the indirect/sequential process is much bigger than the cross section for the direct/simultaneous one, and indirect processes can result in prominent resonance structures in the total photo-double-detachment cross section [6]. For example, the calculated background double ionization cross section is up to 10% of the total in Fe\(^+\) and 20% in Fe [43]. Kjeldsen's experiment [99] shows that for Fe\(^+\) double ionization contributes only about 2% of the single-ionization cross section in the \(3p\rightarrow3d\) region.

The mechanisms leading to photo-double-ionization (sequential ionization or two-step-two (TS2), shake-off, two-step-one (TS1), rescattering) [100] are very complex and only in some cases are experimentally accessible. In case of photoionization, the threshold measurements involving the detection of ‘threshold’ photoelectrons with kinetic energy less than 10 meV are a sensitive probe to the electron correlation [87]. These electrons, easily deflected by stray electrostatic and magnetic fields, make the photo-double-detachment experiments very challenging. The most complete information about photo-double-ionization may be obtained by a simultaneous determination of the energies and ejection angles of both outgoing electrons. This may be achieved by detecting the two electrons in coincidence [101] or by detecting the positively charged core ion in coincidence with one of the ejected electrons, using cold-target recoil-ion momentum spectroscopy (COLTRIM) [102].

The Wannier threshold law has been the subject of extensive theoretical and experimental investigation for almost four decades [85, 97, 100], and for a while all experimental evidence appeared to be consistent with the conventional Wannier approach.

In 1990, experimental studies of the spin dependence in electron-impact ionization of atomic hydrogen [103] revealed deviations from the Wannier threshold
theory. Friedman *et al.* [85] reexamined results of the previous two-electron escape work trying to provide insight into the possible origin of these deviations. The simplicity of the threshold law derived from the assumption that the analysis of threshold behavior is restricted to the mechanics of the escape process alone, instead of requiring a detailed understanding of the dynamics of the whole process. Thus, small deviations from the Wannier Law may be a signature of major differences in the dynamical behavior of the highly correlated two-electron system. Because electron correlations are enhanced in the negative ions, they could be ideal targets to test this two-electron escape process. Clearly new technology to measure the ejected electrons from inner-shell ionization will be necessary in order to make detailed measurements and fully understand these effects.

### 3.5. Post-collision interaction

The formation of singly charged positive ions from inner-shell photodetachment of negative ions is a two step process: first, detachment of the inner-shell electron leads to formation of a core-excited neutral atom; and second, the core-excited neutral atom ejects an Auger electron to form a positive ion, as shown in Fig. 3.15. Typically, the decay lifetime of the core hole is very short (~10^{-14} s) [3, 36], so there is a high probability that the Auger electron is ejected before the photoelectron escapes. The fast Auger electron overtakes the slow photoelectron, and the effective nuclear charge felt by the photoelectron increases. Thus, the attractive potential between the photoelectron and nucleus increases. This implies that the total energy of the photoelectron decreases, and it can be recaptured. Also, the photoelectron screens the nucleus from the Auger electron causing the latter to gain energy. The interaction between photoelectrons and Auger electrons is called the *post-collision interaction*
Inner-shell photodetachment followed by Auger-electron decay is an example of a resonant rearrangement collision in which three charged particles, an ion and two electrons, are formed. The probability that an Auger electron is emitted in the interval \((t, t+dt)\) is given by the rate equation

\[
dP = \frac{(1-P(t))dt}{\tau_h} = \frac{(1-P(t))dt}{\Gamma/\tau} = \frac{(1-P(t))dt}{\Gamma/\tau}.
\] (1.45)

where \(\tau_h\) is the lifetime of the initial hole state and \((1-P(t))\) represents the relative number of atoms at time \(t\) with the hole in the inner-shell.

Assuming that the decay of the hole by fluorescence is negligible, by integrating (1.45) we obtain the probability that the Auger electron has been emitted at any time \(t\) smaller than \(\tau\)

\[
P(\tau) = 1 - \exp(-\tau/\tau_h) = 1 - \exp(\Gamma/\tau).
\] (1.46)

The width of the hole state is \(\Gamma = 1/\tau_h\) and \(P(\tau)\) gives also the probability that the
photoelectron has been recaptured [30].

The energy conservation law for this process is
\[ \hbar \nu + E^- = E^0 + E_{\text{exc}} = E^+ + \varepsilon_{\text{ph}} + \varepsilon_{\text{Auger}} \] (1.47)
where \( \hbar \nu \) is the photon energy, \( E^- \) is the ground state energy of the negative ion, \( E^0 \) is the energy for the neutral atom, and \( E^+ \) is the energy for the positive ion. Thus \( E_{\text{exc}} \) and \( \varepsilon_{\text{ph}} \) are the kinetic energies of the photoelectron before and after Auger-electron emission, respectively. If the photoelectron is recaptured, it has a negative energy \( \varepsilon_{\text{ph}} = -\varepsilon_n \), and the Auger-electron energy is enhanced.

An excess energy \( E_{\text{exc}} = \hbar \nu - E_{\text{bin}} \) is given to the hole. Here \( E_{\text{bin}} \) is the binding energy corresponding to the hole. The question is which time should be associated with this excess energy. This time \( \tau = \tau_{(\text{exc})} \) can be estimated both classically and quantum mechanically.

In the semi-classical picture, time is given by \( \tau = \tau_{\text{ph}} - \tau_{\text{Auger}} \), where \( \tau_{\text{ph}} \) is the time it takes for the photoelectron to reach the distance \( R \) from the nucleus at which point it is overtaken by the fast Auger electron. The Auger electron reaches \( R \) in time \( \tau_{\text{Auger}} \). By assuming that the electrons are released close to the nucleus with constant velocity, and since \( v_{\text{Auger}} \) is much larger than the photoelectron velocity \( v_{\text{ph}} \), we have \( \tau \sim \tau_{\text{ph}} \sim R/v_{\text{ph}} \). Classically, recapture occurs when the sum of the initial photoelectron kinetic energy and the ionic potential energy (-1/R) just after Auger decay, is less than zero. In this situation, the photoelectron can no longer escape the Coulomb attraction and cannot propagate beyond the classical turning point \( R = 2/v_{\text{ph}}^2 \). The classical turning point is calculated including the angular momentum potential as \( R = [1 + (1 - 2\varepsilon l(l+1))]^{1/2}/2\varepsilon \). Since \( v_{\text{ph}} = (2E_{\text{exc}})^{1/2} \), the time is \( \tau \sim 2^{-1/2} E_{\text{exc}}^{-3/2} \). From eq. (1.46) and semi-classical considerations [104], the probability for the photoelectron to be recaptured is
\[ P(\tau) = 1 - \exp\left(-\Gamma/2 \sqrt{E_{\text{exc}}/2}\right). \] (1.48)

In the quantum-mechanical model, \( \tau \) is considered to be the time during which the photoelectron interacts with the Auger electron [105]. Describing the interaction by time-independent perturbation, we have \( \tau \Delta \varepsilon \sim 1 \), where \( \Delta \varepsilon \) is the spread of energies which are released when the photoelectron is recaptured. According to Eq. (1.47), \( \Delta \varepsilon \sim \varepsilon_{\text{ph}} \sim E_{\text{exc}} \) and therefore \( \tau = 1/\Delta \varepsilon \sim 1/E_{\text{exc}} \). From eq. (1.46) and from quantum-mechanical considerations, the probability for the photoelectron to be recaptured is
\[ P(\tau) = 1 - \exp\left(-\Gamma/E_{\text{exc}}\right). \] (1.49)

There is a distinct difference between the quantum-mechanical and the semi-classical results. In the semi-classical model, \( P(\tau) \) depends on \( \tau_{\text{ph}} \) as long as \( \varepsilon_{\text{Auger}} \gg E_{\text{exc}} \), and it does not depend very much on the time \( \tau_{\text{Auger}} \) necessary for the Auger electron to pass the photoelectron.

Consider the photodetachment of a negative ion:
\[ h\nu + A^- \rightarrow A^{0*} + e_{\text{ph}} \]
\[ \downarrow \]
\[ A^+ + e_{\text{Auger}} \]

Given the computed escape probabilities in each channel \( P_{\text{esc}}^i \) which depends only on the energy \( \varepsilon_i \), the angular momentum \( l_i \), and the core Auger width \( \Gamma_i \), the expression for the \( A^+ \) cross section was calculated by Gorczyca et al. [107] to be
\[ \sigma(A^+) = \sum_i P_{\text{esc}}^i \sigma_i \] (1.50)
where \( \sigma_i \) is the photodetachment cross section to channel i, and the sum includes only those channels “i” which can core Auger decay.

The effect of the photoelectron recapture process is the reduction in cross section within about \( \varepsilon \sim 2\Gamma^{2/3} \) above the threshold [106]. Fig. 3.16 shows the
recapture signal in the case of the photodetachment of helium negative ion measured by Bilodeau et al. [107].

In the photoelectron spectrum, PCI causes a shift in spectral lines in energy and produces broadened line shapes. For inner-shell photodetachment from negative ions detecting the positive ion formation, the post collision interaction effect causes a reduction of the positive ion signal above the threshold [104, 106], especially at small photoelectron energies. Thus post collision interaction effects can severely alter the behavior of the near threshold cross section as have been seen in inner-shell photodetachment of Li$^-$ [104] and He$^-$ [107].

Figure 3.16 Recapture signal in the photodetachment of the helium negative ion [107]. The open circles represent the measured He$^+$ production following the photodetachment near the 1$s$ threshold. The solid curves are the theoretical calculated cross section. The inset shows the corresponding recaptured portion of the signal.
CHAPTER 4

EXPERIMENTAL METHOD

The discovery of the photoelectric effect by Hertz in 1881 [108] can be a starting point for a discussion of photoionization in atoms. In 1905, Einstein presented the modern quantum mechanical interpretation of this effect [75], relating the experimental facts of how the electrons are emitted from a metal surface when photons, quanta of electromagnetic radiation impinge on the surface. In the middle 1950s Siegbahn and co-workers [109, 110] developed X-ray photoelectron spectroscopy based on the photoelectric law. Photon sources used in this early work were X-ray anodes and resonance radiation UV lamps, notably He I and He II radiation. When the laser was introduced as a scientific tool new fields in experimental physics were opened up. For many experimental investigations, neutral atoms and molecules have been a natural choice, due to the relatively simplicity of preparing them in high density targets. Technical difficulties in negative ion production determined more limited studies on these systems.

Over the last 30 years, due to the new techniques, such as plasma discharge technology and the merged-beam method, the amount of data for ionic species has been substantially increased. Since 1970s synchrotron radiation has become an increasingly more important photon source since it gave access to the inner-shell electrons. The merged ion-photon beam method, where the ions are collinearly overlapped with a parallel photon beam became the accepted method for atomic ion
measurements using both optical laser and synchrotron radiation [13, 14, 111]. There are now experiments using this technique at different synchrotron facilities around the world, namely the ASTRID (Denmark), SuperACO (France), Photon Factory and SPring-8 (Japan), and ALS and APS (USA).

Schematically, the photoionization (or photodetachment, as it is denoted for \( n = -1 \) and \( m = 1 \)) process can be written as

\[
h \nu + X^{n+} \rightarrow X^{(n+m)+} + me^- \quad (4.1)
\]

Experimentally this process can be investigated by studying the disappearance of the reactants or the appearance of the products (or a combination of these). The technique is called photoabsorption, photodepletion, photoion or photoelectron spectroscopy depending on the choice of analysis; if fluorescent photons are emitted in the process, also photoemission spectroscopy is possible. The total photoionization or photoabsorption cross sections \( \sigma \) are obtained from the absorption of the photons (4.2), the depletion of the target (4.3) or the appearance of the photoions (4.4) using

\[
\frac{I}{I_0} = e^{-n_0 \sigma t} \quad (4.2)
\]

\[
\frac{n}{n_0} = e^{-t_0 \sigma l} \quad (4.3)
\]

\[
S = I_0 n_0 \sigma l \quad (4.4)
\]

where \( I_0 \) and \( I \) label the incoming and outgoing photon-beam intensities, respectively, \( n_0 \) and \( n \) the corresponding densities, \( t \) and \( l \) the interaction time and length, respectively, and \( S \) the photoionization/photodetachment signal [112].

Each of these methods has its own advantages and disadvantages, so the choice of experimental set-up depends on the target, photon source and detection possibilities. Often, the main challenge related to experiments with neutral atoms is to determine the density of the used target. For the ion beams, on the other hand, the target density can be obtained by using their size, current and velocity, but it is
extremely small. The density of the negative ion beams is about $10^6 \text{ cm}^{-3}$ [12], smaller than the density of vacuum gas molecules at ultrahigh vacuum (UHV), implying that very intense photon sources are required to obtain an observable signal. The 3rd generation synchrotron radiation facilities with undulator beamlines provide intense and highly collimated beams of VUV and soft X-ray photons. Such beamlines have made it possible to use the merged-beam technique efficiently in inner-shell photodetachment studies of negative ions. In addition to the intense VUV radiation from the undulators these experiments exploit the fact that the final product of inner-shell excitation is ionic and therefore easier to detect compared to a neutral target.

The merged-beam technique is characterized by co-linearly overlapping beams of ions and VUV/X-Ray photons. It was originally used for electron-impact ionization [113] and later adapted for photoionization by Lyon et al. [114]. An important advantage of this method is that the absolute cross section can be determined, because the density of the target-ion beam can be directly measured. The absolute cross sections are obtained by using the current $I$ of the target-ion beam, the photon-beam intensity ($I_\gamma = J/e\eta$, measured by a calibrated photodiode with quantum efficiency $\eta$), the ion and photon beam profiles (measured by the scanning slits), the velocity $v$ of the target ions, the photoionization signal $S$, the efficiency of the particle detector $\Omega$, and the length of the interaction region $L$ as follows:

$$\sigma = S e^2 \eta v / I \Omega \int dz/\Delta x \Delta y F(z)$$  \hspace{1cm} (4.5)

where $F$ is the form factor, a measure of the photon–ion beam overlap and $\Delta x \Delta y F$ is an effective beam area.

Unlike for atoms and positive ions the number of experiments carried out for negative ions so far is limited. The lack of experimental photodetachment cross-section data can be related to the substantial difficulties involved in such
measurements, e.g. low ion-target density, low signal and high background signal.

The experiments presented in this thesis were performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, using the High Resolution Atomic Molecular and Optical Physics (HRAMO) undulator beamline 10.0.1 with the fixed ion-photon beamline (IPB). The ion-photon-beam (IPB) endstation [16] is based on the merged-beam technique and photoion spectroscopy using tunable synchrotron radiation. The negative ion beam was produced using a cesium sputter source (SNICS II) [17]. The mass selected ions are merged collinearly with the counter-propagating photon beam from beamline 10.0.1., as shown in Fig. 4.1.

![Figure 4.1. Ion-photon-beam endstation and schematic of beamline 10.0.1.](image)

Inner-shell photodetachment and subsequent Auger decay produce positive ions. The positive ions (the signal) are deflected by the de-merging magnet and
detected as a function of photon energy.

4.1. The photon source

Synchrotron radiation is a natural consequence of accelerating charged particles to relativistic velocity. When charged particles are forced to move in a circular orbit photons are emitted. Synchrotron radiation is a low field photon source and its intensity is limited to single-photon processes. This is unlike the high field laser light which is highly monochromatic and whose intensity may initiate multi-photon processes. Synchrotron characteristics, such as high brightness, wide energy spectrum, high polarization, and short pulses, make the synchrotron radiation an excellent spectroscopic tool that may be easily adapted to study a large variety of scientific problems in atmospheric chemistry, astrophysics, plasma physics, interstellar chemistry and fundamental physics.

The Advanced Light Source (ALS) at Berkeley National Laboratory (LBNL) is designed to produce photon beams with high spectral brightness and a considerable degree of spatial coherence. The electrons are produced by a thermoionic gun consisting of a cathode material surface kept at high temperature and situated in a radio frequency (RF) cavity [115]. The electric field generated in the cavity overlaps the AC electric field of the electron gun and produces electron bunches separated by 8 ns. The electron bunches are directed into a linac-to-booster (LTB) transfer line at 50 MeV by a linear accelerator, as shown in Fig. 4.2. In the booster ring the energy of the electrons is increased to 1.5 GeV before their injection into the storage ring through the booster-to-storage ring (BTS) transfer line. In the storage ring the electrons are accelerated to the nominal operating energy of 1.9 GeV. Typically there are 284 bunches of electrons in the ring, and this is so-called multi-bunch mode for
the storage ring. The electrons moving in the curved path will emit electromagnetic radiation, and their energy will decrease in time.

