Near threshold VUV polarization measurements in the noble gases.

Craig David Noren
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NEAR THRESHOLD VUV POLARIZATION MEASUREMENTS
IN THE NOBLE GASES

by

Craig David Norén

A Dissertation
submitted to the
Faculty of Graduate Studies and Research
through the Department of
Physics in Partial Fulfillment
of the requirements for the Degree
of Doctor of Philosophy at the
University of Windsor

Windsor, Ontario, Canada

1995
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ABSTRACT

NEAR THRESHOLD VUV POLARIZATION MEASUREMENTS
IN THE NOBLE GASES

by

Craig David Norén

The linear polarization of resonant VUV radiation emitted from collisionally excited rare gas atoms (He, Ne, Ar, Kr and Xe) has been measured in the threshold region. The apparatus consisted of a hemispherically analyzed electron beam interacting with a gas jet and the normally emitted radiation being analyzed using reflection optics. Conservation of angular momentum arguments predict a threshold polarization of 1 (-1) for direct (exchange) excitation of LS coupled states (i.e. \(^1P\) (\(^3P\) )) and this was demonstrated for the \(^3s2p\) state of helium. The effects of negative ion resonances on the observed polarization have been calculated using the Baranger-Gerjuoy theory and compared with the measured polarization curve. These calculations are expected to be most reliable when the resonance formation is the dominant excitation channel (i.e. at threshold). Also the effects of cascade, as well as competition between direct and exchange excitation (heavy rare gases), were also observed and discussed.
To Mom and Dad
ACKNOWLEDGEMENTS

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Finally, but certainly not least, I would like express my gratitude to Dr. J.W. McConkey for his infinite patience, guidance and enthusiasm throughout my stay.
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Chapter 1

Introduction

Polarized fluorescence occurs when there is an imbalance in the population of the magnetic sublevels of the excited state. This imbalance can occur whenever the excitation process is spatially anisotropic such as occurs when polarized light beams or charged particle beams are used for the excitation process. The importance of the polarization of optical radiation is being increasingly recognized in a variety of fields such as:

1) the development of secondary standards for absolute calibration in the vacuum ultra-violet (VUV) has required the determination of accurate excitation cross-sections for electron-impact excited VUV lines as well as the polarization sensitivity of the photon detection equipment [Shemansky et al., 1985; Forand et al., 1986],

2) in plasma diagnostics where the polarization of the spectral lines can reveal information on the presence of electric and magnetic fields which can cause an anisotropic velocity distribution of the electrons [Fujimoto et al., 1992],

3) in electron-photon coincidence studies, where polarization correlation functions are measured to allow the extraction of the fine details of the excitation processes, linear and circular polarization measurements are needed to calibrate results [Westerveld et al., 1985; Khakoo et al., 1986; Heck and Williams, 1987] and

4) for the evaluation of relative cross-sections within an unresolved multiplet [McConkey, 1988].

Clearly when considering the electron-impact excitation of atoms or molecules, the polarization of the resultant radiation carries important information about the impact excitation process itself. This is likely to be particularly important near the threshold where conservation of angular momentum and its component along the quantization axis (electron-beam) often allows accurate predictions about the magnitude of the polarization in this energy region. Deviations from this expected value can be interpreted as being due
to processes other than direct excitation, such as the formation of negative-ion resonances [Wolcke et al., 1983]. Although there have been numerous reports of near threshold polarization of electron-impact radiation from a variety of targets, these have all been confined to the visible or near UV spectral regions (see review by Heddle and Gallagher [1989] which gives references to earlier work). One difficulty in analyzing the VUV radiation has been the lack of suitable materials for transmission optics and thus reflection optics must be used where deterioration of surfaces, causing changes in optical performance, must be dealt with.

An illustrative example of how polarization measurements can be used to disentangle excitation data is given McConkey [1988] who measured the polarization of the 121.5 nm line of He$^+$ from threshold to 480 eV and discussed their results in terms of the relative importance of the $4s\rightarrow2p$, $4p\rightarrow2s$ and $4d\rightarrow2p$ components. They concluded that, because the threshold polarizations corresponding to these components would be 0, 0.43 and 0.49 respectively, the $4s\rightarrow2p$ component dominates the excitation near threshold.

Information on polarization measurements of resonant VUV radiation resulting from electron-impact on the rare gases has been rare in the literature. Standage [1977] reviewed previous measurements of VUV polarization measurements of helium and highlighted the discrepancies observed in their values. Since that time Steph and Golden [1982] and Hammond et al. [1989] have performed measurements which are in reasonable agreement with each other. Steph and Golden’s data were obtained from coincidence experiments and therefore are cascade-free and specific to the $2^1P$ excitation while Hammond et al.’s data were integrated measurements of all $n^1P\rightarrow1^1S$ transitions. To correct for cascade, Hammond et al. used the fractional cascade component determined by Donaldson et al. [1972] and Westerveld et al. [1979] and assumed that it was unpolarized. The results of Steph and Golden lie between the corrected and uncorrected data of Hammond et al. indicating that part of the cascade must be polarized. Only the results of Hammond et al. extend to threshold where their value of 0.78 is consistent with the theoretical prediction of +1 (see chapter 2) given the energy resolution of approximately 500 meV. However the relatively large spacing of their data points and
poor energy resolution did not permit the detailed analysis of the threshold region where negative-ion resonances have been observed in high resolution measurements of VUV photons [Brunt et al., 1977a] and metastables [Brunt et al., 1977b; Buckman et al., 1983a].