**Figure 4.2.** The schematic layout of the ALS [115].

The energy of the electron beam lost to synchrotron radiation is replenished by radio frequency accelerators, which are cavities with an axial electric field oscillating at the frequency of arrival of sequential electron bunches. The photon beams are directed into beamlines to be used simultaneously for a wide variety of experiments. A summary of the parameters is provided in the Table 4.1, and more technical specifications about the synchrotron facility may be found in the ALS report [116].
Synchrotron radiation is produced in the storage ring as the electrons pass through the bending magnets, undulators, and wigglers. The High Resolution Atomic, Molecular and Optical physics beamline 10.0.1 (HRAMO) is served by a 4.55-m-long, 10-cm-period undulator with 43 full periods. This beamline produces an intense beam of photons at very high spectral resolution over the photon energy range from 17 to 340 eV.

**Table 4.1.** Typical operating parameters for the ALS electron storage ring [116].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron-beam energy</td>
<td>1.0 – 1.9 GeV</td>
</tr>
<tr>
<td>Electron-beam injection energy</td>
<td>1.0 – 1.5 GeV</td>
</tr>
<tr>
<td>Filling pattern (multibunch mode)</td>
<td>276 – 320 bunches</td>
</tr>
<tr>
<td>Bunch spacing: multibunch mode</td>
<td>2 ns</td>
</tr>
<tr>
<td>Bunch spacing: two bunch mode</td>
<td>328 ns</td>
</tr>
<tr>
<td>Storage ring circumference</td>
<td>196.8 m</td>
</tr>
<tr>
<td>Number of straight sections</td>
<td>12</td>
</tr>
<tr>
<td>Radio frequency</td>
<td>500 MHz</td>
</tr>
<tr>
<td>Beam lifetime: multibunch mode</td>
<td>8 hrs at 400 mA</td>
</tr>
<tr>
<td>Beam lifetime: two bunch mode</td>
<td>35 min. at 40 nA</td>
</tr>
<tr>
<td>Horizontal emittance</td>
<td>6.75 nm-rad</td>
</tr>
<tr>
<td>Vertical emittance</td>
<td>0.15 nm-rad</td>
</tr>
<tr>
<td>Energy spread ($\Delta E/E$, rms)</td>
<td>$1 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
A spherical-grating monochromator delivers a highly collimated photon beam of spatial width of 1 mm and divergence less than 0.5°. The beamline produces a photon flux of $\sim 10^{12}$ photons per second in a bandwidth of 0.01% at the energy of 40 eV [115].

The photon beamline layout is shown in Fig. 4.3. The photons coming out from the undulator are directed and focused first horizontally by a spherical mirror (M1), then vertically by another spherical mirror (M2) with a demagnification of 8, onto the entrance slit of the spherical grating monochromator (SGM).

![Figure 4.3. Schematic layout of ALS Beamline 10.0.1 [115].](image)

The spherical grating monochromator consists of three parts: a fixed-position entrance slit, three interchangeable diffraction gratings, and translating exit slit. The gold-surfaced spherical gratings are 19 cm long each having a 21-m radius of curvature. The ruling densities and energies covered by the three gratings are given in Table 4.2, where LEG, MEG, and HEG are abbreviations for low, mid and high energy gratings.

The SGM was designed such that the angle between the entrance and exit slit is held constant. The photon energy can be changed by rotating the grating and
translating the exit slit to the focal point of the grating while simultaneously adjusting the undulator gap to maximize the photon beam intensity.

**Table 4.2.** The parameters of the diffraction gratings in ALS beamline 10.0.1 [115].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LEG</td>
<td>380</td>
<td>17.8</td>
<td>75</td>
</tr>
<tr>
<td>MEG</td>
<td>925</td>
<td>40</td>
<td>160</td>
</tr>
<tr>
<td>HEG</td>
<td>2100</td>
<td>100</td>
<td>360</td>
</tr>
</tbody>
</table>

The photon energy resolution is determined by the width of the entrance and exit slits of the SGM. The optimum flux of monochromatic photon beam is obtained by vertically refocusing and positioning with a third spherical mirror (M3) which also directs the photon beam into the experimental station. Focusing is achieved by adjusting the curvature of the mirrors using piezoelectric actuators [117]. The mirrors also optimize the photon flux and the photon beam trajectory in the endstation which houses our instrumentation.

Each of the optical elements in the beamline has losses in reflectivity that are difficult to predict and may change with time. An absolutely calibrated silicon X-ray photodiode [118] is installed permanently in the IPB endstation, and was used to calibrate the photon flux for the three gratings at the beamline 10.0.1.

The quantum efficiency of the photodiode, i.e. the number of electron-hole pairs generated per absorbed photon, was determined by the manufacturer using a standard photon source absolutely calibrated by the National Institute of Standards and Technology (NIST). The photon flux can be expressed as the ratio of the current generated in the photodiode and the quantum efficiency of the photodiode. The
photodiode currents measured at beamline 10.0.1 are typically in the 2-200 μA, depending on the photon energy and resolution set by the slits. Figure 4.4 presents, on a log-log scale, the measurements of the absolute photon flux performed under optimized undulator conditions as a function of photon energy. The beamline 10.0.1 produces a photon flux of ~$10^{12}$ photons per second in a bandwidth of 0.01% at energy of 40 eV.

![Figure 4.4](image.png)

**Figure 4.4.** Photon flux versus photon energy for monochromator ALS beamline 10.0.1 at 400 mA electron storage ring current and 10,000 resolved power (red fill circle-LEG, green square-MEG, blue fill triangle-HEG first harmonic of the undulator; open triangle –third harmonic; solid lines –theoretical calculations) [115].

The measured quantum efficiency of the photodiode is presented in Fig. 4.5 and the values have been interpolated over the photon energy range using best-fit polynomials to the calibration points provided by the manufacturer. These measurements correspond to the maximum flux available, and are important reference
data to assure that the photon beamline is performing optimally during the photodetachment measurements.

The three diffraction gratings at the ALS beamline 10.0.1 are mechanically interchangeable, and the photon energy calibration is only reproducible within approximately 0.1% whenever the grating is changed. For each experiment it is necessary to calibrate the photon energy using well-known ionization resonances.

![Figure 4.5. Photodiode quantum efficiency as a function of photon energy.](image)

The photon energy calibration measurements are performed with a gas-ionization cell installed on one branch of beamline 10.0.1. The cell contains two parallel plates placed parallel with the photon-beam axis and is filled with a neutral gas (He, Ne, Ar, Kr, Xe, SF₆, CO, etc) at mTorr pressure. A schematic view of the gas cell is presented in Fig. 4.6. One electrode, used as a repeller electrode is held at +100 V, while the other electrode is connected to a commercial femtoampere-meter recording the photoionization current as a function of photon energy. The gas-
ionization cell is separated from the ultrahigh vacuum (UHV) region of the monochromator by an Al window. In order to avoid disturbing effects due to the absorption edges of the window, the window material is selected according to the photon energy studied.

To accurately calibrate the energy scale over the entire range of each grating at least two and typically three points are required. Often the second order radiation from the grating offers additional calibration energies at half of the reference values.

**Figure 4.6.** Schematic view of the gas-ionization cell.

When an ion moves with velocity $v$ in the interaction region, the photon energy experienced by the ion, is given by the Doppler formula [30]:

$$h\nu' = h\nu(1-v/c \cos \theta)$$

(4.6)

where $\theta$ is the angle between the direction of the moving ion and the photon beam, and $h\nu$ is the photon energy in the lab frame.

There are two different effects causing Doppler broadening in an experiment using photon and ion beams, namely variations in the ion velocities and variations in the interception angles between the beams. In the collinear geometry the interception angle is better constrained by the beamline apertures, so the geometrical Doppler
broadening is negligible, therefore the initial ion velocity spread becomes the dominant broadening mechanism. Ions produced in the negative cesium sputter source will have different velocities due to the scattering mechanism in the cathode. However, the initial velocity spread is reduced when the ions are accelerated in an electric field [119].

In all experiments presented in this thesis the calibration of the photon energy scale was done in two steps. First, the Doppler shift was applied to all nominal photon energies; second, the Doppler corrected scale was calibrated using well-known ionization resonances and applying a linear transformation. For example, in the case of the Fe\(^{-}\) beam having energy of 8.5 keV, the ion-frame Doppler shift was 30 to 42 meV for photon energies of 50 to 70 eV. In this photon energy range, the calibration amounted to maximum energy changes of 40 meV and the error in the resulting calibrated energy scale was less than ±4 meV [120].

One of the most important characteristic of ALS beamline 10.0.1 is the high spectral resolution achievable over a broad spectral range. The spectral resolution depends on the properties of the target ion and the photon source, and in favorable cases a resolution close to 1 meV [121] was obtained at ALS beamline 10.0.1.

### 4.2. The negative ion source

Formation of high-intensity negative ion beams has long been of interest in several areas of physics. Each specific application requires different characteristics for the ion beam as charge state, intensity, purity, divergence, etc. Despite a large number of different types of sources are in use worldwide, and no universal ion source exists that is able to comply with all different demands.

The photodetachment process of a negative ion is fairly weak, so in order for
an experiment to be successful, two points are important: first, the extracted negative ion beam should be stable for precise measurements; second, the intensity of the negative ion beam should be as high as possible, since the measured photodetachment signal is directly proportional to the target ion current.

The ion source used for the production of negative ions in the experiments presented in this thesis is a cesium sputter source (SNICS) which was originally designed by Middleton [17]. The main advantage of this source is that usable negative ion beams can be made from almost every element of the periodic table. Also, the source design makes it extremely easy to reload without breaking the vacuum, and the negative ion beams obtained using SNICS are stable.

### 4.2.1. Production of negative ions

In order to form a negative ion, a loosely bound electron needs to be attached to an atom. A free electron cannot be directly attached to an atom since the momentum and energy conservation cannot be fulfilled simultaneously. In the process leading to negative ion formation, the energy given up for the capture of the electron could be taken by a photon, or by another electron, atom or molecule.

The simplest possible scheme for negative ion formation is the radiative capture of an electron by an atom [7].

\[
e^- + A \rightarrow A^- + h\nu
\]

The photon removes the excess energy in this reaction. The probability for radiative attachment is very low so the process cannot be used to create the density of negative ions often required in photodetachment studies.

In dense gas media three body collisions lead to formation of negative ions [68]:

---

[68]:
\[
e^- + A + B \rightarrow A^- + B \\
A + 2e^- \rightarrow A^- + e^-
\]

In a collision between two atoms it is possible that an electron is transferred from one atom to another, resulting in the formation of a negative ion:

\[
A + B \rightarrow A^- + B^+
\]

In dissociative attachment [68], an electron collides with a molecule which dissociates with the electron attached to one of the fragments:

\[
e^- + AB \rightarrow A^- + B^+ + e^-
\]

From all the above processes, charge transfer is the most suitable for obtaining a negative ion beam, and it is also the method used in this work. A fast moving atom captures an electron from a target atom. The binding energy of the outermost electron in the target atom is a very important parameter in this process. Charge exchange is most efficient when the electron affinity of the formed negative ion is equal to the ionization potential of the target atom. However, the highest electron affinity of any negative ion is smaller than the lowest ionization potential of any atom [112]. So, the elements with low ionization potential, i.e. alkali metals, are the most suitable targets. The charge transfer efficiency strongly depends on the center of mass energy of the collision and the density of the target atoms [122, 123, 124].

4.2.2. The cesium sputter ion source

In the experiments described in this thesis the negative ions were produced by using a cesium sputter ion source (SNICS) [17]. The cesium vapors produced by a cesium oven are introduced in the source chamber (p \( \sim \) 10\(^{-8}\) torr, where 1 torr = 133.322 Pa). The main parts of the source are a conical surface ionizer
constructed of molybdenum and a cathode made of the element of interest, see Fig. 4.7.

Cesium atoms play a double role in the formation of negative ions. First, Cs atoms are positively ionized by the hot surface of the ionizer. A potential bias applied between the ionizer and the target cathode accelerates the positive Cs ions toward the cathode and they sputter the material from its surface. Second, some of the Cs vapors condense on the front of the cathode which is kept at low temperature by a water cooling system. The sputter atoms will pick up electrons as they pass through the condensed Cs layer, producing negative ions. The negative ions are accelerated back across the ionizer-cathode bias, focussed by an electrostatic Einzel lens and accelerated by an additional extraction voltage to reach a specific total energy.

Figure 4.7. The source of negative ions by cesium sputtering (SNICS) [17].

By changing the material that makes the cathode, negative ions of many elements of the periodic table can be produced. The cathode material consists of the element of interest such as either a pure solid metal, or a powder, or a granular
sample (mixed with silver powder) compacted into a copper sleeve. If a material has poor thermal conductivity or low melting points, a compound with more suitable properties can be used. A good guide for the selection of cathode materials is Middleton’s report entitled ‘A Negative Ion Cookbook’ [17] where the production of a large variety of negative ions using Cs sputtering technology is described.

At the present time there is no microscopic theory describing negative ion formation by sputtering. The experimental data suggests that the process is similar to surface ionization [125]. Neglecting the statistical factors, the negative ion yield is proportional to \( \exp \left( \frac{E_A - \Phi_s}{kT} \right) \), where \( E_A \) is the electron affinity, \( \Phi_s \) is the effective work function of the sputter surface, \( k \) is the Boltzmann constant and \( T \) is the temperature of the sputter surface. The negative ion yield will be high only when \( \Phi_s \leq E_A \). The work functions of most elemental surfaces lie between 3.5 and 4.5 eV and electron affinities are 1 – 2 eV [125], so sputtering seems to be inefficient for negative ion formation. But the presence of a thin layer of cesium on the sputter surface reduces the work function and dramatically increases the negative ion yield.

The sputter process is inefficient or unstable until a sputter crater is formed on the cathode. Usually a new cathode is “burnt in” for hours, or even days before an experiment can start. Generally the sputtering is accompanied by the formation of a small ball of bright plasma, and is largely concentrated within a circle of less than 1 mm diameter. Furthermore, the negative ion yield or current depends sensitively on the position of the cathode. In order to obtain reasonable ion beam currents plasma temperatures range between 500 K and 1500 K. The ideal ion source will produce a stable beam with only one electronic state populated, but this cannot always be achieved. In reality, the Boltzmann distribution describes the population of the excited states of the negative ions. Thus studies of the ground states of negative ions
need a lower temperature in order to have a lower background signal from the excited states. On the other hand, larger sputter temperature yields larger excited state populations which are favorable for studies of these states.

So far we used the SNICS II ion source to produce intense and stable ion beams of: Li$^-$, B$^-$, C$^-$, Si$^-$, S$^-$, Fe$^-$, Ni$^-$, Se$^-$, Ru$^-$, Pd$^-$, Ag$^-$, Pt$^-$, CN$^-$, and C$_{60}$$^-$. The measured ion currents after shaping and spatial trimming of few of the negative-ion beams are presented in Table 4.3.

<table>
<thead>
<tr>
<th>Negative Ion</th>
<th>Ion Current [nA]</th>
<th>Origin of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^-$</td>
<td>150</td>
<td>Berrah et al. [13]</td>
</tr>
<tr>
<td>B$^-$</td>
<td>100</td>
<td>Berrah et al. [46]</td>
</tr>
<tr>
<td>C$^-$</td>
<td>100</td>
<td>Walter et al. [47]</td>
</tr>
<tr>
<td>S$^-$</td>
<td>280</td>
<td>Bilodeau et al. [83]</td>
</tr>
<tr>
<td>Fe$^-$</td>
<td>40</td>
<td>Dumitriu et al. [120]</td>
</tr>
<tr>
<td>Pt$^-$</td>
<td>100</td>
<td>Bilodeau et al. [84]</td>
</tr>
</tbody>
</table>

4.3. The negative ion beam

The negative ion beam extracted from the cesium sputter source passes through a mass analyzer magnet. Once the ion of interest is selected, it is merged collinearly with the counter-propagating photon beam from ALS beamline 10.0.1, as illustrated in Fig. 4.8. Merging the ion and photon beam require considerable tuning of their position with respect to each other. This is accomplished by changing the
voltages on the steering plates, Einzel lenses, merger spherical deflector and the field-strength of the analyzing magnet. Beam profile monitors and slit scanners are used in order to check the overlap between the negative ion and photon beam. Inner-shell photodetachment and subsequent Auger decay produce positive ions. The positive ions are deflected by the de-merging magnet and detected with a channeltron detector. The charge pulses produced by the detector are directed to a fast amplifier then separated from the electronic noise by a constant-fraction discriminator. This produces TTL logic pulse which is directed to the data acquisition system.

Figure 4.8. Schematic of photon-ion beam (IPB) endstation at beamline 10.0.1 [115].

4.3.1. The analyzing magnet

In addition to the element of interest, negative ions are also formed from contaminants present in the cathode material and from the background gas. The negative ion beam is therefore mass-analyzed by a transverse magnetic field produced
by a sector C-magnet with 10-cm pole gap, and bending radius of 59 cm, see Fig.4.9. The horizontal and vertical slits, before and after the magnet, define the ion beam trajectory and its cross-sectional area, and the mass resolution.

A deceleration Einzel lens with the same polarity as the ion beam charge focuses the negative ion beam. Two sets of mutually perpendicular electrostatic steering plates are used to control the position of the negative ion beam in the vertical and horizontal directions as well as the vertical angle of the ion beam. Adjustable beam slits located after the steering section defines the size of the ion beam.

**Figure 4.9.** The analyzing magnet, merger and interaction region IPB endstation.
4.3.2. **Merger and interaction region**

The ion beam is merged onto the axis of the counter-propagating photon beam by a pair of 90° spherical-sector bending plates. A hole in the back plate of the merger allows the photon beam to pass through and be detected by a calibrated silicon photodiode [126]. Fine-tuning overlap of the beams is achieved by the two sets of steering plates. The trajectory of the ion beam in the interaction region may be shifted applying slightly asymmetric voltages on the spherical bending plates. An Einzel lens, consisting of two grounded cylinders and a central biased one, focuses the beam in the center of the interaction region.

The interaction region is an isolated stainless-steel-mesh cylinder. A series of entrance and exit apertures accurately define the effective length of the interaction region (L=29.4 cm). An electrical potential may be applied on the interaction region. In this case the photoions produced inside of this region are energy-labeled and can be separated downstream from the photoions produced outside the interaction region.

The intensity distribution of both beams is measured by rotating-wire beam profile monitors installed upstream and downstream of the interaction region. The overlap between the ion and photon beam is monitored by three translating slit-scanners, located near the entrance, middle and exit of the interaction region. Typical two-dimensional spatial intensity profiles of the ion and photon beams are shown in Fig. 4.10. The positions and profiles of the two beams are continuously monitored while tuning the beam. The monitors are removed from the beam path during data collection. Typically, the magnetically mass-selected negative ion beam with a diameter of ≈ 5 mm overlapped the counter-propagating photon beam with a spatial width of 1.2 mm over a distance of about 1.5 m.
The products resulting from the photodetachment process (positive ions) are separated from the parent beam (negative ions) by a 45° dipole analyzing magnet located downstream of the interaction region, called the demerger, see Fig. 4.11.

**Figure 4.11.** Side view of the demerger section of IPB endstation.
The negative ion beam is collected by a large Faraday cup located below the magnet and its current is measured by a sensitive electrometer whose analog output is directed to a voltage-to-frequency converter, providing a normalization signal to the data acquisition system. The magnetic field of the demerger is set such that the product ions pass through an aperture and a cylindrical tube, and thus the dispersion in the vertical plane is removed.

The positive ions (signal) are directed onto a stainless steel plate biased at –550 V by a spherical 90º electrostatic deflector. Secondary electrons emitted by the steel plate are accelerated and detected by a channeltron detector used in a pulse-counting mode. The deflection planes of the demerger magnet and the spherical deflector are orthogonal. This geometry permits the products to be swept across the detector in mutually perpendicular directions. A cylindrical Einzel lens located downstream of the interaction region provides further diagnosis of complete collection for the positive ions.

The charge pulses produced by the channeltron are directed to a fast amplifier then separated from electronic noise by a constant-fraction discriminator. This produces a TTL logic pulse which is directed to the data acquisition system. The schematic of the electronics set-up is presented in Fig. 4.12.

![Figure 4.12. The schematic of the electronic set-up.](image-url)
A source of background signal arises from photodetachment events due to collisions of the negative ions with the residual background gas. In order to reduce the background signal ultra-high vacuum conditions are required. This is accomplished by a 1000 l/s turbomolecular pump located in the section between the analyzing magnet and the merger, a 2000 l/s cryopump below the merger (see Fig. 4.9). Oil-free scroll backing pumps are used for turbomolecular pumps to prevent hydrocarbon contamination of the beamline elements. Two 500 l/s mag-ion pumps, one located under the interaction region and the other downstream of the demerger magnet maintain a pressure of ~5 x 10^{-10} torr in the interaction region (see Fig. 4.9 and Fig. 4.11). The ALS and IPB endstation are protected from accidental loss of vacuum by a system of on-line gate valves interlocked to pressure ionization gauges.

The background count rate is not negligible even under the ultra-high vacuum conditions. These positive ions produced by stripping collisions of the primary ion beam with the residual gas will be also detected and counted together with the photoions. The background signal must be subtracted by mechanically chopping the photon beam on and off. A stepping-motor-driven paddle installed upstream of the endstation chops the photon beam at a frequency of 6 Hz. By chopping the photon beam and subtracting the "photon-off" from the "photon-on" counts, the background signal is accounted and the photodetachment signal is determined.

4.4. Absolute photodetachment cross section

Absolute photodetachment cross sections for negative ions are essential for testing the many theoretical predictions available dealing with many-body effects in negative ion photodetachment [127]. They are also needed to model different types of plasmas in astrophysics. Absolute photodetachment cross section measurements are
very challenging, so experimental data on photodetachment cross sections for negative ions are very limited compared with the cross section data on neutral atoms and positive ions. The merged-beam technique has the significant advantage of measuring directly the absolute cross section, since the density of the target ion beam can be determined. The main disadvantage of this method is that the metastable states of the target ions are often populated. When an unknown fraction of metastable target ions is present in the beam, the cross section can not considered to be absolute [112].

Also, it is important to distinguish between absolute measurements and ion-yield measurements normalized to few absolute data points. The main difference is that in the absolute measurements the form factor, a measure of the ion-photon beam overlap, is determined for all photon energies, while this is only done for the few photon energies (the measured absolute points) in the ion-yield measurements. Typically, the accuracy of the measured cross sections is 10-35% [112]. Since the form factor may vary significantly with photon energy and time, the second method may produce normalized ion-yield data which apparently differ by much more than 20% from the absolute cross section [6]. Photodetachment of negative ions has received intense interest during the last few years and Table 4.4 gives an overview of measured inner-shell photodetachment cross sections [6].

The IPB endstation at the ALS beamline 10.0.1 has been designed to facilitate absolute cross section measurements for interactions of photons with negative/positive ions. The IPB endstation has two modes of operation: spectroscopy and absolute mode [135]. In spectroscopy mode, the interaction region bias voltage is set to zero, so the length of the merged path photon-ion beam is maximum. Spectroscopy mode is used to record the photoion-yield spectrum as a function of photon energy. In absolute mode, a bias voltage is applied to the interaction region,
thus the interaction length photon-ion beam is accurately defined for cross-section measurements.

The absolute cross section data presented in this thesis are ion-yield measurements normalized to few absolute data points. The absolute cross section measurements are performed at a number of photon energies where there are no resonant features in the photon-yield spectra. For each photon energy (hv) point, the total absolute photodetachment cross section (σ) is given by the formula:

$$\sigma(hv) = \frac{(qvR)}{(\Gamma \Phi F)} \quad (4.7)$$

Where q is the charge state of the parent ion [C], v is the ion velocity inside the interaction region (cm/s), R is the signal rate [Hz], \(\Gamma\) is the primary ion beam current [A], \(\Phi\) is the photon flux [photons/s], F is the total form factor [cm⁻¹].

**Table 4.4.** Experimental cross section data for inner-shell photodetachment of negative ions [6].

<table>
<thead>
<tr>
<th>Target</th>
<th>Cross Section Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>He⁻</td>
<td>Bilodeau <em>et al.</em> [107, 128, 83]; Berrah <em>et al.</em> [87]</td>
</tr>
<tr>
<td>Li⁻</td>
<td>Berrah <em>et al.</em> [13]; Kjeldsen <em>et al.</em> [14]</td>
</tr>
<tr>
<td>B⁻</td>
<td>Berrah <em>et al.</em> [129,46,106]</td>
</tr>
<tr>
<td>C⁻</td>
<td>Walter <em>et al.</em> [47]; Gibson <em>et al.</em> [130]</td>
</tr>
<tr>
<td>Na⁻</td>
<td>Covington <em>et al.</em> [91]</td>
</tr>
<tr>
<td>S⁻</td>
<td>Bilodeau <em>et al.</em> [83, 131]</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Aguilar <em>et al.</em> [92]; Sandstrom <em>et al.</em> [132]</td>
</tr>
<tr>
<td>Fe⁻</td>
<td>Dumitriu <em>et al.</em> [120]</td>
</tr>
<tr>
<td>Ru⁻</td>
<td>Dumitriu <em>et al.</em> [175]</td>
</tr>
<tr>
<td>Te⁻</td>
<td>Kjeldsen <em>et al.</em> [133]</td>
</tr>
<tr>
<td>I⁻</td>
<td>Kjeldsen <em>et al.</em> [134]</td>
</tr>
<tr>
<td>Pt⁻</td>
<td>Bilodeau <em>et al.</em> [84]</td>
</tr>
</tbody>
</table>
The signal rate is \( R = \frac{R_0}{\Omega_{\text{det}} \Omega_{\text{elecr}}} \), where \( R_0 \) is the measured count rate, \( \Omega_{\text{det}} \) is the detector efficiency and \( \Omega_{\text{elecr}} \) is the pulse detection efficiency of the electronics. The detector efficiency includes the possibility of \( \Omega_{\text{det}} > 100\% \) to account for possible double-counting events arising from electronic ringing and other effects.

The total form factor (or the beam overlap integral), \( F = \int F(z) dz \), defines the spatial overlap of the photon and ion beams along the common interaction path. The propagation direction of the ion beam is considered as the z-axis. The 2D form factors \( F(z_i) \) were estimated based on ion and photon beam profiles measured by the slit scanners at three positions \( z_i \) using the following relation:

\[
F(z_i) = \frac{\iint I(x,y) \Gamma(x,y) dx dy}{\iint I(x,y) dx dy} \frac{\iint \Gamma(x,y) dx dy}{\iint \Gamma(x,y) dx dy}
\]

To a good approximation, it is assumed that the primary beam current density \( \Gamma(x,y) \), and the photodiode current density \( \Gamma'(x,y) \) are separable in the form \( \Gamma(x,y) = \Gamma(x) \Gamma'(y) \), and \( \Gamma'(x,y) = \Gamma'(x) \Gamma'(y) \) since the scanner integrates over two perpendicular directions rather than providing two-dimensional beam intensity profiles [112, 136]. The variation of the form factors along the z-axis is approximated by a second order polynomial, and \( F(z) \) was obtained interpolating \( F(z_i) \), as shown in Fig. 4.12. The total form factor, \( F = \int F(z) dz \), was determined integrating along the length of the biased interaction region, \( L = 28.3 \) cm.

The main sources of background signal, the signal observed without photons present, are ions scattered by the apertures etc., ionization as a result of collisions between the negative ions and the vacuum gas, and highly-excited state metastable ions that are emitted by the ion source and spontaneously decay in the interaction region by autodetachment. The total background is minimized by the design of the apparatus and by keeping the interaction region under UHV conditions, typically \( 5 \times 10^{-10} \) Torr. Fortunately, in the case of the SNICS source the background from the
metastable ions is dependent on the ion source temperature, and can be reduced by applying appropriate settings.

**Figure 4.13.** Form factors for different \( z_i \) in the interaction region.

In the case of Fe\(^-\) negative ions, the absolute cross section was measured at four discrete photon energies and the photoion yield spectrum was normalized by fitting a slowly varying function to their measured ratio as a function of photon energy. Typical experimental parameters for absolute photodetachment cross section measurements for Fe\(^-\) at a photon energy 53.71 eV are listed in Table 4.5 [120].

Absolute measurements need accurate photon and ion detector calibrations. The transmission and efficiencies must be measured. For the photon flux calibration, two identical absolutely calibrated silicon X-ray photodiode are installed permanently in the IPB endstation and gave consistent measurements within 2%. The photodiode manufacturer provided a batch calibration traceable to NIST, with quoted uncertainty of 5%.
Table 4.5. Typical experimental parameters for Fe\textsuperscript{−} absolute cross section measurements.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value at photon energy of 53.71 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Beam Energy, E</td>
<td>9.25 keV</td>
</tr>
<tr>
<td>Ion Beam Current, I\textsuperscript{−}</td>
<td>8 nA</td>
</tr>
<tr>
<td>Photodiode Current, I\textsuperscript{γ}</td>
<td>0.200 mA</td>
</tr>
<tr>
<td>Interaction Region Bias, V\textsubscript{int}</td>
<td>+0.75 keV</td>
</tr>
<tr>
<td>Ion Interaction Velocity, v</td>
<td>2.7 x 10\textsuperscript{5} m/s</td>
</tr>
<tr>
<td>Fe\textsuperscript{+} Signal Rate, R</td>
<td>470 Hz</td>
</tr>
<tr>
<td>Fe\textsuperscript{+} Background Rate</td>
<td>370 Hz</td>
</tr>
<tr>
<td>Form Factors: F(z\textsubscript{1}), F(z\textsubscript{2}), F(z\textsubscript{3})</td>
<td>6.79 cm\textsuperscript{2}, 8.73 cm\textsuperscript{2}, 8.89 cm\textsuperscript{2}</td>
</tr>
<tr>
<td>Total Form Factor, F</td>
<td>243.4 cm\textsuperscript{1}</td>
</tr>
<tr>
<td>Merge-path Length, L</td>
<td>28.3 cm</td>
</tr>
<tr>
<td>Detector Efficiency, Ω\textsubscript{det}</td>
<td>97.5 %</td>
</tr>
<tr>
<td>Pulse Detection Efficiency for electronics, Ω\textsubscript{electr}</td>
<td>100 %</td>
</tr>
<tr>
<td>Cross Section, σ</td>
<td>5.7 x 10\textsuperscript{-18} cm\textsuperscript{2}</td>
</tr>
</tbody>
</table>

The detector calibration required us to operate the detector alternately as a Faraday cup and as a single-particle detector. The absolute detection efficiency is obtained by comparing the count rate \( S \) observed into the detector and the number of negative ions per second \( i\textsuperscript{−} \) that reach the detector measured by an averaging sub-femtometer

\[
Ω = \frac{Sq e}{i\textsuperscript{−}} \tag{4.9}
\]

where \( q \) is the charge of the ion and \( e \) is the electron charge.

The efficiencies depend slightly on the energy, mass and charge of the ions. The detector efficiency has been periodically measured for a variety of ions ranging from singly charged ions to multiply charged ions for the last two years of use and gave a consistent value of 100(5) % [137]. The double-counting events arising from electronic ringing and other effects may lead to \( Ω_{\text{det}} > 100\% \). However, due to the very
low density of the negative ion beam the detector calibration is an extremely sensitive measurement.

The accuracy of the cross section data is determined by easily quantified statistical fluctuations (random errors) and a number of systematic contributions which are more difficult to estimate. The systematic uncertainty is more likely to be 10-15% and is dominated by the uncertainty in the determination of the absolute photon flux (5-10%), the uncertainties in the total form factor F (2-5%), and the detector efficiency (1-3%) [112]. Table 4.6 presents the uncertainties in the absolute cross section measurements for Fe⁻ negative ion.

**Table 4.6.** Uncertainties reported to 1 SD in absolute cross section measurements of Fe⁻ leading to Fe⁺ production.

<table>
<thead>
<tr>
<th>Source</th>
<th>Systematic</th>
<th>Random</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary ion collection</td>
<td>4%</td>
<td>1%</td>
<td>4%</td>
</tr>
<tr>
<td>Primary ion velocity</td>
<td>1%</td>
<td>-</td>
<td>1%</td>
</tr>
<tr>
<td>Photodiode calibration</td>
<td>5%</td>
<td>1%</td>
<td>5%</td>
</tr>
<tr>
<td>Form factor measurement and integration</td>
<td>8%</td>
<td>3%</td>
<td>9%</td>
</tr>
<tr>
<td>Interaction region length</td>
<td>5%</td>
<td>-</td>
<td>5%</td>
</tr>
<tr>
<td>Photoion detector efficiency</td>
<td>5%</td>
<td>-</td>
<td>5%</td>
</tr>
<tr>
<td>Photoion collection efficiency</td>
<td>3%</td>
<td>3%</td>
<td>4%</td>
</tr>
<tr>
<td>Pulse counting efficiency</td>
<td>2%</td>
<td>-</td>
<td>2%</td>
</tr>
<tr>
<td>Quadrature sum</td>
<td>13%</td>
<td>5%</td>
<td>14%</td>
</tr>
</tbody>
</table>
All errors are assumed to be independent and added in quadrature and reported to one standard deviation (1 SD), therefore the total systematic instrumental error in this case is ±14 [120].