Theoretical calculations of the excitation cross-section for different $LS$ states have been performed in the threshold region [Freitas et al., 1984; Konovalov and McCarthy, 1995; Sawey and Berringlon, 1993] and clearly show the effects of negative-ion resonances. However theoretical polarization calculations have been limited to the region above the first ionization limit [Csanak et al., 1992; Vriens and Carrière, 1970]. These calculations are based on the Born approximation and give good agreement with the measured polarization at higher energies ($\geq 100$ eV).

Results of the polarization of VUV radiation for the heavy rare gases have also been sparse. The measurements by Karras [1988] (some of which were published in Hammond et al. 1989) and Uhrig et al. [1994a,b] focused primarily in the high energy regime where the Born theory was found to hold. However at near-threshold energies, where the effects of negative ion resonances (VUV photons [Brunt et al., 1977c] and metastables [Brunt et al., 1976; Buckman et al., 1983b]) and cascading significantly influence the observed polarization, very little work has been done at a resolution which can discern these effects.

Other polarization measurements of VUV radiation for the heavy rare gases were performed by Dassen et al. [1977] on the 106.7 nm line of argon and by Al-Shamma and Kleinpoppen on krypton [1977] and xenon [1978] (within the first 3 eV above threshold). The measurements by Karras and Uhrig et al., while agreeing very well with each other and reasonably well with Dassen et al., show considerable disagreement with those of Al-Shamma and Kleinpoppen. Recently, one of the authors [Kleinpoppen, 1994] has indicated that their measurements are probably in error. The poor energy resolution and widely spaced data points of Karras and of Uhrig et al. prevent detailed analysis of the threshold region.

Other polarization measurements have been recently performed by Furst et al. [1993] on the light emitted from the $np^4(n+1)l^5[5/2]_3$ states in Ne ($n=2$; 640.2 nm), Ar

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\((n=3; 811.5 \text{ nm}), \text{Kr} (n=4; 811.2 \text{ nm})\) and \(\text{Xe} (n=5; 881.9 \text{ nm})\), and the \(np^3(n+1)p[5/2]_2\) states in \(\text{Kr} (n=4; 877.7 \text{ nm})\). The \(np^3(n+1)p[5/2]_3\) level is the only \(J=3\) state in the \(p\) manifold and is a pure \(LS\) state \((^3D_3)\) to the extent that configuration mixing is unimportant while for the \(np^3(n+1)p[5/2]_2\) level, neither \(L\) nor \(S\) are good quantum numbers. The \(np^3(n+1)p[5/2]_2\) state can be represented in an intermediate coupling representation as

\[
\psi(J=2) = \alpha \psi(^3D_2) + \beta \psi(^1D_2) + \gamma \psi(^3P_2) \tag{1.1}
\]

where \(\alpha, \beta\) and \(\gamma\) are mixing coefficients. Their results for \(J=3\) states at threshold are in good agreement with the \(LS\) coupled threshold predictions (see section 2.3) while the \(J=2\) state did not (as would be expected from equation 1.1). The data also do not show any indications of resonant structure in the near threshold region.

Theoretical calculations for the excitation of the VUV emitting states of the heavy rare gases have been limited to neon [Savada et al., 1971; Noro et al., 1979; Clark and Taylor, 1982; Taylor et al., 1985 and Bentley, 1991] and argon [Ohja et al., 1982]. These calculations determined only the total excitation cross-sections over the first 2 eV above threshold and thus no polarization results can be determined. To the author's knowledge there have been no theoretical excitation cross-sections, let alone polarization functions, calculated for krypton and xenon in the region between the threshold and the first ionization potential.

In this work, polarization measurements of the rare gases (He, Ne, Ar, Kr, Xe) using a medium resolution electron beam were performed in the near threshold region. The polarization functions were analyzed using threshold predictions based on the theory of Percival and Seaton [1958] (chapter 2) as well as polarizations predicted for negative-ion resonances based on the Baranger-Gerjuoy theory [1958] (chapter 3). A description of the apparatus is presented in chapter 4. The results for helium are given in a separate chapter (chapter 5) since it has different ion-core parity and coupling schemes from the other gases. The results for the heavy rare gases are presented as a unit (chapter 6) where systematics that occur are highlighted.
Chapter 2

Theoretical Considerations

2.1 Introduction

The theoretical development of the polarization of atomic line radiation resulting from electron beam excitation has been treated in the classic paper by Percival and Seaton [1958]. Their treatment extended earlier analysis to account for the fine structure and the hyperfine structure when these features are comparable to the line width and permitted the calculation of the polarization as a function of electron energy in terms of the magnetic sublevel excitation cross-sections and their appropriate coefficients. An overview of their procedure along with predictions relevant to this work will be presented in section 2.3.

A second approach for determining the polarization has been to use the density matrix formalism [Blum 1981]. This method was developed to describe electron-atom interactions where both the scattered electron and the emitted photon are measured. The results of this technique can be applied to experiments where only photons are measured by integrating over all scattering angles. This method is particularly useful in determining threshold polarizations and first order corrections to the polarization function due to negative ion resonances (see section 6.3) since it is possible to express these values in terms of 3-j (or Clebsch-Gordon coefficients), 6-j and 9-j symbols involving the angular momentum of the atom before and after electron impact excitation. An overview of this method will be presented in section 2.4.

First, predictions based on simple angular momentum arguments will be presented.
2.2 Threshold Polarization

The linear polarization (Stokes parameters $P_1$) of atomic line radiation resulting from electron impact is given by

$$P_1 = \frac{I_{\|} - I_{\perp}}{I_{\|} + I_{\perp}} \quad (2.1)$$

where $I_{\|}$ and $I_{\perp}$ are the intensities of the radiation whose electric vector is parallel and perpendicular to the quantization axis respectively. The quantization axis (or $z$ axis) is generally defined as being parallel to the electron beam and therefore $I_{\|}$ has its electric vector parallel to the $z$ axis while $I_{\perp}$ has its electric vector parallel to either the $x$ or $y$ axis.