The merged-beam set-up at ALS has proven its capabilities through numerous photodetachment and photoionization experiments involving various negative ions and positive ions, respectively. The present set-up is permanent, so once the experiment is aligned it remains aligned, and both the photodiode and the photoion detector can be calibrated in situ. This allows for a much more efficient use of the beam time since the ion sources can be tested before the actual experiment, and many different sources can be used with the set-up. The entire system is computer controlled and the parameter settings can be stored for documentation. The data acquisition software designed by Dr. John Bozek is using Lab Windows, and the codes are written in C+.

The ALS set-up is versatile and successful, therefore ten (out of twelve) inner-shell absolute photodetachment cross-section measurements, presented in Table 4.4, were performed at beamline 10.0.1. At the present moment, the beamline photon energy range is 17 - 340 eV. If higher energy is required to access the inner-electrons, e.g. the binding energy of oxygen K-shell electrons is 543.1 eV [138], the experiment can not be performed at beamline 10.0.1. Furthermore the fixed set-up can not be moved to another ALS beamline. For this reason, our group built a Mobile Ion Photon Beamline (MIPB) which can be easily mounted at different beamlines in order to access photon energies not available at ALS beamline 10.0.1.
CHAPTER 5

INNER-SHELL PHOTODETACHMENT OF IRON NEGATIVE ION

This chapter presents the inner-shell photodetachment from Fe⁻ in the 48-72 eV photon energy range. The absolute photodetachment cross sections of Fe⁻ leading to Fe⁺ and Fe²⁺ ion production were measured. The 3p → (3d + ed) photoexcitation in the Fe⁻ negative ion gives rise to shape resonances. In the near-threshold region, shape resonance profiles with l=2 accurately fit the single photodetachment cross section. Simultaneous double-photo-detachment was also observed, resulting in an increased Fe²⁺ production which obeys a Wannier law. Despite the large number of possible terms resulting from the Fe⁻ 3d -open shell, a simple calculation using the R-matrix method qualitatively agrees well with the experimental data.

5.1. Introduction

Throughout the universe, transition 3d metals are abundant [18], and the interaction of 3d metal atoms and ions with radiation is of great importance for astrophysics. Extensive theoretical work has been performed in order to calculate the photoionization cross sections for atoms and ions of astrophysical relevance (see the Opacity [19] or Ferrum [20] Projects). In addition, 3d metals and their compounds are of extreme practical importance in metallurgy, magnetism, and data storage systems [21]. The spectra of transition metals are very complex due to the coupling of 3d
electrons with core holes and strong interaction with the underlying continua [6]. The $3d$ orbital retains to a high degree the same characteristics in solids [22], so the atomic and ionic data could be very useful to contribute information toward understanding intra- and inter-atomic effects.

Iron, lying at the maximum of the nuclear stability curve, is an important astrophysically abundant element [6]. Ionization of positive iron ions by electron impact has been extensively studied in crossed-beam experiments [140]. Several photoionization measurements with synchrotron radiation studying $3p$-photoionization resonances in neutral atomic iron have also been reported [141]. The absolute photoionization cross section of Fe$^+$ has been measured in a relevant energy region for astrophysical applications (15.8 – 180 eV) using the merged ion-photon beam technique [99]. Photoionization of higher charge states of iron has been explored theoretically as part of both the Opacity [19] and the Iron [142] Projects. However the accuracies of these calculations are questionable as shown by a recent systematic photoionization study along the iron isonuclear sequence [143]. Despite numerous research activities for neutral iron and its positive ions, there are only a few valence-shell photodetachment studies for the iron negative ion. The electron affinity of Fe$^-$ (0.151(3) eV [16]) has been determined by laser photoelectron spectroscopy. Measurements of partial photodetachment cross sections and photoelectron angular distributions of Fe$^-$ at visible photon wavelengths have also been reported [24].

The fundamental physics of the interaction of iron atoms and ions with photons is interesting but difficult to analyze in detail. Due to angular momentum coupling there are a large number of possible terms resulting from the open $3d$ shell. Thus, for an accurate description of the photoionization process, strong correlations between these terms as well as relativistic effects have to be taken into account [6, 21,
The main features in the spectra of the neutral transition metals are the so-called “giant resonances” which appear in the vicinity of the $3p$ threshold [6]. Comparing the resonances in the iron negative ion photodetachment cross section with the “giant resonances” in neutral atoms and positive ions will allow detailed insights into the nature of the resonances.

### 5.2. Experimental method

The experiment was performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, using the High Resolution Atomic Molecular and Optical Physics (HRAMO) undulator beamline 10.0.1 with the ion-photon beamline (IPB). The IPB endstation [16] uses the merged beam technique for photoion spectroscopy, where ions and photons travel collinearly in order to increase the interaction volume between photons and the dilute ion beam (see Chapter 4 for a detailed description of this technique).

The negative ion beam with energy of 8.5 keV was produced using a cesium sputter source (SNICS II from NEC) [17]. The magnetically mass selected ions were deflected by a 90° spherical electrostatic deflector and merged collinearly with the counter-propagating photon beam. Inner-shell photodetachment from Fe⁻ followed by Auger decay produced Fe⁺ positive ions that were steered out of the primary beam by a 45° de-merger magnet and detected as a function of photon energy with an electron multiplier. The de-merger magnet also deflected the primary negative ion beam into a Faraday cup where typical ion currents of 20 nA were recorded after shaping and spatial trimming of the negative ion beam.

In the apparatus, the negative ion beam with a diameter of 5mm overlapped the collimated photon beam with a spatial width of 1.2 mm over a distance of about
1.5 m. However, the photon-ion interaction region was defined by a 29.4 cm long stainless-steel cylinder. The 8.5 keV incoming ions were kinetic energy tagged by applying a constant potential of +0.75 kV to the interaction region. The negative Fe$^-$ ions entering in the interaction region were thus accelerated to 9.25 keV, and the positively charged ions Fe$^+$ (Fe$^{2+}$) resulting from the photodetachment process exited the interaction region experiencing a second kinetic energy boost of +0.75 keV (+1.50 keV), leaving with 10 keV (10.75 keV) of kinetic energy. The Fe$^+$ and Fe$^{2+}$ ions formed outside of the interaction region, having a lower kinetic energy of 8.5 keV, could then be selected against by the de-merger magnet and spherical electrostatic deflector located before the detector. Only charged products can be detected with the present apparatus. Therefore, if neutral Fe atoms were produced, they could not be detected.

In order to optimize the ion-photon beam overlap, two rotating wire beam profile monitors were used at the front and the rear of the interaction region. In addition, the beam was characterized by three translating-slit scanners, located near the entrance, middle and exit of the interaction region. The outputs through these monitors were recorded by a computer and thus two-dimensional profiles of the ion and photon beams were obtained. The monitors were removed from the beam path during the data collection.

The significant background signal produced by collisions between the negative ions and the residual gas ($\approx 4 \times 10^{-10}$ torr) or apertures in the beamline could be accounted for by chopping the photon beam at 6 Hz, and subtracting the "photon off" from the "photon on" counts. The photon energy was scanned by rotating the spherical-grating monochromator and translating the exit slit of the monochromator while simultaneously adjusting the undulator gap to maximize the photon beam
intensity. Several sweeps over the photon energy of interest were recorded and summed in order to improve the signal-to-noise ratio. The photon energy scale was calibrated using accurately known (2 to 4 meV uncertainties are quoted to 1 standard deviation (SD) throughout) absorption lines in He [144]. The total uncertainty in the calibrated lab-frame photon energy was estimated to be 40 meV. By the direct measurement of the interaction bias potential and the ion source acceleration potentials, the beam energy in the interaction region was determined to be 9.25(17) keV which gives sufficient ion velocity to produce a significant Doppler shift. In this experiment, the ion-frame Doppler shift is 30 meV to 42 meV for the photon energy of 50 eV to 70 eV. The energy correction has been applied to all the spectra here reported.

5.3. Results and discussions

The absolute cross sections for photoexcitation of Fe$^-$ leading to Fe$^+$ production were measured for the four photon energy points listed in Table 5.1. The absolute cross sections ($\sigma$) are calculated from the measurements of the target-ion current ($I$), velocity ($v$), charge ($q$), signal rate ($R$), form factor ($F$), and photon flux ($\Phi$) as follows: $\sigma = (q \cdot v \cdot R) / (I \cdot F \cdot \Phi)$ [18]. The signal rate is $R = R_0 / (\Omega_{\text{det}} \cdot \Omega_{\text{electr}})$, where $R_0$ is the measured count rate, $\Omega_{\text{det}}$ is the detector efficiency and $\Omega_{\text{electr}}$ is the electronics pulse detection efficiency. In the present experiment the detector efficiency $\Omega_{\text{det}}$ was estimated to be 100(5)% [137] and $\Omega_{\text{electr}}$ was 97.5(20)%. Note that we include the possibility of $\Omega_{\text{det}} > 100\%$ to account for possible double-counting events arising from electronic ringing and other effects. The total (one standard deviation) systematic instrumental error was ±14%.

The two dimensional form factors, $F_z = \int \Phi_x dx \int \Phi_y dy$, were estimated based
on ion $(i)$ and photon $(\Phi)$ beam profiles which are measured by the slit scanners. The total form factor $(F)$, a measure of the quality of the overlap of the ion beam with the photon beam, is obtained by integration of the quadratic interpolation of these three 2D form factors over the interaction region length. For an accurate determination of the form factor, the ion-photon interaction volume must be well defined.

**Table 5.1.** Measured absolute cross section $\text{Fe}^- \rightarrow \text{Fe}^+$ and $\text{Fe}^{2+}$ and ratio of channel strengths $(\text{Fe}^{2+}/\text{Fe}^+)$ reported to 1 SD.

<table>
<thead>
<tr>
<th>Photon Energy [eV]</th>
<th>Cross Section $\text{Fe}^+$ [Mb]</th>
<th>Cross Section $\text{Fe}^{2+}$ [Mb]</th>
<th>Ratio of the channel strengths $\text{Fe}^{2+}/\text{Fe}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.23</td>
<td>0.89(13)</td>
<td>0.125(21)</td>
<td>0.141(11)</td>
</tr>
<tr>
<td>53.71</td>
<td>5.7(9)</td>
<td>0.59(10)</td>
<td>0.103(8)</td>
</tr>
<tr>
<td>58.24</td>
<td>4.5(7)</td>
<td>0.58(10)</td>
<td>0.128(10)</td>
</tr>
<tr>
<td>70.24</td>
<td>2.5(4)</td>
<td>0.69(12)</td>
<td>0.275(21)</td>
</tr>
</tbody>
</table>

This was accomplished with the $+0.750(15)$ keV applied to the interaction region. The effective interaction region length of 28.3(14) cm was determined from electrostatic simulations using SIMION 7.00 [145] and the ion kinetic energy acceptance of the spherical-sector deflectors positioned just before the positive-ion detector.

The ratio of channel strengths $(\text{Fe}^{2+}/\text{Fe}^+)$ was measured at the same photon energies as the absolute cross sections following the same procedure as previous experiments [83, 131]. With the present apparatus only one channel can be monitored at any particular time. So, the signal rates $R(\text{Fe}^+)$ and $R(\text{Fe}^{2+})$ were recorded in rapid succession (1-4 minutes per product per energy point) and the measurements were repeated six times to verify that no significant fluctuations in the overlap, ion current,
or other such effects were present. The ratio of channel strengths \((\text{Fe}^{2+}/\text{Fe}^+\)) is reported in Table 5.1. Figure 5.1 shows the absolute photodetachment cross section of \(\text{Fe}^-\) to the \(\text{Fe}^+\) and \(\text{Fe}^{2+}\) product channels. The large circles with error bars in Fig. 5.1 represent the absolute cross section measurements to which the spectra are normalized by using the same method as in previous experiments [16, 83, 131].

Photodetachment of \(\text{Fe}^-\) ([Ar] 3d\(^7\)4s\(^2\) \(^{4}\text{F}_{9/2}\)) proceeds from the inner 3\(p\) shell via three channels. The relevant states in the negative ion, the parent Fe atom, and the positive ion \(\text{Fe}^+\) are presented in Fig. 5.2. According to dipole selection rules, the emitted photoelectron can be either an \(\varepsilon s\) or an \(\varepsilon d\) electron (\(\varepsilon\) represents the kinetic energy of the outgoing electron), and the majority of \(\text{Fe}^+\) and \(\text{Fe}^{2+}\) formation probably happens in step-wise processes that can be written schematically as:

\[
\text{hv} + \text{Fe}^- (3p^63d^74s^2)^{4}\text{F}_{9/2}) \rightarrow \text{Fe}^-^* (3p^53d^84s^2 \ [{}^4\text{D,} \ ^4\text{F,} \ ^4\text{G}])
\]

\[
\downarrow \text{first step}
\]

\[
\text{Fe}^{++} + \text{e}_\text{photoelectron}
\]

\[
\downarrow \text{second step}
\]

\[
\text{Fe}^{+*} + \text{e}_\text{Auger}
\]

\[
\downarrow \text{third step}
\]

\[
\text{Fe}^{2+} + \text{e}_\text{Auger}
\]

The photodetachment may also lead to the production of neutral Fe and possibly \(\text{Fe}^{3+}\), but neutral Fe cannot be detected with the present system, and no \(\text{Fe}^{3+}\) ions were observed.

Excitation of a 3\(p\) electron in \(\text{Fe}^-\) leads to quasidiscrete \(3p^53d^84s^2 \ [{}^4\text{D,} \ ^4\text{F,} \ ^4\text{G}]\) \textit{shape} resonances. In this case the one-electron potential produced by the short-range attraction and the centrifugal repulsion form a barrier large enough to trap the electron behind it. The primary decay mechanism is tunneling through the barrier,
and thus the width and strength of the resonances are influenced by the particular form of the potential. This resonance behavior has been reported for other photodetachment studies such as in Li$^-$ [14, 13, 45, 104], B$^-$ [46, 106, 146], and C$^-$ [47, 130, 147]. In contrast, negative ions for which the valence shell can be filled completely (or become half full) by photoexcitation of an inner-shell electron may exhibit Feshbach resonances due to the enhanced stabilization [83, 128, 133].

Figure 5.1. The measured photodetachment cross section for Fe$^+$ and Fe$^{2+}$ from Fe$^-$. The cross-section scale was established by making absolute measurements (denoted by filled circles) at the four energies shown.
Theoretical predicted energy for this state is ~66 eV [19].

*Resonance energies measured in the present experiment.

**Figure 5.2.** Simplified energy-level diagram for Fe⁻ and the relevant states in the parent Fe atom and positive ion Fe⁺ and Fe²⁺. For clarity purpose the diagram is not to scale. The electron affinity of atomic Fe 0.151(3) eV [23], and all other energies are reported relative to the ground state of the negative ion Fe⁻. The solid lines represent the measured resonance energies. The dotted lines represent the ground state for the positive ions Fe⁺ and Fe²⁺ [155]. The dashed lines are the theoretically calculated energies of 3p excited states of Fe⁺ [19].

Based on the above studies, and since promoting the 3p electron into the 3d
orbital in Fe$^-$ ([Ar]3d$^7$4s$^2$ 4F$_{9/2}$) does not result in filling the subshell, the formation of shape resonances is the most likely. Indeed, three large shape resonances dominate the photodetachment spectrum for Fe$^-$ leading to Fe$^+$, as discussed below.

In order to gain a qualitative understanding of the resonance phenomena occurring in the complete photodetachment process, we performed simple calculations using the R-matrix method [148]. Whereas an enormous amount of configuration interaction and a large number of neutral Fe target states would be needed to obtain any type of converged atomic description, and relativistic effects are certainly non-negligible, we were only concerned with the gross features of the photodetachment process, so the problem was simplified as follows. First, all relativistic effects, including the spin-orbit interaction, were omitted, so that an LS description was valid. (We later included relativistic effects in a separate structure calculation, neglecting the continuum, so as to study the fine-structure splitting of resonance states, as mentioned below.) Second, our atomic basis consisted of a single-configuration description for the initial Fe$^-$ 3p$^6$3d$^7$4s$^2$ ($^4$F$_{9/2}$) ground state, the photodetached neutral Fe 3p$^6$3d$^6$4s$^2$ ($^5$D$^0$) ground state, and some of the 3p-excited Fe* states, namely the 3p$^5$3d$^7$4s$^2$ ($^5$G$^0$), 3p$^5$3d$^7$4s$^2$ ($^5$F$^0$), 3p$^5$3d$^7$4s$^2$ ($^5$D$^0$), 3p$^5$3d$^7$4s$^2$ ($^3$G$^0$), 3p$^5$3d$^7$4s$^2$ ($^3$F$^0$), and 3p$^5$3d$^7$4s$^2$ ($^3$D$^0$) states. The partial and total theoretical absolute photodetachment cross sections for Fe$^-$ are shown in Fig. 5.3. By examining the partial cross sections, the dominant contribution in each partial wave is found to be from the 3p$^5$3d$^7$4s$^2$ ($^5$G$^0$)$_{ed}$ channel. This channel gives rise to two $^4$D shape resonances, 3p$^5$[3d$^8$($^3$P)] ($^4$D) and 3p$^5$[3d$^8$($^3$F)] ($^4$D), but only one resonance in each of the other two partial waves 3p$^5$[3d$^8$($^3$F)] ($^4$F) and 3p$^5$[3d$^8$($^3$F)] ($^4$G).

We have assessed that post collision interaction (PCI) recapture is negligible. As in the earlier cases of B$^-$ [46] and C$^-$ [47] inner-shell photodetachment, even if
recapture does occur, only doubly-excited Fe** states remain following the departure of the intermediate Auger electron, and these doubly-excited states subsequently undergo a second Auger decay, yielding an Fe^+ ion that is detected.

In order to align the photon energies between the experimentally (50.5(5) eV) and theoretically determined thresholds a global shift of -2.4 eV has been applied to the theoretically calculated cross sections, as shown in Fig. 5.3.

Figure 5.3. Theoretical results are shown for the individual \(^4\)G, \(^4\)F, and \(^4\)D symmetry contributions (dotted lines) and the total, summed cross section (solid line).
The resonance energies and parameters predicted by theory and the measured values are shown in Table 5.2. Since we were unable to include relativistic interactions in our R-matrix calculations, we performed separate multi-configurational Hartree-Fock (MCHF) structure calculations, where the spin-orbit operator was included, to obtain fine-structure-resolved resonance energies.

The resonance widths, on the other hand, were obtained by fitting the R-matrix cross section with shape resonance profiles. Our crude atomic description of the resonances, using only a single configuration, led to severe overestimates of the resonance energies. Thus, a global shift of -9.4 eV was applied to the theoretical resonance energies in Table 5.2 in order to align them with the measured values.

<table>
<thead>
<tr>
<th>Resonance</th>
<th>Energy\textsuperscript{\textit{experiment}}</th>
<th>Width\textsuperscript{\textit{experiment}}</th>
<th>Energy\textsuperscript{\textit{theory}}</th>
<th>Width\textsuperscript{\textit{theory}}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[eV]</td>
<td>[eV]</td>
<td>[eV]</td>
<td>[eV]</td>
</tr>
<tr>
<td>3p^{5}[3d^{9}(3F)]4s^{2}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4G_{11/2}$</td>
<td>51.21\textsuperscript{(5)}</td>
<td>0.20\textsuperscript{(4)}</td>
<td>51.02</td>
<td></td>
</tr>
<tr>
<td>$^4G_{9/2}$</td>
<td>51.57\textsuperscript{(5)}$^*$</td>
<td>0.22\textsuperscript{(6)}</td>
<td>51.51</td>
<td>0.63</td>
</tr>
<tr>
<td>$^4G_{7/2}$</td>
<td>51.81\textsuperscript{(6)}$^+$</td>
<td>0.47\textsuperscript{(8)}</td>
<td>51.94</td>
<td></td>
</tr>
<tr>
<td>3p^{5}[3d^{9}(3P)]4s^{2}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4D_{7/2}$</td>
<td>53.23\textsuperscript{(6)}$^+$</td>
<td>0.46\textsuperscript{(24)}</td>
<td>55.22</td>
<td>0.65</td>
</tr>
<tr>
<td>3p^{5}[3d^{9}(3F)]4s^{2}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4F_{9/2}$</td>
<td>53.62\textsuperscript{(5)}$^*$</td>
<td>1.11\textsuperscript{(9)}</td>
<td>56.84</td>
<td>2.25</td>
</tr>
<tr>
<td>$^4F_{7/2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4D_{7/2}$</td>
<td>55.07\textsuperscript{(9)}$^*$</td>
<td>4.32\textsuperscript{(20)}</td>
<td>60.44</td>
<td>8.34</td>
</tr>
</tbody>
</table>

\textsuperscript{+}Data shown in Fig. 5.5.
\textsuperscript{*}Data shown in Fig. 5.4 The $^4F_{9/2}$ and $^4F_{7/2}$ resonances were not resolved in the present experiment.
\textsuperscript{a} Present multi-configurational Hartree-Fock (MCHF) calculation to include fine structure splitting. The reported theoretical energies are shifted by -9.4 eV in order to match the energy of the $^4G_{11/2}$ state.
\textsuperscript{b} Present R-matrix results neglecting spin-orbit splitting.

Nevertheless, overall a qualitatively good agreement between theory and experiment can be seen from Fig. 5.4. We can attribute the three peaks to
$3p \rightarrow (3d + \varepsilon d)$ transitions, with the first sharper structure at about 51.6 eV representing $3p^63d^74s^2 \ (^{4}F_{9/2}) \rightarrow \ 3p^53d^84s^2 \ (^{4}G_{7/2, \ 9/2 ,11/2})$ excitation, the middle structure at 53.62(5) eV representing $3p^63d^74s^2 \ (^{4}F_{9/2}) \rightarrow \ 3p^53d^84s^2 \ (^{4}G_{7/2, \ 9/2})$ excitation, and the last structure with a long tail at 55.07(9) eV representing $3p^63d^74s^2 \ (^{4}F_{9/2}) \rightarrow \ 3p^5[3d^8(^3F)]4s^2 \ (^{4}D_{7/2})$ excitation. The peak widths were found by fitting shape resonance profiles [72, 149] to the resonance peaks giving 1.11(9) eV and 4.32(20) eV for the second and third peak respectively in Fig. 5.4 (see Table 5.2). The theoretical $^{4}F_{9/2} - ^{4}F_{7/2}$ fine structure splitting is 174 meV and given the 1.11(9) eV experimental width of these two peaks combined, the broad natural line width does not allow these two resonances to be resolved.

The energy separation of the $^{4}G$ and $^{4}F$ peaks (first and second peak in Fig.5.4) is 2.045(30) eV, slightly lower than the value of 2.78(70) eV determined from the M$_{2,3}$-shell Auger and autoionization spectra of free Fe atoms [150]. Three similar structures shifted at higher photon energy (57.4 eV, 60.6 eV, and 62.7 eV) and with a larger splitting between peaks were observed in the isoelectronic neutral atomic Co [151]. The 3$p$ photoionization cross section of atomic Fe presents only two broad resonances at 53.5 eV and 56.2 eV [151]. The absolute photoionization cross section data for the positive ion Fe$^+$ in the 3$p$→3$d$ region [99] and the present data for Fe$^-$ exhibit a strong resemblance. The Fe$^+ \rightarrow$ Fe$^{2+}$ single-photodetachment cross section, similar to Fe$^− \rightarrow$ Fe$^+$, presents three broad structures around 53.5 eV, 57.0 eV, and 57.5 eV. The Fe$^+ \rightarrow$ Fe$^{3+}$ double-photoionization cross section presents a strong perturbation near the lowest Fe$^{2+}$ 3$p^{-1}$ threshold (~67 eV) showing that the interaction between simultaneous and sequential double photoionization is strong [99].
Figure 5.4. (upper panel) High-resolution (100 meV) cross section of Fe\(^+\) ions following photodetachment of Fe\(^-\) [see Equation (1)] over a broad photon energy range. The open circles are the experimental data. The solid lines are the results of three shape-resonance profile fits to the data. The cross-section scale was established by making absolute measurements (denoted by filled circles) at the four energies shown.

(lower panel) Theoretical results were shifted by \(\Delta E = -2.4\) eV in order to match the experimental threshold position.

5.3.1. Single photodetachment threshold

The near-threshold photodetachment cross section of Fe\(^-\) was obtained by measuring the positive ion production for Fe\(^+\) in the photon energy range from 50.5 eV to 53.5 eV with a photon energy resolution of 100 meV, shown in Fig. 5.5. Fe\(^+\)
production above the 3p threshold is dominated by the photodetachment of a single electron followed by further autoionization.

In photodetachment from a negative ion, the near-threshold cross section can be described by the Wigner threshold law [79]: \( \sigma \sim (h\nu - \varepsilon_{thr})^{l+1/2} \), where \( h\nu \) is the photon energy, \( \varepsilon_{thr} \) is the threshold energy and \( l \) is the angular momentum of the photoelectron. This threshold law has been verified in countless valence-shell detachment experiments [3].

**Figure 5.5.** (upper panel) High-resolution (100 meV) cross section of Fe\(^-\) leading to Fe\(^+\) over the photon energy range of the first structure shown in Fig. 5.4. The open circles are the experimental data. Dotted curves are the best fit shape resonance profiles of the second and third structures in the large photon energy range (see, Fig. 5.4). (lower panel) The same data with this underlying shape-resonance profile (the solid line in the upper panel) from the higher-energy resonances subtracted. The solid lines are the result of four shape-resonance profile fits to the data.
Recent work in He\(^{-}\) (1s), S\(^{-}\) (2p) [83], and Pt\(^{-}\) (4f) [84] has shown that the Wigner threshold law is also valid in inner-shell detachment and \(p\)-, \(s\)-, and \(d\)-wave detachment laws were observed, respectively. However, the presence of a shape resonance near threshold, as in the case of Fe\(^{-}\), significantly distorts the spectrum. This has been observed in a number of valence studies [72, 152, 153], and also in inner-shell studies in C\(^{-}\) [47, 130], and B\(^{-}\) [46]. In previous studies, it was observed that a modified shape resonance profile described near-threshold resonances very well in inner-shell processes [46, 47, 130]. This profile follows that first suggested by Peterson et al. [72, 149] and successfully used in valence detachment studies. For a shape resonance \(i\) near the threshold, we have

\[
\sigma_{\text{fit}}(\nu) = \sigma_0 + A_i \left( \frac{(\nu - \varepsilon_{\text{thr}})}{(\varepsilon_i - \varepsilon_{\text{thr}})} \right)^{l+\frac{1}{2}} \frac{\Gamma_i / 2\pi}{(\nu - \varepsilon_i)^2 + (\Gamma_i / 2)^2}
\]

(2)

Here \(\nu\) is the photon energy, \(\varepsilon_{\text{thr}}\) is the threshold energy, \(l\) is the orbital angular momentum of the photoelectron, \(\varepsilon_i\) is the energy of the resonance, \(\Gamma_i\) is the corresponding natural (Lorentzian) width, \(\sigma_0\) is the total cross section at the threshold energy, and \(A_i\) is the amplitude factor [46]. For the 3\(p\) photodetachment of Fe\(^{-}\), the photoelectron can leave with \(l = |l_\theta \pm 1| = 0\) or 2, i.e. as an \(s\) or a \(d\) wave.

The large photon energy region, corresponding to our experimental data shown in Fig. 5.4, was fit using the sum of three modified shape resonance profiles with \(l=2\) in order to model the observed structures. Results of this fit, the solid thin green lines shown in the top panel of Fig. 5.4, were then used to model the signal in the 3\(p\) threshold region. The tails of these two large underlying resonances, represented by the dashed green lines in the top panel of Fig. 5.5, could be subtracted from the data in order to isolate the resonances in the 3\(p\) threshold region, as shown in the lower panel of Fig. 5.5.

The resulting near-threshold data was then fit with the sum of shape resonance
profiles \((l=2)\), which reproduce the resonances very well (see the lower panel of Fig. 5.5). The details of the results from the fit are presented in Table 5.2. Note that four shape resonance profiles are used since, given the initial state \(3p^63d^74s^2\) \((^4F_{9/2})\) and the \(3p^53d^84s^2\) \((^4G_{5/2,...,11/2})\) final states, the \(|\Delta J| \leq 1\) selection rules allow three excitations: \(^4F_{9/2} \rightarrow ^4G_{7/2}\), \(^4F_{9/2} \rightarrow ^4G_{9/2}\), and \(^4F_{9/2} \rightarrow ^4G_{11/2}\). The fourth resonance arises from \(^4F_{9/2} \rightarrow ^4D_{7/2}\) \((3p^5[3d^8(^3P)]4s^2)\) excitation, and the energy for this resonance is predicted about 2 eV higher than the measured value (see Fig. 5.3). The theoretical calculation predicts the order of the different \(J\) states as shown in Fig. 5.2. The measured splitting of almost all terms is smaller than calculated, see Table 5.3.

**Table 5.3.** The fine structure splitting for the resonances.

<table>
<thead>
<tr>
<th>Term</th>
<th>(\Delta E_{\text{experiment}}) [eV]</th>
<th>(\Delta E_{\text{theory}}) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^4G_{11/2} \rightarrow ^4G_{9/2})</td>
<td>0.36(7)</td>
<td>0.49</td>
</tr>
<tr>
<td>(^4G_{9/2} \rightarrow ^4G_{7/2})</td>
<td>0.24(7)</td>
<td>0.42</td>
</tr>
<tr>
<td>(^4G_{7/2} \rightarrow ^4D_{7/2}) (3p^5[3d^8(^3P)]4s^2)</td>
<td>1.42(8)</td>
<td>0.92</td>
</tr>
<tr>
<td>(^4D_{7/2}) (3p^5[3d^8(^3P)]4s^2 \rightarrow ^4F_{9/2})</td>
<td>0.39(7)</td>
<td>1.62</td>
</tr>
<tr>
<td>(^4F_{9/2} \rightarrow ^4F_{7/2})</td>
<td>–</td>
<td>0.17</td>
</tr>
<tr>
<td>(^4F_{7/2} \rightarrow ^4D_{7/2}) (3p^5[3d^8(^3F)]4s^2)</td>
<td>1.45(10)</td>
<td>3.43</td>
</tr>
</tbody>
</table>

* The \(^4F_{9/2}\) and \(^3F_{7/2}\) resonances were not resolved in the present experiment.

### 5.3.2. Simultaneous double photodetachment threshold

In the present experiment no distinction can be made between the different final states of the detected \(\text{Fe}^+\) or \(\text{Fe}^{2+}\) ions and thus the data shown in Fig. 5.1 represent the sum of all the partial cross sections. Below about 57 eV, the signal for \(\text{Fe}^+\) and \(\text{Fe}^{2+}\) product channels shows no qualitative difference; this is evidence that both charge states in this region are sampling the same process (i.e., the initial \(3p\)
photodetachment) and are simply formed via different decay routes. However, above 57 eV the Fe\(^+\) production continues to decrease monotonically while that of Fe\(^{2+}\) instead increases indicating some new channel may be opening for Fe\(^{2+}\) production, but is blind to Fe\(^+\) production.

Decay of a Fe\(^-\) 3p\(^{-1}\)3d\(^8\)4s\(^2\) shape resonance by autodetachment of the 3d electron leaves the system in the Fe 3p\(^{-1}\)3d\(^7\)4s\(^2\) state. Calculations of Fe\(^+\) term energies carried out by Berrington and Ballance [19] have determined the energy levels of interest above the Fe\(^{2+}\) limit, which are reproduced in Fig.5.2. The main formation of Fe\(^+\) can be explained through simple Auger decay to Fe\(^+\) 3d\(^5\)4s\(^2\), Fe\(^+\) 3d\(^6\)4s\(^1\), or Fe\(^+\) 3d\(^7\). However these states lie below the Fe\(^{2+}\) ground state, so further autodetachment is not possible. Sequential Auger decay cannot produce Fe\(^{2+}\) and production of this ion must proceed through a three-electron process, such as simultaneous double-Auger decay or Auger + shakeup process populating the higher-lying doubly excited states followed by a second autodetachment process. However, simultaneous multi-electron photodetachment could also lead to the formation of Fe\(^{2+}\).