Note that because of cylindrical symmetry about the $z$ axis, $I_x = I_y = I_{\perp}$.

The total emission intensity $\bar{I}$ is therefore given by

$$\bar{I} = I_x + I_y + I_z = I_{\|} + 2I_{\perp} \quad (2.2)$$

and therefore equation 2.1 can be rewritten as

$$P_1 = \frac{3I_{\|} - \bar{I}}{I_{\|} + \bar{I}}. \quad (2.3)$$

For electric dipole transitions involving $J' = 1$ ($M_{J'} = 0, \pm 1$) $\rightarrow J'' = 0$ ($M_{J''} = 0$) the linear polarization gives information concerning the relative population of the magnetic sublevels. The light is polarized parallel to the quantization axis for the transitions $\Delta M_J = 0$ while the light is polarized perpendicular to the quantization axis for $\Delta M_J = \pm 1$ (see figure 2.1).

It is now possible to make predictions concerning the polarization of the radiation emitted by an atom which is excited by electron impact from a $^1S_0 \rightarrow ^2S + 1P_1$. If we assume that $L$ and $S$ are conserved separately, as is the case with helium, then the following relations for the magnetic sublevels must hold:

$$M_S + m_z = M_{S'} + m_{z'} \quad (2.4)$$

$$M_L + m_l = M_{L'} + m_{l'} \quad (2.5)$$
where $M_L$ ($M_L'$) is the orbital angular momentum magnetic quantum number before (after) electron impact, $M_S$ ($M_S'$) is the projection of the spin angular momentum magnetic sublevel before (after) electron impact, $m_l$($m_l'$) is the projection of the orbital angular momentum of the incident (scattered) electron onto the quantization axis and $m_s$ ($m_s'$) is the projection of the spin of the incident (scattered) electron onto the quantization axis. If the incident electron defines the quantization axis, it therefore has no angular momentum about this axis and $m_l = 0$ and since the atom is initially in an $L=0$ state, therefore $M_L = 0$. At threshold the scattered electron carries off very little energy and therefore no angular momentum (i.e. $m_s = 0$) which results in $M_L = 0$. Thus in the case of helium the threshold excitation of the $^1P$ state results in only parallel polarized light (i.e. $P=1$).

For the heavy rare gases $LS$ coupling is not valid and therefore only the total angular momentum is considered. The conservation of the $z$-component of angular momentum requires that
be satisfied where \( M_j (M) \) is the total angular momentum magnetic quantum number before (after) electron impact. As above, \( m_t = m_r = 0 \) and \( M_j = 0 \) (because \( J=0 \)) which means that the magnetic sublevel of the total angular momentum for the excited state of the atom is determined by the spin sublevel component. For direct excitation (i.e. the scattered electron is the incident electron) \( m_t = m_r \) in the absence of spin-dependent forces and therefore \( \Delta M_j = 0 \) which results in only parallel polarized light being produced. For exchange excitation there are two possible outcomes: 1) \( m_t = m_r \) and 2) \( m_t = -m_r \) (see figure 2.2). For case (1) \( M_j = 0 \) (singlet excitation) and the radiation is parallel polarized while for case (2) \( M_j = \pm 1 \) (triplet excitation) and therefore the radiation is perpendicularly polarized (\( P_t = -1 \)). Note that \( M_j = \pm 1 \) is excited only through exchange excitation. Thus a measurement of the polarization at threshold for the heavy rare gases will determine which mechanism is dominating. For mercury, which also has a \(^1S_0\) ground state, exchange was observed to be dominant [Hanne et al., 1981].

![Electron exchange: e\(^-\) + A\(^1S_0\) \rightarrow A\(^2P_{\text{g}}\) + e\(^-\)](Taken from Hanne and Kessler, 1976)  

\( M_j + m_t + m_r = M_j' + m_t' + m_r' \)  \hspace{1cm} (2.6)

**Figure 2.2** Exchange collision leading to triplet excitation of a two-electron atom by electron impact. The incident electron is indicated by the hatching [taken from Hanne and Kessler, 1976]
Note that the above considerations have not taken into account the hyperfine structure due to the presence of nuclear spin \( I \) from naturally occurring isotopes. The effect of the hyperfine structure tends to depolarize the radiation and will only affect krypton and xenon which have significant amounts of isotopes with non-zero \( I \).

### 2.3 Oppenheimer-Penney Theory

The theoretical basis for the polarization of atomic line radiation resulting from electron impact was first developed by Oppenheimer [1927a,b; 1928] and later extended to include hyperfine structure by Penney [1932]. Their method involved calculating the probabilities for excitation of individual quantum states and the probabilities for emission of polarized radiation from their subsequent decay. While fine structure (f.s.) and hyperfine structure (h.f.s.) were accounted for, Percival and Seaton [1958] demonstrated the Oppenheimer-Penney (O.-P.) theory was valid only when f.s. and h.f.s was significantly larger or smaller than the line width of the observed radiation. In the present work, the separation of the h.f.s. is large enough for the O.-P. theory to be valid.