Simultaneous double photodetachment is a highly correlated process in which two electrons are simultaneously ejected from the negative ion following the absorption of a single photon. The sequential double photodetachment process is a two-step process involving the formation of an intermediate core-excited state of the Fe atom which rapidly decays into the two-electron detachment continua, resulting in Fe\(^+\) ions. The reaction can be written as:

\[
\text{hv} + \text{Fe}^- (i) \rightarrow \text{Fe}^* (j) + e^- \\
(1) \quad \text{Fe}^* (j) \rightarrow \text{Fe}^{**} (f) + e^- \\
(2) \quad \text{Fe}^* (j) \rightarrow \text{Fe}^{*+} (f) + e^- \rightarrow \text{Fe}^{2+*} (f) + e^- + e^-
\]
(3) \( \text{Fe}^* (j) \rightarrow \text{Fe}^{2+*} (f) + e^- + e^- \)

The initial state (i) is the \( 3p^63d^74s^2 \) ground state of \( \text{Fe}^- \). The intermediate state is an atomic Fe core excited state \( [\text{Fe}^* (j)] \), mainly \( 3p^53d^74s^2 \). In general, a core excited Fe atom may produce neutrals that are not detected in the experiment. As previously mentioned, however, recapture of the photoelectron from PCI effects leaves Fe in an auto-detaching state, resulting in the formation of \( \text{Fe}^+ \), and radiative decay is expected to be insignificant compared with the efficient Auger decay process.

In case (1), the Auger process leaves the \( \text{Fe}^+ \) in final state (f), being the ground state \( (3p^63d^64s) \) or some excited state that does not subsequently autodetach (e.g., \( 3p^63d^7 \) or \( 3p^63d^54s^2 \)). Shake-up processes are also possible, in which case other doubly-excited states may be formed (e.g., \( 3d^64p, \ 3d^54s4p, \ 3d^64d, \ 3d^54s5s, \ 3d^54s4d \), etc). Some of these states may decay into a \( \text{Fe}^{2+} \) state, which is depicted by case (2). Finally case (3) depicts the formation of \( \text{Fe}^{2+} \) by double-Auger decay of the \( \text{Fe}^* \) state. The measured ratio of \( \text{Fe}^{2+}/\text{Fe}^+ \) production over the photon energy interval 51-57 eV is 9.34(12)% (when the background is correctly accounted for, see below). This is consistent with the range observed in other systems (see, e.g. \( \text{He}^- \) [128] and \( \text{S}^- \) [131]). The resonant structures observed in the measured cross sections here are therefore very likely associated with these sequential processes (shape resonances, by their nature, decay by a single-electron tunneling process).

In the *simultaneous* process two electrons are simultaneously detached from the \( \text{Fe}^- \) ion and the reaction can be written as:

\[
\text{hv} + \text{Fe}^- (i) \rightarrow \text{Fe}^+^* (j) + 2e^- \\
\text{Fe}^+^* (j) \rightarrow \text{Fe}^{2+} (f) + e^- 
\]

The initial state (i) is the \( 3p^63d^74s^2 \) ground state of \( \text{Fe}^- \). The intermediate state (j) is
an excited state of the Fe\(^+\) ion that can decay to either the ground state or an excited final state (f) of the Fe\(^{2+}\) ion.

Usually the cross section for the sequential process is much larger than the cross section for the simultaneous one [97]. For example, the calculated background double ionization cross section is up to 10% of the total ionization in Fe\(^+\) and 20% in Fe [19]. Kjeldsen's experiment [99] shows that for the photoionization of Fe\(^+\), double ionization contributes only about 2% of the single-ionization cross section in the \(3p \rightarrow 3d\) region.

To further understand the spectrum, it is of interest to remove the resonant structure from the Fe\(^{2+}\) channel in order to more easily see the underlying continuum. Assuming that both the Fe\(^{2+}\) and Fe\(^+\) signals are primarily due to the sequential process, as indicated by their very similar cross section, at least below 57 eV, we can use the Fe\(^+\) signal to estimate the simultaneous process in Fe\(^{2+}\). To do this, we first remove the background signal arising from photodetachment to lower-lying states in order to isolate the \(3p\) detachment cross section. For Fe\(^+\), this background is almost entirely due to the photo-double-detachment of valence electrons to the Fe\(^+\) \(3d^6 4s\), \(3d^7\), and \(3d^5 4s^2\) states. A power law fit to the below-threshold Fe\(^+\) signal returned a power of \(-4.3(1.7)\), consistent with the theoretical value for single-electron detachment of \(-4.5\) [154]. A slightly sloped line was sufficient to describe the Fe\(^{2+}\) background. The modeled backgrounds (shown on Fig. 5.6 as dashed lines) were subtracted from the measured Fe\(^+\) and Fe\(^{2+}\) data. The resulting Fe\(^+\) signal was then scaled by a factor of 0.0934(12) to match the magnitude of the Fe\(^{2+}\) cross section over the resonances photon energy interval (51 to 57 eV). This scaled signal is the estimated sequential process cross section in Fe\(^{2+}\), and can be subtracted from the total measured Fe\(^{2+}\) cross section in order to effectively isolate the signal resulting
from photo-double-detachment (the simultaneous process) with subsequent autodetachment to Fe$^{2+}$. A clear threshold for this process can be seen in Fig. 5.6.

Figure 5.6. (upper panel) Photo-double-detachment cross section Fe$^{-}$ → Fe$^{2+}$. The circles are the experimental data. The dashed lines are the modeled backgrounds. (lower panel) Simultaneous 2-electron detachment producing Fe$^{2+}$ estimated by assuming that the Fe$^{+}$ signal is representative for the single-electron detachment signal. See text for details. The black open diamonds represent the extracted photo-double detachment cross section and the solid red line is the result of power law fits to the extracted photo-double-detachment cross section.
In photo-double-detachment two electrons emerge from a positively charged ion core. In 1953 Wannier made the prediction about the variation of the double photoionization cross section with energy in a critical zone where the electron correlation effects dominate [80]. Since then much effort has gone into testing the Wannier law and its range of validity [85]. There have been several previous investigations of double photodetachment cross sections for negative ions such as H\(^-\) [86], He\(^-\) [87, 88, 89], Li\(^-\) [14, 89], K\(^-\) [90], Na\(^-\) [91], Cl\(^-\) [92] and F\(^-\) [93].

The near-threshold total cross section for this double electron escape process [80, 94, 95, 96] has the form:

\[
\sigma_{\text{total}} = \sigma_0 (h\nu - \varepsilon_{\text{thr}})^m,
\]

where \(\sigma_0\) is the total cross section at the threshold energy and \(\varepsilon_{\text{thr}}\) is the threshold energy. For the case of photo-double-ionization, \(m\) is predicted to be 1.056 [97] and the difference from unity is due to the electron correlation effects.

According to the theoretical calculations [19], the Fe\(^+\) states 3d\(^4\)4s\(^2\)4p, 3d\(^4\)4s\(^2\)4d, 3d\(^4\)4s\(^2\)5s, and 3p\(^5\)3d\(^6\)4s\(^2\) lie above the ground state of the Fe\(^2+\) ion, as shown in Fig. 5. The formation of the first three excited states in Fe\(^+\) is less likely since it implies correlation effects involving up to four \(d\) electrons, while the last one involves only two electrons, a 3\(p\) and 3\(d\) electron in a knock-off type process.

A power law fit to the extracted photo-double-detachment signal returns a threshold position at \(\varepsilon_{\text{thr}} = 57.0(6)\) eV and a power of \(m = 0.95(20)\) in good agreement with the Wannier threshold law. (This error includes an estimate of our confidence in modeling the background which we determined by repeating the procedure using various reasonable functional forms for the background). The energy of the 3p\(^5\)3d\(^6\)4s\(^2\) state was calculated to be \(~66\) eV [19] above the ground state of the negative Fe\(^-\) ion, about 9 eV above the measured Wannier threshold. Considering the difficulty of
calculating this highly excited state in such a complicated system, this overestimation of the energy may be expected, and the threshold in the $\text{Fe}^- \rightarrow \text{Fe}^{2+}$ photodetachment cross section likely arises from this state. In order to determine its range of validity we plot the power and the threshold position returned by the fit versus the upper limit of the photon energy range used to fit the data, see Fig. 5.7.

![Graph](image)

**Figure 5.7.** The threshold and power returned by the fit versus the upper limit of the photon energy range used to fit the extracted photo-double-detachment cross section. The horizontal red lines are the estimated best values for the Wannier law fit parameters.
A fit of the Wannier law to the near-threshold photo-double-detachment extracted signal shows excellent agreement up to 67 eV. The fitted threshold and power values change substantially if photon energies above 67 eV are included in the fit range, due to additional structure in the Fe\textsuperscript{2+} cross section above the Wannier curve over the range 67-72 eV.

5.4. Conclusions

We have reported absolutely-scaled inner-shell photodetachment cross section data for the Fe\textsuperscript{−} negative ion near and above the 3\textit{p} excitation region. In the photon energy range 48-72 eV, the Fe\textsuperscript{−} photodetachment spectrum is dominated by shape resonances which can be assigned to the $3p \rightarrow (3d + \epsilon d)$ excitation lying just above the $3p$ threshold. In the near-threshold region, the single-photodetachment cross section can be accurately fit using shape resonance profiles with $l=2$. The Wannier law was observed and fit well to the near-threshold region of the extracted Fe\textsuperscript{−} photo-double detachment cross section, observed in the Fe\textsuperscript{2+} production channel. Furthermore, the absolute photodetachment cross sections for Fe\textsuperscript{−} leading to Fe\textsuperscript{+} and Fe\textsuperscript{2+} were measured at four photon energies, providing important reference data for astrophysics and plasma physics.
CHAPTER 6

INNER-SHELL PHOTODETACHMENT OF RUTHENIUM NEGATIVE ION

This chapter presents inner-shell photodetachment from Ru\(^{-}\) near and above the 4\(p\) excitation region in the 29-91 eV photon energy range using a merged ion-photon beam technique. The absolute photodetachment cross sections of Ru\(^{-}\) ([Kr] 4\(d^75s^2\)) leading to Ru\(^{+}\), Ru\(^{2+}\), and Ru\(^{3+}\) ion production were measured. In the near-threshold region, a Wigner s-wave law, including estimated PCI effects, locates the 4\(p_{3/2}\) detachment threshold between 40.10 and 40.27 eV. Additionally, the Ru\(^{2+}\) product spectrum provides evidence for simultaneous 2-electron photodetachment (likely to the Ru\(^{+}\) 4\(p^54d^55s^2\) state) located around 49 eV. Resonance effects are observed due to interference between transitions of the 4\(p\)-electrons to the quasi-bound 4\(p^54d^55s^2\) states and the 4\(d\rightarrow\epsilon\)f continuum. Despite the large number of possible terms resulting from the Ru\(^{-}\) 4\(d\)-open shell, the cross section obtained from a 51-state LS-coupled R-matrix calculation agrees qualitatively well with the experimental data.

6.1. Introduction

The demand for materials of special qualities has focused attention on the properties of the transition elements containing partially filled \(d\)-orbitals. Transition
metals are of interest because of their catalytic properties and the participation of $d$-orbital electrons in bonding properties. The transition metals and their compounds are of extreme practical importance in metallurgy, utilization of marine resources, cosmochemistry and geology [25]. In addition, understanding the magnetic properties of transition metal thin films is crucial for modern data storage technology [21]. The interaction of transition metal atoms and ions with electromagnetic radiation generates very complex spectra due to the coupling of $d$-electrons with core holes and the underlying continua [22]. The angular momentum coupling leads to a large number of possible terms from the open $d$-shell, thus for an accurate description of the photoionization process, strong correlations between these terms as well as relativistic effects have to be taken into account [21, 22, 156]. The $d$-orbital retains, to a high degree, the same characteristics in solids [22, 156], so the atomic and ionic data could be very useful to contribute information toward understanding intra- and inter-atomic effects.

Throughout the Universe, transition metals are abundant and ruthenium is the most abundant of the platinum-group metals (i.e., Ru, Rh, Pd, Os, Ir, and Pt) in meteoritic matter [157]. The ruthenium atom is of interest for providing an efficient conversion of solar energy into chemical energy by photoinduced electron transfer [26]. Due to the experimental difficulties of producing a usable atomic beam, mainly the high temperature required to vaporize the metal (boiling point 4150 °C [158]), there have been few experimental and theoretical studies of free ruthenium atoms [25, 27, 28, 159] compared to the situation for solids [156, 160-163]. Only one valence-shell photodetachment study exists for the ruthenium negative ion [29], in which laser photodetachment spectroscopy was used to measure the binding energies of the ground state Ru$^-$ ([Kr] 4d$^7$5s$^2$ 4F$_{9/2}$) (1.04638(25) eV, the electron affinity of Ru) and
the first excited fine structure level $^4F_{7/2}$ (0.8653(10) eV) together with calculations for the $^4F_{5/2}$ (0.795 eV) and $^4F_{3/2}$ (0.725 eV) levels.

It is well known that the photoionization cross sections of $d$-photoelectron bands of gas-phase molecules are highly structured. A massive variation in the cross section, the so-called "giant resonance", has been observed, for example, at about 55 eV in the $d$-band photoelectron spectrum of Ru($\eta$-C$_5$H$_5$)$_2$ [156], as well as seen or predicted in other transition metals [21, 22, 164]. It is therefore of interest to determine if a similar "giant" resonance is also present in the photodetachment cross section of the Ru$^-$ atomic negative ion.

### 6.2. Experimental method

The experiment was performed at the Advanced Light Source (ALS) using the High-Resolution Atomic, Molecular and Optical Physics (HRAMO) undulator beamline 10.0.1 with the fixed ion-photon beamline (IPB) endstation [16]. The IPB is based on a counter-propagating merged-beam technique for photoion spectroscopy in order to increase the interaction volume between photons and the dilute ion beam.

The experimental technique has been described previously [84, 120, 83, 131, 46]. A 7.54 keV negative ion beam of Ru$^-$ was produced using a cesium sputter source (SNICS II, from NEC) [17], with an ion current of about 40 nA obtained in the interaction region after shaping and spatial trimming. The magnetically mass-selected negative ion beam with a diameter of ~5 mm overlapped the counter-propagating photon beam with a spatial width of ~1.2 mm over a distance of about 1.5 m. Inner-shell photodetachment and subsequent Auger decay produce positive ions that were deflected by the demerger magnet and counted as a function of photon energy with an electron multiplier based detection system.
The photon-ion interaction region was defined by a ~30 cm long stainless-steel cylinder, held at +0.55 kV in order to kinetic-energy tag the Ru\(^{-}\) ions. Negative ions entering in the interaction region were thus accelerated to 8.09 keV, and the positively charged ions Ru\(^{+}\) (or Ru\(^{2+}\)) resulting from the photodetachment process exited the interaction region experiencing a second kinetic energy boost of +0.55 keV (or +1.10 keV), leaving with 8.64 keV (or 9.19 keV) kinetic energy. The Ru\(^{+}\) and Ru\(^{2+}\) ions formed outside of the interaction region, having a lower kinetic energy of 7.54 keV, could then be easily selected against by the de-merger magnet and spherical electrostatic deflector located before the detector. The ion-photon beam overlap was optimized by using two rotating-wire beam profile monitors near the entrance and exit of the interaction region. In addition, three translating-slit scanners located near the entrance, middle and exit of the interaction region were used to obtain two-dimensional (2D) profiles of the photon and ion beam. In this way the interaction volume was well defined which allowed for absolute cross section measurements (see section 6.3.1 below). The monitors were removed from the beam path during the data collection.

The ground states of Ru, Ru\(^{+}\), Ru\(^{2+}\), Ru\(^{3+}\), and Ru\(^{4+}\), relative to the Ru\(^{-}\) ground state are respectively, 1.04638(25) [29], 8.4069(3) [28], 25.167(10) [165], 58.8(26) [166], 108(5) eV [166] [uncertainties are quoted to 1 standard deviation (SD) throughout]. Ru\(^{4+}\) and higher charged state products are therefore not energetically possible to produce with the photon energies used in the present experiment. All three energetically allowed ionic products were measured. Note that only charged products can be detected with the present apparatus and neutral Ru, although very likely produced, could not be detected.

A significant background signal was produced by collisions between negative
ions and residual vacuum gas (~4 x 10^{-10} torr) or apertures in the beamline. The photon beam was chopped at 6 Hz in order to continuously monitor and subtract the background signal. The resulting photodetachment signal was normalized to the incident photon flux and the negative ion current. The incident photon flux was recorded by an absolutely calibrated silicon x-ray photodiode [118] and the ion current was monitored with a Faraday cup placed after the de-merging magnet. The effects of any variations over time of the experimental parameters (ion-photon beam overlap, negative ion current, incident photon flux, vacuum gas pressure) could therefore be monitored and corrected for (see section 6.3.1 for details on the effects of these experimental parameters on the cross section). Several sweeps over the photon energy of interest were recorded and summed in order to improve the signal-to-noise ratio.

The photon energy was scanned by rotating the spherical-grating monochromator and translating the exit slit of the monochromator while simultaneously adjusting the undulator gap to maximize the photon beam intensity. The Ru¯ beam energy in the interaction region was determined to be 8.09(20) keV, which gives sufficient ion velocity to produce a small Doppler shift, between 12 meV and 37 meV for photon energies between 29 eV and 91 eV. The monochromator photon energy was calibrated using accurately known absorption lines of Ar [167], Ne [168], and He [169]. The resulting uncertainty in the calibration was between 10 meV (at 30 eV) and 180 meV (at 90 eV). Corrections for the photon energy calibration and Doppler shift have been applied to all the spectra reported here.
6.3. Results and discussions

6.3.1. Absolute cross sections

The absolute photodetachment cross section has been introduced in the previous chapters and is given by the formula: \( \sigma = qvR/I\Phi F \) [16], where \( q \) is the charge of the target ion, \( R \) is the signal rate, \( \Phi \) is the photon flux, \( I \) is the target-ion current, \( v \) is the velocity of negative ions, and \( F \) is the form factor. The signal rate is \( R = R_0 / (\Omega_{\text{det}}\Omega_{\text{electr}}) \), where \( R_0 \) is the measured count rate, \( \Omega_{\text{det}} \) is the detector efficiency and \( \Omega_{\text{electr}} \) is the pulse detection efficiency of the electronics. In the present experiment the detector efficiency \( \Omega_{\text{det}} \) was estimated to be 100(7)% [137] and \( \Omega_{\text{electr}} \) was 99(1)%. (Note that we include the possibility of \( \Omega_{\text{det}} > 100\% \) to account for possible double-counting events arising from electronic ringing and other effects.)

The 2D form factors \( F_z = \int_i \Phi_x dx \int_y \Phi_y dy \) were calculated based on ion \( i \) and photon \( \Phi \) beam profiles measured at three positions by slit scanners, where \( x \) and \( y \) are orthogonal directions in the plane normal to the ion and photon beam propagation direction. The total form factor \( F \), a measure of the photon–ion beam overlap quality, is then obtained by integrating the quadratic interpolation of 2D form factors (measured at 3 positions) over the biased interaction region length of 28.3(14) cm, determined from electrostatic simulations using SIMION 7.00 [145], and the ion kinetic energy acceptance of the positive-ion detection system. The total (one standard deviation) systematic instrumental error in the absolute cross section was ±20%.

The measured absolute cross sections for photoexcitation of Ru⁰ leading to Ru⁺, \( \sigma(\text{Ru}^+) \), are listed in Table 6.1. The cross sections for Ru²⁺ and Ru³⁺ production were obtained by multiplying these by the ratio of the cross sections, \( \sigma(\text{Ru}^{2+})/\sigma(\text{Ru}^+) \) and \( \sigma(\text{Ru}^{3+})/\sigma(\text{Ru}^+) \), also listed in Table 6.1. As in previous experiments [84, 120, 83,
these ratios were determined by recording the signal rates for each photoionization product in rapid succession (typically 1-4 minutes per product per energy point). The measurements were repeated several times to verify that no significant fluctuations in the overlap, ion current, or other such effects were present during the data collection.

### Table 6.1. Absolute photodetachment cross sections $\sigma$ for the production of Ru$^+$, Ru$^{2+}$, and Ru$^{3+}$ from Ru$^-$, obtained from the measured $\sigma$(Ru$^+$) cross section and the ratios, $\sigma$(Ru$^{2+}$)/$\sigma$(Ru$^+$) and $\sigma$(Ru$^{3+}$)/$\sigma$(Ru$^+$), which are also reported. All values are reported to 1 SD.

<table>
<thead>
<tr>
<th>Photon Energy [eV]</th>
<th>Cross Section [Mb]</th>
<th>Measured Ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru$^+$</td>
<td>Ru$^{2+}$</td>
</tr>
<tr>
<td>48.663(15)</td>
<td>9.5(19)</td>
<td>1.03(22)</td>
</tr>
<tr>
<td>69.26(5)</td>
<td>5.3(11)</td>
<td>2.1(4)</td>
</tr>
<tr>
<td>89.35(18)</td>
<td>1.35(29)</td>
<td></td>
</tr>
</tbody>
</table>

### 6.3.2. Broad range spectra-giant resonance region

The total photodetachment cross sections for Ru$^+$ from Ru$^-$ were measured in the 29 - 91 eV photon energy range, as shown in Fig. 6.1. Below the $4p$ threshold at ~40 eV (binding energies of 43.2 eV for the $4p_{3/2}$ and 46.3 eV for the $4p_{1/2}$, relative to the Fermi surface, have been measured in Ru metal samples [170]) a significant photodetachment cross section is observed. While some of this Ru$^+$ signal may be produced by simultaneous (direct) double photodetachment of $5s$ and/or $4d$ electrons, we find from multi-configuration Hartee-Fock (MCHF) calculations (see below) that there are several excited triplet states of Ru above the $4d^7\,^4F$ ground state of Ru$^+$. 
Photodetachment into one of these states would quickly autoionize, explaining the strong signal below the 4$p$ threshold. Below 40 eV there is a strong dip, followed by a sharp increase in the cross section near the 4$p_{3/2}$ threshold. This is followed by a large structure with a maximum cross section of more than 10 Mb at about 46.5 eV, and a slow-broad decay of the underlying continua.

**Figure 6.1.** The measured photodetachment cross section for Ru$^+$, Ru$^{2+}$, and Ru$^{3+}$ from Ru$^-$.

The reported spectra were normalized to the absolute cross section measurements, represented as large circles with 1 SD error bars. The relevant states in the Ru atom and ions are presented in Fig. 6.2.
Figure 6.2. Energy-level diagram (to scale) showing ground [28, 165, 166] and some relevant core excited states of Ru−, Ru, Ru+, Ru2+, and Ru3+, relative to the ground state of Ru− [29] (the 4s detachment threshold is estimated from [171]). Included is a preliminary assignment of 4p 54d65s2 for the core-excited state responsible for the 2-electron detachment threshold discussed in section 6.3.3. For clarity of presentation, fine structure states are not shown. An asterisk (*) indicates the level energy is obtained from this work. The very broad “giant” Ru− 4p 54d65s2 resonant excitations observed in this work are indicated as a range of energies around the 4p detachment threshold based on the measured and calculated theoretical spectra. The arrows indicate channels leading to the main structures described herein.

In the previous chapter we investigated the photodetachment cross section of Fe−, where three large, well separated shape resonances were observed in the 48 – 72 eV photon energy range [120]. Despite the similar electronic configuration of Fe− ([Ar] 3d74s2 4F) and Ru− ([Kr] 4d75s2 4F), the behavior of their photodetachment
cross sections in the \( np \rightarrow nd \) excitation region \( (n = 3 \text{ for Fe}^-, \text{ and } n = 4 \text{ for Ru}^-) \) is strikingly different.

Shape resonances are situated just above their parent atomic state. In this case the one-electron potential produced by the short-range attraction and the centrifugal repulsion forms a barrier large enough to trap the electron behind it. The primary decay mechanism is tunneling through the barrier, and thus the width and strength of the resonances are influenced by the particular form of the potential. This resonance behavior has been reported for other inner-shell photodetachment studies such as in Li\(^-\) [14, 13, 45,104], B\(^-\) [46, 106, 146], C\(^-\) [47, 130, 147], and Fe\(^-\) [120]. As a consequence of their decay mechanism, the resonances are broad structures in the photodetachment cross section and since they are often located very close to a threshold, the corresponding Wigner threshold behavior is severely altered by their presence, as pointed out by Peterson \textit{et al.} [72, 149]. Such shape resonances describe the Fe\(^-\) photodetachment spectrum very well, as can be seen by the excellent fit of a sum of three modified shape resonance profiles to the experimental data in Fig. 5.4 previous chapter. However, these profiles poorly describe the Ru\(^-\) photodetachment cross section, indicating that the nature of these structures is likely different.

The Ru\(^-\) spectrum resembles much more closely that which is expected from Cr\(^-\)([Ar]\(3d^54s^2\)\(6S_{5/2}\)), where a giant resonance is predicted (see \textit{ab initio} calculations of Ivanov \textit{et al.} [164], which appear to be in reasonable agreement with unpublished experiments reported in [6]). This resonance is similar to giant autoionizing resonances in the 3\(p\) photoionization spectra of the neutral 3\(d\) transition metals and their positive ions [21, 22]. Unlike Fe\(^-\), the Cr\(^-\) spectrum appears to be highly modified by interchannel interaction [164]. There, the 3\(p\rightarrow3d\) resonance is expected to have a large effect on the 3\(d\rightarrow\epsilon f\) channel, appearing as a pronounced Fano-profile
structure in that partial wave. It appears that such interchannel coupling is also more prominent in Ru\(^{-}\) than the lighter Fe\(^{-}\) system, and may explain some of the differences between these two systems. It is also interesting to note in this regard that the ground state configurations of neutral Cr and Ru both have a single \(s\)-electron in the valence shell as opposed to Fe, in which the outer \(s\)-shell is filled. As in Cr\(^{-}\), the dip and enhancement around the \(4p\) threshold observed in Ru\(^{+}\) production appears to be due to transitions of the \(4p\)-electrons to a quasi-bound state \(4p^54d^85s^2\) in the \(4d\rightarrowef\) continuum and is supported by our R-matrix calculations discussed below.

In order to study the photodetachment of Ru\(^{-}\) theoretically, we use the R-matrix method [148] as follows. First, a Hartree-Fock calculation was performed for the configuration-averaged \(4p^64d^65s^2\) state to generate a basis set of \(1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d,\) and \(5s\) orbitals. Then a 51-state LS-coupled R-matrix calculation was performed including all 20 even-parity target states of Ru that could be coupled from the \(4p^64d^65s^2, 4p^64d^75s\), and \(4p^64d^8\) configurations. In addition, all 31 odd-parity target states that could be coupled from the \(4p^54d^75s^2, 4p^54d^85s\), and \(4p^54d^9\) configurations were included. Since the ground state of Ru\(^{-}\) is of \(^4F\) symmetry, dipole selection rules dictate that the \(^4G, ^4F,\) and \(^4D\) final symmetries can be populated via photodetachment.

We first present the total photodetachment cross section, summed over all three final symmetries and all energetically available channels (Th\(_{tot}\)) in Fig. 6.3, which shows strong distortion arising from \(4p\rightarrow4d\) excitations.
Most of the cross section is due to the $4d$ and $5s$ photodetachment to the lowest 20 even-parity states. MCHF calculations locate the majority of these states below the Ru$^+$ ground state, which therefore cannot autoionize to ionic products, with only 5 triplet states above the Ru$^+$ ground state (in particular, in order of energy, the $4d^6[^3\text{F}_2]5s^2\ ^3\text{F}$, $4d^6[^3\text{P}_2]5s^2\ ^3\text{P}$, $4d^7[^2\text{D}_1]5s\ ^3\text{D}$, $4d^8\ ^3\text{F}$, and $4d^8\ ^3\text{P}$ states). The large discrepancy in the magnitude of the calculated total cross section and the measured cross section is therefore due to the fact that neutral Ru channel is not observed. Nonetheless, the shape of the total calculated cross section is very similar to the measured Ru$^+$ cross section, although shifted by about 2 eV to lower energies. This
includes details such as a kink observed on the rising slope of the cross section, just above 40 eV in the experiment. Also well reproduced is the dip seen just below the 4\(p\) threshold and the maximum just above, arising from 4\(p\)→4\(d\) interference with the \(\varepsilon f\) continuum.

To attempt to better understand the observed Ru\(^+\) spectrum, we calculate the sum of the auto ionizing states, i.e., those we expect to lie above the Ru\(^+\) ground state. These states include the 5 triplet states mentioned above and the 31 4\(p\) core-hole states. The partial cross section to these highest 36 target states (Th\(_{\text{auto}}\)) is also shown in Fig. 6.3. The strength and shape of the 4\(p\) continua is reasonably well reproduced (with a shift to higher energies) and part of the below-threshold signal is explained. However, almost all of the strong 4\(p\)→4\(d\) resonance strength is lost. One possibility is that the MCHF calculation is underestimating the energies of the excited Ru states. Indeed, including some additional lower-lying states restores the resonance structure (see Fig. 6.4), although the calculated cross section is approximately twice as large as the experiment. An alternate likely explanation is that the calculated oscillator strength is confined to low-lying Ru states by the limited basis used and should actually be redistributed to various other higher-lying states. We note, for example, that if configuration interaction is allowed with higher states for the Ru\(^-\) ground state, we obtain roughly 16% mixing of the 4\(d^75s^2\) and 4\(d^75p^2\) configurations. This makes photodetachment into Ru 4\(d^65p^2\) states possible, for example, which are autoionizing and could easily account for the missing oscillator strength in Th\(_{\text{auto}}\). Therefore the calculations reproduce almost all the major features observed quite well, however it would appear that there are additional autodetaching Ru excited states which carry some of the 4\(p\)→4\(d\) excitation cross section to Ru\(^+\) that are missed in the sum.
Figure 6.4. Comparison of theory with experiment. Experimental curves are for Ru$^+$ and the sum of all detected ionic products, as labeled (curves are smoothed over 5 data points to reduce statistical scatter). The sum of the 36 predicted autodetaching states ($\text{Th}_{\text{auto}}$) is seen to be lacking the resonant enhancement observed in the experiment. Including the 42 highest lying states ($\text{Th}_{42}$) recovers the structure, but has a cross section approximately a factor of 2 too large.

6.3.3. Highly charged ion production

Further differences between Fe$^-$ and Ru$^-$ can be observed by comparing the doubly charged product, as shown in Fig. 6.1. While the resonance region was essentially identical in Fe$^+$ and Fe$^{2+}$, Ru$^{2+}$ appears to show a remarkably modified spectrum. There are two main differences between the Ru$^{2+}$ and Ru$^+$ spectra. First, the dip below, and the maximum above the $4p$ threshold are not present anymore in the Ru$^{2+}$ spectrum. This is because the $4p \rightarrow 4d$ resonance structure is not observed in the $4p \rightarrow ed$, continuum, in striking contrast to Fe$^-$. Therefore these excitations are only
seen as an interference with the even states, all of which are well below the Ru\textsuperscript{2+} ground state. In order to compare our data with the calculations, Fig. 6.5 shows the measured Ru\textsuperscript{2+} spectrum with the calculated cross section leading to states with a 4p hole only. The theory curve has been reduced by a factor of 10, reflecting that most of the cross section leads to single ionization, and shifted up by 0.2 Mb to estimate the observed below-threshold signal.

![Graph showing Ru\textsuperscript{2+} and Ru\textsuperscript{+} spectra.]

**Figure 6.5.** Comparison of the measured Ru\textsuperscript{2+} spectrum with the calculated cross section including only 4p core-hole states (Th\textsubscript{4p}). The theory curve has been reduced by a factor of 10, to account for the low branching decay leading to Ru\textsuperscript{2+} and shifted up by 0.2 Mb, to estimate the small photodetachment background observed below the 4p threshold.

There is a small shift, and perhaps stretch, in the photon energy scale (as also seen with comparison to Ru\textsuperscript{+} above), but the calculations offer a reasonable description of the near threshold region until \(~49\text{eV}, where the second difference with Ru\textsuperscript{+} is seen. There appears to be an onset of a strong channel present in Ru\textsuperscript{2+} at
~49 eV, that is absent in Ru$^+$. This energy corresponds roughly to where the excited state of Ru$^+$ 4$p^54d^65s^2$ might be expected. This would represent a simultaneous (direct) 2-electron detachment process from Ru$^-$, i.e., where a 4$d$ electron is “knocked off” in the 4$p$ photodetachment process. While the energy of this state is not known, it can be roughly estimated assuming similar 4$d$ binding energy as in the ground state neutral atom [155], i.e., ~8.5 eV above the 4$p$ threshold. Due to the efficiency of Auger decay processes, this state will result almost exclusively in Ru$^{2+}$ production, with no Ru$^+$ production, thus explaining why it is seen only in the Ru$^{2+}$ channel. To further support this interpretation, we note that the same 2-electron photodetachment process (except involving the 3$p$ and 3$d$ electrons) was observed in Fe$^-$ at 57.0 eV (6.5 eV above the 3$p$ threshold), although in Ru$^-$ this channel appears to be relatively stronger.