The development of the O.-P. theory requires the following assumptions:

1. There are three atomic energy levels (or groups of closely spaced sublevels) labeled \( a \), \( b \) and \( c \) which contain \( \alpha \), \( \beta \) and \( \gamma \) sublevels that can be represented by the quantum states \( \psi_\alpha, \psi_\beta \) and \( \psi_\gamma \) respectively. The statistical weight of each sublevel is equal to the number of sublevels present for each energy level and is denoted \( w_\alpha, w_\beta \) and \( w_\gamma \) respectively. Further, \( a \) is defined as the initial state, \( b \) is the excited state produced by electron impact and \( c \) is the final state.

2. The incident electron beam and the initial atomic state \( a \) have a completely isotropic spin distribution.

3. The initial orbital angular momentum of the atom is zero which results in any anisotropy of the emitted radiation being due to the interaction with the incident electron.

4. The total spin and the total orbital angular momentum are separately conserved throughout the interaction.
With these assumptions it is now possible to express the polarization function in terms of excitation cross-sections. To do this we assume that a mono-energetic beam of electrons with number density \( n(e) \) and velocity \( v_0 \) is incident on atoms in state \( \alpha \). The atoms are assumed to be distributed evenly in all sublevels \( \alpha \) (i.e. the number density \( n(\alpha) \) is the same for all \( \alpha \) so that the number density for state \( \alpha \) is \( w_{\alpha}n(\alpha) = n(\alpha) \)). The transition rate for \( \alpha \rightarrow \beta \) is

\[
W(\alpha \rightarrow \beta) = n(e)n(\alpha)v_0 Q(\alpha \rightarrow \beta)
\]

and the total transition rate \( W(\beta) \) from state \( \alpha \) to sublevel \( \beta \) is found by summing over \( \alpha \) and yields

\[
W(\beta) = n(e)n(\alpha)v_0 Q(\beta) = n(e)n(\alpha)K(\beta)
\]

where

\[
Q(\beta) = w_{\alpha}^{-1} \sum_\alpha Q(\alpha \rightarrow \beta)
\]

is the total excitation cross-section for sublevel \( \beta \) and

\[
K(\beta) = v_0 Q(\beta)
\]

is the rate coefficient.

Next we consider the probability for decay (\( \beta \rightarrow \gamma \)) by photon emission. The energy spacings of the sublevels within \( b \) and \( c \) are considered to be much smaller than the energy separation between \( b \) and \( c \) and therefore the photon energy will be treated as the same for all transitions. The emission of radiation \( \nu_{bc} = (E_b - E_c)/h \) from an electric dipole lying in the \( \xi \)-direction \((\xi=x,y,z)\) is denoted by \( A_\xi(\beta \rightarrow \gamma) \). The total probability for emission from \( \beta \) is

\[
A(\beta) = \sum_{\xi,\gamma} A_\xi(\beta \rightarrow \gamma).
\]

The probability for radiative emission from any state \( \beta \) is the same (i.e. \( A(b) = A(\beta) \)) and therefore the probability for emission from \( \beta \) is \( A(b)n(\beta) \).

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In equilibrium, the excitation rate equals the emission rate for each $\beta$ and therefore

$$n(\beta)A(h) = n(e)u(\alpha)K(\beta)$$  \hspace{1cm} (2.12)

and

$$n(\beta)A_1(h) = n(e)u(\alpha)K_1(\beta).$$  \hspace{1cm} (2.13)

Combining 2.12 and 2.13 and using 2.10 yields the following relation for the rate coefficient for the emission of $\xi$-photons from sublevel $\beta$

$$K_\xi(\beta) = \frac{A_\xi(\beta)}{A(b)} u(\alpha) Q(\beta).$$  \hspace{1cm} (2.14)

The total emission rate coefficients for $\xi$-photon and all photons are

$$K_\xi = \sum_\beta K_\xi(\beta) = \frac{u(\alpha)}{A(b)} \sum_\beta A_\xi(\beta)Q(\beta)$$  \hspace{1cm} (2.15)

and

$$K = \sum_\xi K_\xi = u(\alpha) \sum_\beta Q(\beta)$$  \hspace{1cm} (2.16)

respectively.

Finally, if we define the electron beam as being along the $z$-axis and the observed photons as propagating along the $x$-axis, then the observed photon intensity with electric vectors parallel (I$_\parallel$) and perpendicular (I$_\perp$) to the $z$-axis are given by

$$I_\parallel = D \sum_\beta n(\beta)A_y(\beta)$$  \hspace{1cm} (2.17)

$$I_\perp = D \sum_\beta n(\beta)A_z(\beta)$$

where $D$ is a constant. Using equation 2.13, equations 2.17 can be expressed as

$$I_\parallel = D \frac{n(e)n(\alpha)u(\alpha)}{A(b)} \sum_\beta Q(\beta)A_y(\beta)$$

$$I_\perp = D \frac{n(e)n(\alpha)u(\alpha)}{A(b)} \sum_\beta Q(\beta)A_z(\beta).$$  \hspace{1cm} (2.18)

Substituting equations 2.17 into the polarization formula (2.1) and noting that $A_y(\beta) = A_\xi(\beta) = \frac{1}{2}(A(b) - A_z(\beta))$ due to cylindrical symmetry, we obtain equation (2.3)
\[ P_1 = \frac{3l_{11} - \tilde{l}}{l_{11} + \tilde{l}} \]  
(2.3)

where

\[ \tilde{l} = l_{11} + 2l_1 = Dn(b)A(b). \]  
(2.19)

The rate coefficient \( K \), which is proportional to the observed radiation intensity (compare equations 2.15, 2.16 with 2.18), equation 2.3 can be rewritten as

\[ R = \frac{3K_z - K}{K_z + K}. \]  
(2.20)

In order to use equation (2.20) the cross-sections for the excitation of the quantum states \( \beta \) must be determined. Using the \( LS \) coupling scheme we have

\[ \beta = \Delta S L M_S M_L, \]
\[ \alpha = \Delta' S L' M'_S M'_L, \]
\[ \gamma = \Delta^* S L^* M'_S M'_L, \]

where \( \Delta, \Delta' \) and \( \Delta^* \) denote all other quantum numbers and will be suppressed hereafter.

If the spin of the incident electron \( (m_s) \) and scattered electron \( (m'_s) \) are not observed then the total cross-section \( Q(SLM_S M_L) \) must be averaged over \( m'_s \) and summed over \( m_s \). This results in

\[ Q(SLM_S M_L) = \frac{v_b}{v_o} \frac{1}{2(2S+1)(2L'+1)} \sum_{M_L} \int |f_{m_m}(am'_s, M_L)k_b|^2 \, dv(k_b) \]  
\[ Q(SLM_S M_L) \]  
(2.21)

where \( f_{m_m} \) is the scattering amplitude, \( k_b \) is the direction of the scattered electron and \( k_o \) is the direction of the incident electron.

Because there is no preferred spin direction and spin and orbital angular momentum are conserved separately, \( Q(SLM_S M_L) \) is independent of \( M_S \). Also, \( Q(SLM_S M_L) \) does not depend on the sign of \( M_L \) due to symmetry about the \( z \)-axis. Therefore

\[ Q(SLM_S M_L) = \frac{Q_{M_L}}{(2S+1)} \]  
(2.22)
\[ Q(SL) = \sum_{M_J} Q(SL M_J) = \sum_{M_L} Q_{M_L}. \quad (2.23) \]

Now if there is a weak spin-orbit interaction we can use the representation
\[ \beta = SL M_J \]
and the scattering amplitude is transformed as
\[ f_{SL M_J \sigma} = \sum_{M_J M_L} (SL M_J M_L, J) f_{SL M_J \sigma M_L}. \quad (2.24) \]

where the term in the brackets is a Clebsch-Gordon coefficient. The cross-section transforms as
\[ Q(SL M_J) = \sum_{M_J M_L} (SL M_J M_L, J)^2 Q(SL M_J) \]
\[ = \frac{1}{2S+1} \sum_{M_J M_L} (SL M_J M_L, J)^2 Q_{M_L}. \quad (2.25) \]

Summing (2.25) over \( M_J \) and using equation (2.22) results with
\[ Q(SL J) = \sum_{M_J} \frac{Q_{M_J}}{2S+1} \sum_{M_J M_L} (SL M_J M_L, J)^2 \]
\[ = \frac{(2J+1)}{(2S+1)(2L+1)} \sum_{M_L} Q_{M_L}. \quad (2.26) \]

If nuclear spin is present then the excited states can be represented by
\[ \beta = SL J I F_M \]
where \( I \) is the nuclear spin and \( F \) is the resultant of \( I \) and \( J \). The cross-sections in this representation can be expressed in terms of \( Q(SL M_J) \) by the transformation
\[ Q(SL J I F_M) = \frac{1}{(2J+1)} \sum_{M_J M_I} (J M_J M_I, F M_M)^2 Q(SL M_J). \quad (2.27) \]

A second representation which is convenient to use is
\[ \beta = SL T L M_M M_L \]
where \( T \) is the resultant of \( S \) and \( I \). In this representation the cross-section is given by

\[
Q(SITLM_f M_L) = \frac{1}{(2S+1)(2I+1)} Q_{M_f m_f}
\]  

(2.28)

since all spin was assumed to be isotropic (see equation 2.22).

The two representations can be related by the following transformation

\[
\langle SITLM_f M_L | SLJFM_F \rangle = \langle TLM_f M_L | FM_F \rangle \langle SI(T) LF | SL(J) IF \rangle
\]  

(2.29)

where

\[
\langle SI(T) LF | SL(J) IF \rangle = \left[ (2T+1)(2J+1) \right]^{1/2} (-1)^{-L-I-T-J} [SLJ]_{FI T}.
\]  

(2.30)

This results in the following expression for the cross-section

\[
Q(SLJFM_F) = \frac{2J+1}{(2S+1)(2I+1)} \sum_{T,M_T} \left( 2T+1 \right) [SLJ]_{FI T}^2 \langle TLM_f M_L | FM_F \rangle^2 Q_{M_f m_f}.
\]  

(2.31)

The transition probabilities are also more conveniently expressed by expanding the electric dipole transition operator \( r \) in terms of the spherical harmonics \( Y_{l \mu}(r) \). This results in the transition probabilities being written as

\[
A_z(\beta \rightarrow \gamma) = A^{(\mu)}(\beta \rightarrow \gamma)
\]

\[
A(\beta \rightarrow \gamma) = \sum_{\mu} A^{(\mu)}(\beta \rightarrow \gamma)
\]  

(2.32)

where \( \mu \) has the values \(-1,0,1\).

Using the Wigner-Eckhart theorem we obtain

\[
A^{(\mu)}(JM_f \rightarrow J'M_f) = (J'M_f - \mu J M_f)^2 A(J \rightarrow J')
\]  

(2.33)

where

\[
A(J \rightarrow J') = \sum_{JM_f \mu} A^{(\mu)}(JM_f \rightarrow J'M_f),
\]  

(2.34)

Note that equations 2.33 and 2.34 do not depend on \( LS \) or \( L "S" \) and therefore can be used for electric dipole transitions which depart from \( LS \) coupling.