Finally, as noted previously, it is possible to form Ru$^{3+}$ at the higher photon energies explored here. However, only a very small cross section was observed [measured to be 65(15) kb at 89 eV, see Table 6.1]. This is largely because the ground state of Ru$^{3+}$ [at 58.8(26) eV relative to the ground state of the negative ion, see Fig. 6.2] is above the 4$p$ detachment threshold, and therefore Auger decay channels from this core-hole are not available. Note however, that a very small, slowly varying signal (< 5 kb) is observed even below 58.8 eV. It is energetically impossible to form Ru$^{3+}$ at these photon energies, and this signal must therefore arise from some contamination. The most likely source is from higher-order light in the photon beam. This type of contamination has been observed previously (see, e.g., [84]), especially with very low signal rate products with cross sections that increase substantially with photon energies, as is the case here. Finally, we note that the 4$s$ threshold should open around 75 eV (estimated from measurements in solid samples
and therefore could contribute to 4-electron detachment at these higher energies, but cannot explain the turn-on in the signal observed around 56 eV. The location of this apparent threshold is suggestive of a simultaneous (or “direct”) 4-electron detachment process to the ground state of Ru\(^{3+}\). Such a process would be described by a Wannier threshold law \[80\], which for 4-electron detachment the cross section would obey a power law with an exponent of 3. The magnitude of the cross section, however, would be surprisingly large for such a 4-electron process; as <1 kb at about 20 eV above threshold is expected based on measurements in other systems \[172\]. It may then be more likely that the process is a 3-electron photodetachment into an autodetaching Ru\(^{2+}\) state. This would be described by a power law exponent of 2. Unfortunately, due to the underlying, possibly non-linear, background observed in this channel and the extreme sensitivity of the threshold position and power law to variations in the background signal, conclusive fits could not be made to the data. Fits nonetheless suggest a threshold position of between 49 and 60 eV, and a power law exponent between 2 and 3, which is consistent with the above interpretations.

### 6.3.4. 4p photodetachment threshold region

Negative ions are bound in a short-range potential (~1/r\(^4\)) and this leads to a near-threshold photodetachment cross-section behavior significantly different than the behavior of atoms and positive ions, which are bound in the long-range Coulomb potential (~1/r). In the case of negative ions, the near-threshold cross section follows the Wigner law \[79\]

\[
\sigma = \sigma_0 (h\nu - \varepsilon_t)^{l+1/2},
\]

where \(\sigma_0\) is the amplitude, \(h\nu\) is the photon energy, \(\varepsilon_t\) is the threshold energy, and \(l = |l_0 \pm 1|\) is the photoelectron angular momentum, with \(l_0\) the angular momentum of the
bound electron being detached.

The threshold photodetachment cross section of Ru\(^-\) is shown in Fig. 6.6.

**Figure 6.6.** High-resolution (30 meV) photodetachment cross section of Ru\(^-\) leading to Ru\(^+\) and Ru\(^2+\) near the 4\(p\) threshold. The open circles are the experimental data. The solid curve is a Wigner s-profile fit to the data with inclusion of PCI effects, assuming an Auger width of 40 meV. The dotted curve is a Wigner s-wave law obtained from the fit with the PCI effects removed. The dashed curve represents the linear background included in the fit.

In the present experiment if a 4\(p\) electron (\(l_0 = 1\)) is detached from Ru\(^-\), the photoelectron angular momentum (\(l = |l_0 \pm 1|\)) can be 0 or 2, i.e. an s- or d-wave. It has been seen in previous outer-shell photodetachment experiments [1, 5, 173] that the d-wave is greatly suppressed by the centrifugal barrier and the photodetachment
cross section near threshold is described by the Wigner $s$-wave law. Fig. 6.6 shows the near-threshold photodetachment cross section of $\text{Ru}^-$ obtained by measuring the positive ion production for $\text{Ru}^+$ and $\text{Ru}^{2+}$ in the photon energy range from 39 eV to 42.5 eV with a photon energy resolution of 30 meV.

The Wigner threshold law has been verified in countless valence-shell detachment experiments [1, 5, 173]. Recent work in $\text{He}^-$ ($1s$), $\text{S}^-$ ($2p$) [83], $\text{Pt}^-$ ($4f$) [84], and $\text{Fe}^-$ ($3p$) [120] has shown that the Wigner $p$-, $s$-, and $d$-wave detachment threshold laws are also valid in inner-shell detachment, despite possibly significant post-collision interaction (PCI) effects.

At photon energies very near a photodetachment threshold, the photoelectron has little kinetic energy, and recedes from the atomic core very slowly. It is then possible for the fast electron released from the subsequent Auger decay to overtake the photoelectron before it has moved very far from the atomic core. Once overtaken, the photoelectron can get trapped in the exposed Coulomb potential of the residual ionic core. This results in a neutral atom instead of a positive ion product, and hence the suppression of the detected positive ion production near the photodetachment threshold (unless the electron is recaptured in an autodetaching state [47]). The result is mainly an apparent shift of the threshold position to higher energies, dependent on the Auger decay lifetime, with some “smearing” of the threshold that is especially apparent in the sharp (infinite slope) turn-on of $s$-wave threshold laws (see [83]). This signal suppression effect can be accurately accounted for by using a semi-classical reduction factor theoretical method [104].

The $\text{Ru}^+$ near-threshold data suffer from significant distortion due to the strong variations in the underlying photodetachment continua due to the $4d$ resonant interference discussed above, which significantly obscures the threshold behavior.
We note that studies in Pt\textsuperscript{−} had similar difficulties for the Pt\textsuperscript{+} product [84]. However, in the case of Ru\textsuperscript{2+}, the continuum is near constant and a Wigner s-wave law fits the threshold region very well except very near to the threshold, where PCI effects become important as discussed above. Unfortunately, the Auger decay lifetime for the Ru 4p\textsuperscript{5}4d\textsuperscript{7}5s\textsuperscript{2} state is not known, and the decay width of the state couples very sensitively to the position of the threshold in the fit. The solid curve in Fig. 6.6 is a Wigner law (with the inclusion of the PCI effects assuming an Auger width of 40 meV) fit to the Ru\textsuperscript{2+} data from 39.5 to 41.5 eV, yielding a 4p\textsubscript{3/2} threshold position of 40.2 eV. The dashed curve is the Wigner law obtained from the fit with the PCI effects removed, and highlights the significant (~200 meV) apparent shift in the threshold position due to the PCI photoelectron recapture effect. While the solid curve is an excellent fit to the data up to 42 eV, good fits are also obtained for Auger widths ranging from 30 to 70 meV, resulting in an uncertainty in the fit threshold position. We deduced from multiple fits, using various Auger widths in the above mentioned range, that the 4p\textsubscript{3/2} threshold is between 40.10 and 40.27 eV. (We note that these Auger widths may be somewhat smaller than expected, but still reasonable given 4p decay widths measured in Xe, which are as small as 150 meV [173]). It is of interest to note that this also demonstrates a means to determine rough experimental values of the Auger decay widths of core-excited neutral atomic states.

An additional small feature can be noticed about 2 eV above the 4p threshold in both the Ru\textsuperscript{+} and Ru\textsuperscript{2+} spectra, where there appears to be a new channel opening at ~42.2 eV. We believe this feature is likely due to the \textit{p}\textsubscript{1/2} fine-structure threshold. In solid Ru, the \textit{p}\textsubscript{1/2} threshold is expected to be about 3 eV above the \textit{p}\textsubscript{3/2} [171], but may be lower in the atomic negative ion. However, a cusp associated with \textit{5s} \rightarrow \textit{5p} discrete excitations produced by inelastic 4p photoelectron scattering could
potentially also explain this feature. Such a feature is seen, for example, in the partial $3p \rightarrow \varepsilon d$ photodetachment of Cr$^-$ [164], when the dynamic polarization interaction for an outgoing electron is included in the theoretical calculations. If we assume a similar excitation energy for the scattering process (i.e., excitation from the $4p \rightarrow 4d$ core-excited neutral atomic state) as the first $5s \rightarrow 5p$ excitation ($4d^2 5p^5 5D_4$) from the ground state of Ru (3.262375 eV [155]), the cusp should appear at ~43.4 eV. This is larger than the data suggest, but the currently very poor knowledge of the relevant core-excited Ru states does not allow us to exclude this possibility.

6.4. Conclusions

We have reported absolutely-scaled inner-shell photodetachment cross section measurements for the Ru$^-$ negative ion near and above the $4p$ excitation region in the photon energy range 29 to 91 eV. The absolute photodetachment cross sections for Ru$^-$ leading to Ru$^+$, Ru$^{2+}$, and Ru$^{3+}$ were measured at three photon energies, providing reference data for astrophysics. From high statistic measurements near the $4p$ detachment onset, our best estimate for the $4p_{3/2}$ detachment threshold is determined to be between 40.10 and 40.27 eV, assuming an estimated Auger decay width of 30 to 70 meV. A direct 2-electron detachment process, likely to Ru$^+ 4p^5 4d^6 5s^2$, is observed in the Ru$^{2+}$ spectrum, locating this state at approximately 49 eV. Ru$^{3+}$ is also observed, most likely originating from direct 3-electron photodetachment to an autodetaching Ru$^{2+}$ state near the Ru$^{3+}$ ground state.

There is evidence that the existence of vacant states in the $4d$ inner-shell of the Ru$^-$ negative ion causes resonance interference effects between 4p-electrons to the quasi-bound $4p5d85s2$ excitations and the $4d\rightarrow\varepsilon f$ continuum, resulting in a net dip in the Ru$^+$ cross section (and the total calculated cross section) just below the $4p$
threshold and an enhancement just above the threshold. The interpretation is supported by theoretical calculations. The calculations reproduce most of the major features observed fairly well, although it would appear that there are additional autodetaching Ru excited states which carry some of the $4p \rightarrow 4d$ excitation cross section to Ru$^+$ that are missed in the sum. There remains, however, some structure not well described by the calculations, which suggests that not all important channels/processes have been accounted for. The role of many-particle effects, intershell interaction, and polarization seems much more significant in Ru$^-$ than in Fe$^-$ photodetachment, as would be expected given the additional complexity of the heavier Ru$^-$ ion. A more complete understanding of Ru$^-$ photodetachment will have to await more elaborate theoretical calculations.
CHAPTER 7

SUMMARY

Although negative ions are identical to neutral atoms and positive ions in terms of the constituent particles, the loosely added charge enables them to form systems with strikingly different properties. The effective screening of the attractive nucleus by the remaining electrons prevents the additional electron from experiencing the long-range Coulomb attraction which determines the characteristics of neutral atoms and positive ions. Instead, negative ions owe their existence to the significant rearrangement (polarization) of the neutral atom core. Since electron correlation effects are very enhanced in negative ions, these systems are particularly well suited as theoretical test objects within atomic physics.

Photodetachment is an important process in many physical systems in nature such as astrophysical objects, the upper atmosphere, and fission or fusion plasmas. Previously, photodetachment studies were limited to outer-shell electrons due to the lack of an appropriate light source. In the last decade, the intense photon flux available from the undulator beamlines opened up the possibility of studying inner-shell photodetachment.

It is known that 90% of matter in the Universe is ionized and transition metals are abundant, so the interaction of transition metal atoms and ions with radiation is of great importance for astrophysics. In addition, transition metals and their compounds are of practical importance in metallurgy, magnetism, and data storage systems.
7.1. Conclusions

Inner-shell photodetachment of transition metal negative ions of iron and ruthenium has been studied at the Advanced Light Source at Lawrence Berkeley National Laboratory using the merged beam technique. Iron, lying at the maximum of the nuclear stability curve, is an important astrophysically abundant element. In the photon energy range 48-72 eV, the Fe$^-$ photodetachment spectrum is dominated by shape resonances which can be assigned to the $3p \rightarrow (3d + \varepsilon d)$ excitation lying just above the $3p$ threshold. In the near-threshold region, the single-photodetachment cross section can be accurately fit using shape resonance profiles with $l=2$. The Wannier law was observed and fit well to the near-threshold region of the extracted Fe$^-$ photo-double detachment cross section observed in the Fe$^{2+}$ production channel. Furthermore, the absolute photodetachment cross sections for Fe$^-$ leading to Fe$^+$ and Fe$^{2+}$ were measured at four photon energies, providing reference data for astrophysics and plasma physics.

Ruthenium, the most abundant of the platinum-group metals (i.e., Ru, Rh, Pd, Os, Ir, and Pt) in meteoritic matter, is of interest for providing an efficient conversion of solar energy into chemical energy by photoinduced electron transfer. The inner-shell photodetachment of the Ru$^-$ negative ion was investigated near and above the $4p$ excitation region in the photon energy range 29 to 91 eV. The absolute photodetachment cross sections for Ru$^-$ leading to Ru$^+$, Ru$^{2+}$, and Ru$^{3+}$ were measured at three photon energies. In the near-threshold region, a Wigner $s$-wave law, including estimated PCI effects, locates the $4p_{3/2}$ detachment threshold between 40.10 and 40.27 eV. Resonance effects are observed due to transitions of the $4p$-electrons to a quasi-bound state $4p^54d^85s^2$ in the $f$-wave continuum. Additionally, the Ru$^{2+}$ product spectrum provides evidence for simultaneous 2-electron
photodetachment (likely to the Ru$^+$ 4$p^54d^65s^2$ state) located around 49 eV. Despite the large number of possible terms resulting from the Ru$^-$ 4$d$-open shell, the cross section obtained from a 51-state LS-coupled R-matrix calculation agrees qualitatively well with the experimental data.

There is evidence that the existence of vacant states in the 4$d$ inner-shell of the Ru$^-$ negative ion causes resonance interference effects in the total cross section, resulting in a net dip in the Ru$^+$ cross section just below the 4$p$ threshold and an enhancement just above the threshold. The role of many-particle effects, intershell interaction, and polarization seems much more significant in Ru$^-$ than in Fe$^-$ photodetachment, as would be expected given the additional complexity of the partially filled 4$d$ shell of Ru$^-$.  

7.2. Future inner-shell photodetachment studies of transition metal negative ions

The use of synchrotron radiation for inner-shell photodetachment studies of negative ions is still a young field. Therefore, there are still a lot of unresolved issues that need to be investigated. Our work could be extended to future projects which include studies of transition metal negative ions such as:

1. Inner-shell 2$p$– photodetachment of Fe$^-$

The 3$p$ photoelectron spectra for the transition metal neutral atoms from Mn to Ni are dominated by the large 3$p$–3$d$ Coulomb exchange splitting and the term-dependent decay of the 3$p$ core-hole states. In contrast to the 3$p$ photoabsorption, the 2$p$ photoabsorption can be described in a single configuration approximation and the 2$p$ spin-orbit splitting dominates the spectra. It will be interesting to find out if the 3$p$ and 2$p$ spectra for the transition metal negative ion Fe$^-$ exhibit also the same difference as the neutrals spectra. The comparison of the atomic spectra with the
spectra of the corresponding metals, compounds, thin films, or multilayers, therefore, yields basic information about the interplay of interatomic and intra-atomic interactions.

2. Inner-shell photodetachment of Os\textsuperscript{−} negative ion

A laser spectroscopy experiment indicated Os\textsuperscript{−} as the only known atomic negative ion with bound states of opposite parity. This is making Os\textsuperscript{−} a very interesting candidate for an inner-shell photodetachment experiment. The inner-shell photodetachment of Os\textsuperscript{−} will complete the systematic study of the entire Fe, Ru, and Os column in the periodic table. In this way, a comparison between the transition metal negative ions of the same column can be done.

3. Inner-shell photodetachment of Fe\textsuperscript{−} and Ru\textsuperscript{−} clusters

Clusters are the bridge between the gas phase and the solid phase and have been studied using mostly laser techniques. Investigation of cluster negative ions using synchrotron radiation is a novel direction. Studies of neutral as well as ionic clusters allow us to understand the complex behavior of bulk materials. In a previous experiment, our group investigated the photodetachment of small iron clusters and a change in the resonance structure was observed for the Fe\textsubscript{2}\textsuperscript{−} and Fe\textsubscript{3}\textsuperscript{−} clusters. It will be interesting to look for larger Fe and Ru clusters, and see how their electronic and structural properties evolve with their size.

There is no doubt that inner-shell photodetachment studies will bring valuable new insights into the structural and dynamical properties of negative ions in the coming years. In this research field, theory and experiment currently are developing in parallel, and we hope that our measurements of Fe and Ru transition metal negative ions will inspire theorists to further refine their methods and experimental physicists to extend their investigations to more complex negative ions.
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