For transitions involving the h.f.s. states the following relations are obtained:
\[ A^{\mu}(JIFM_F \rightarrow J^*IF'M'_F) = (F^*1M_F - \mu|FM_F)^2 A(JIF \rightarrow J^*IF'), \]
\[ A(JIF \rightarrow J^*IF') = (2J + 1)(2F^* + 1) \sum_{|J^*\rangle} A(J \rightarrow J^*). \] (2.35)

Now the polarization functions can be determined in terms of excitation cross-sections for individual sublevels. First, the case without h.f.s. will be considered. The rate coefficients \( \mathcal{K}_x \) are determined by substituting equations 2.25 and 2.33 into 2.15 and 2.16 (where the sum is now over \( n \) instead of \( \xi \)). This results in the following expressions

\[ \mathcal{K}_x(SLJ \rightarrow J^*) = \frac{\nu_a A(SLJ \rightarrow J^*)}{(2S + 1)A(SLJ)} \sum_{M_F,M_J} [(S)(M_F,M_J)(J^*\rangle 1M_J,0|J\rangle)^2 Q_{M_J} \] (2.36)
\[ \mathcal{K}(SLJ \rightarrow J^*) = \frac{\nu_a A(SLJ \rightarrow J^*)}{(2S + 1)A(SLJ)} 2J + 1 \sum_{M_F,M_J} Q_{M_J}. \] (2.37)

These equations are of use for He and heavy rare gas isotopes with \( I=0 \).

Using equations 2.36 and 2.37 in 2.20 the following results are obtained

i) \( L = 0 \ S = 0,1 \)
\[ R_l = 0 \] (2.38)

ii) \( L = 1 \ S = 0,1 \)
\[ R_l = \frac{G(Q_0 - Q_1)}{h_0 Q_0 + h_1 Q_1}, \] (2.39)

iii) \( L = 2 \ S = 0,1 \)
\[ R_l = \frac{G(Q_0 + Q_1 - 2Q_2)}{h_0 Q_0 + h_1 Q_1 + h_2 Q_2}, \] (2.40)

where \( G, h_0, h_1 \) and \( h_2 \) are given in Table 2.1 for various \( (LSJ \rightarrow J^*) \). As noted in section 2.2, threshold excitation for singlet states is only to the \( M_L = 0 \) state and therefore \( Q_1 = 0 \) which sets the threshold polarization equal to \( G/h_0 \). For helium this gives \( P_1 = 1 \). For neon and argon \( M_J = \pm 1 \) can be populated if exchange occurs and this gives a threshold polarization of \( G/h_1 = -1 \) (i.e. \( Q_0 = 0 \)).

To calculate the polarization for states with h.f.s. and for species with a mixture of \( I \) it is more convenient to find \( I_{\mu} \) and \( I_1 \) for each \( I \) and average these values [Bonham, 1982]. To do this equation 2.27 and 2.33 are substituted into 2.18 which yields

\[ I_{\mu}(JM_J) = \frac{C_{\mu}}{2I + 1} \sum_{FM_F} [(\mu|FM_F)^2 \langle JM_J,0|FM_F \rangle^2 Q(JM_J)A(J \rightarrow J^*)] \] (2.41a)

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Table 2.1 Polarization Formula Coefficients for He lines ($SLJ \rightarrow J^*$) [Percival and Seaton 1958]

<table>
<thead>
<tr>
<th>$SLJ$</th>
<th>$J^*$</th>
<th>$G$</th>
<th>$h_0$</th>
<th>$h_1$</th>
<th>$h_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>011</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1</td>
<td>7</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>022</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-3</td>
<td>3</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>15</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td>110</td>
<td>1</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>111</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-1</td>
<td>13</td>
<td>27</td>
<td>-</td>
</tr>
<tr>
<td>112</td>
<td>1</td>
<td>21</td>
<td>47</td>
<td>73</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-7</td>
<td>11</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1</td>
<td>7</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>121</td>
<td>0</td>
<td>3</td>
<td>5</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-3</td>
<td>7</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>41</td>
<td>81</td>
<td>78</td>
</tr>
<tr>
<td>122</td>
<td>1</td>
<td>3</td>
<td>9</td>
<td>17</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-3</td>
<td>7</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>29</td>
<td>57</td>
<td>54</td>
</tr>
<tr>
<td>123</td>
<td>2</td>
<td>18</td>
<td>41</td>
<td>76</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-9</td>
<td>11</td>
<td>25</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3</td>
<td>15</td>
<td>29</td>
<td>26</td>
</tr>
</tbody>
</table>

\[
I_1(JM_f) = \frac{C_0}{2(2I+1)} \sum_{FM_F} \left[ (IJM_F || FM_F) - (IJM_F - || FM_F) \right]^2 \times Q(JM_f) A(J \rightarrow J^*)
\]  

where $C_0$ is a constant. For the transition $J=1 \rightarrow J^*=0$ the results are given in Table 2.2.

Now the polarization for species with mixed nuclear spin can be obtained using

\[
P_I = \frac{\sum \%(I)(I_{1s}(I)-I_{1s}(I))}{\sum \%(I)(I_{1s}(I)+I_{1s}(I))}
\]

where $I$ is the nuclear spin and $\%(I)$ is the relative population of this isotope. The results for krypton and xenon are given in Table 2.3 along with the threshold polarization for singlet and triplet excitation.
Table 2.2 Intensity relations for various isotopes \( I \). It has been assumed that cross-sections for \( M_j = \pm 1 \) are identical.

<table>
<thead>
<tr>
<th>( I )</th>
<th>( I_n / C_0 Q(1\rightarrow0) )</th>
<th>( I_\perp / C_0 Q(1\rightarrow0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( Q(1,0) )</td>
<td>( Q(1,1) )</td>
</tr>
<tr>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{6} [5Q(1,0)+4Q(1,1)] )</td>
<td>( \frac{1}{6} [2Q(1,0)+7Q(1,1)] )</td>
</tr>
<tr>
<td>( \frac{3}{2} )</td>
<td>( \frac{1}{450} [224Q(1,0)+226Q(1,1)] )</td>
<td>( \frac{1}{450} [113Q(1,0)+337Q(1,1)] )</td>
</tr>
<tr>
<td>( \frac{5}{2} )</td>
<td>( \frac{1}{37725} [17521Q(1,0)+19604Q(1,1)] )</td>
<td>( \frac{1}{37725} [9802Q(1,0)+27323Q(1,1)] )</td>
</tr>
</tbody>
</table>

2.4 Density Matrix Formalism

An alternative approach to determining the polarization has been to use density matrices in conjunction with state multipole moments. The development of this treatment has been discussed in detail in the literature [e.g. Blum, 1981; Blum and Kleinpoppen, 1979] and therefore only a highlight of the results relevant to the present experiment will be presented.

The assumptions used are the same as those presented in section 2.2. The initial, excited and final atomic state are represented by

\[
\begin{align*}
\Gamma_0 &= \Delta_0 L_0 S_0 M_{L_0} M_{S_0} \\
\Gamma_1 &= \Delta_1 L_1 S_1 M_{L_1} M_{S_1} \\
\Gamma_2 &= \Delta_2 L_2 S_2 M_{L_2} M_{S_2}
\end{align*}
\]

respectively.

The incident and scattered electrons are characterized by \( p_0 m_0 \) and \( p_1 m_1 \) respectively where \( p_i \) is the momentum and \( m_i \) is the spin component. Since the initial atomic state is assumed to have zero orbital angular momentum therefore \( L_0 = M_{L_0} = 0 \).

Finally, the emitted photons will be represented by the quantum number \( \lambda \) which is the component of spin about the quantization axis (i.e. the direction of the photon \( n \)). In the helicity representation \( \lambda \) has values of +1 and -1 and is related to the \( x-y \) representation (\( z \) is the quantization axis) by
Table 2.3 Polarization function coefficients and threshold values for triplet (\(P_0^\prime\)) and singlet (\(P_0\)) excitation.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>I</th>
<th>%</th>
<th>G</th>
<th>(h_0)</th>
<th>(h_1)</th>
<th>(P_0^\prime)</th>
<th>(P_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe(^{129})</td>
<td>½</td>
<td>26.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe(^{131})</td>
<td>½</td>
<td>21.2</td>
<td>.664</td>
<td>.888</td>
<td>1.112</td>
<td>.748</td>
<td>-.597</td>
</tr>
<tr>
<td>Xe(^{(a)})</td>
<td>0</td>
<td>52.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr(^{83})</td>
<td>½</td>
<td>11.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr(^{(a)})</td>
<td>0</td>
<td>88.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) denotes all other naturally occurring isotopes

\[ \begin{align*}
|+1\rangle &= -\frac{1}{\sqrt{2}}(|e_x\rangle + |i|e_y\rangle) = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\
|-1\rangle &= +\frac{1}{\sqrt{2}}(|e_x\rangle - |i|e_y\rangle) = \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\end{align*} \] (2.43)

The density matrix for the radiative decay process is given by

\[ \lambda_\lambda' \rho_{\lambda\lambda'} = \begin{pmatrix} \rho_{11} & \rho_{1-1} \\ \rho_{-11} & \rho_{-1-1} \end{pmatrix} \] (2.44)

where \(\rho_{1-1} = \rho_{-11}^*\) due to hermiticity. The total intensity observed is found by taking the trace

\[ I = tr \rho = \rho_{11} + \rho_{-1-1} \] (2.45)

The linear polarization (denoted \(\eta_3\) in the literature and is equivalent to \(P_1\) of the previous sections) is found using the following relations

\[ I_{1\prime} = \langle e_x | \rho | e_x \rangle = \frac{1}{2}(-1) \begin{pmatrix} \rho_{11} & \rho_{1-1} \\ \rho_{-11} & \rho_{-1-1} \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{2}(\rho_{11} - \rho_{1-1} - \rho_{-11} + \rho_{-1-1}) \] (2.46)

\[ I_{1} = \langle e_y | \rho | e_y \rangle = \frac{1}{2}(\rho_{11} + \rho_{1-1} + \rho_{-11} + \rho_{-1-1}) \]
where \(|\epsilon_z,\lambda\rangle,|\epsilon_y\rangle\) are determined by inverting equation 2.43. Substituting 2.45 and 2.46 into 2.1 yields

\[
\ln_0 = -(\rho_{0,1} + \rho_{1,0}).
\]  

(2.47)

The problem now becomes one of determining \(\rho\) for the interaction.

To do this we start with the density operator \((\rho_0)\) describing the initial system (before impact)

\[
\rho_0 = \rho_A \times \rho_e
\]

(2.48)

where

\[
\rho_A = \frac{1}{2S_0 + 1} \sum_{\lambda_M_x} |\Delta_0 S_0 M_0 \times \Delta_0 S_0 M_0 |
\]

(2.49)

is the atomic density operator and

\[
\rho_e = \frac{1}{Z} \sum_{m_0} |\psi_0 m_0 \times \psi_0 m_0 |
\]

(2.50)

is the electron density operator. The matrix elements of \(\rho_0\) are given by

\[
\langle \Delta_0 S_0 M_0 \times \rho_0 M_0 \times \Delta_0 S_0 M_0 | \phi_0 m_0 \rangle = \frac{\delta_{M_0 M_0} \delta_{m_0 m_0}}{2(2S_0 + 1)}.
\]

(2.51)

The scattering process is characterized by the scattering amplitude \(f(\Gamma_1, \Gamma_0)\) which are the matrix elements of the corresponding transition operator \(T\)

\[
f(\Gamma_1, \Gamma_0) = \langle \Gamma_1 | T | \Gamma_0 \rangle
\]

(2.52)

normalized such that

\[
|f(\Gamma_1, \Gamma_0)|^2 = \alpha(\Gamma_1, \Gamma_0)
\]

(2.53)

where \(\alpha(\Gamma_1, \Gamma_0)\) is the differential cross-section for the \(\Gamma_0 \rightarrow \Gamma_1\) transition.

The density matrix for the excited state is given by

\[
\rho_1 = T \rho_0 T^\dagger
\]

(2.54)
with the matrix elements

$$\langle \Gamma | \rho ( \Gamma ) | \Gamma \rangle = \frac{1}{2(2S_0 + 1)} \sum_{M_{S_S} m_{S_S}} f(\Gamma, \Gamma_0) f^*(\Gamma, \Gamma_0).$$  \hspace{1cm} (2.55)$$

If the spins of the excited atoms and the scattered electrons are not observed, then equation 2.55 must be summed over the diagonal elements of the unobserved spin components;

$$\langle M_{L_L} | \rho (L_L) | M_{L_L} \rangle = \frac{1}{2(2S_0 + 1)} \sum_{M_{S_S} m_{S_S}} f(M_{L_L}, M_{S_S}, m_{S_S}, m_{S_S}) f^*(M_{L_L}, M_{S_S}, m_{S_S}, m_{S_S})$$

$$= \langle f(M_{L_L}) f^*(M_{L_L}) \rangle.$$  \hspace{1cm} (2.56)$$

\(\rho(L_L)\) is called the reduced density matrix and describes only the orbital states of the atom. The diagonal elements of equation 2.56 are the excitation differential cross-sections \((\sigma(M_{L_L}))\) for the magnetic substates

$$\alpha(M_{L_L}) = \langle M_{L_L} | \rho (L_L) | M_{L_L} \rangle$$

$$= \frac{1}{2(2S_0 + 1)} \sum_{M_{S_S} m_{S_S}} \left| f(M_{L_L}, M_{S_S}, m_{S_S}, m_{S_S}) \right|^2$$  \hspace{1cm} (2.57)$$

and the trace gives the total differential cross-section

$$\sigma = tr\rho = \sum_{M_L} \alpha(M_{L_L}).$$  \hspace{1cm} (2.58)$$

Not all the elements of \(\langle M_{L_L} | \rho (L_L) | M_{L_L} \rangle\) are independent but are subject to the following conditions:

1) Hermiticity

$$\langle M_{L_L} | \rho (L_L) | M_{L_L} \rangle = \langle M_{L_L} | \rho (L_L) | M_{L_L} \rangle^*$$  \hspace{1cm} (2.59)$$

2) Symmetry (i.e. invariance under reflection in the scattering since there is no "up" or "down" in the present experiment)

$$f(M_L, M_{S_S}, m_{S_S}, m_{S_S}) = (-1)^{M_{L_L}+S_S - S} f(-M_{L_L}, -M_{S_S}, -m_{S_S}, -m_{S_S})$$  \hspace{1cm} (2.60)$$
which gives for the density matrix
\[ \langle M_1^\ell | \rho | M_2^\ell \rangle = (-1)^{M_1^\ell + M_2^\ell} \langle -M_2^\ell | \rho | -M_1^\ell \rangle \] (2.61)
and in particular results in
\[ \sigma(M_2^\ell) = \sigma(-M_1^\ell). \] (2.62)

At this point 5 independent parameters are needed to describe the density matrix for the case \( L_1 = 1 \). If \( i) \) spin conservation is taken explicitly into account and \( ii) \) the special case of \( S_0=S_1=0 \) is considered, the number of parameters is reduced to 3 and the parameterization used in the literature is
\[ \sigma = \sigma(0) + 2\sigma(1) \]
\[ \lambda = \frac{\sigma(0)}{\sigma} \]
\[ \cos \chi = \frac{\text{Re}[\sigma(0)/\sigma(1)]}{\sqrt{\sigma(0)/\sigma(1)}}. \] (2.63)

In general it is possible to excite states of different total angular momentum and the density matrix for the \(| M_1 \rangle \) basis is
\[ \rho(J J') = \sum_{M J M J'} \rho(J M J J' M J') \langle J M J J' | \rho(J M J J') | J M J J' \rangle \] (2.64)
where \( \rho(J M J J') \) are the density matrix elements. It is convenient to express the density matrix in terms of its irreducible components, or state multipoles, by defining a new set of tensor operators \( T(J J')_{K Q} \):
\[ T(J J')_{K Q} = \sum_{M M} (-1)^{J' - M'} (2K + 1)^{1/2} \left( \begin{array}{c} J' \\ M' \\ -M \end{array} \right) \left( \begin{array}{c} J \\ M \\ -M \end{array} \right) \langle J M' | \rho(J M') | J M \rangle. \] (2.65)

The state multipoles are defined as
\[ \langle T(J J')_{K Q} \rangle = \sum_{M M} (-1)^{J' - M'} (2K + 1)^{1/2} \left( \begin{array}{c} J' \\ M' \\ -M \end{array} \right) \left( \begin{array}{c} J \\ M \\ -M \end{array} \right) \langle J M' | \rho(J M') | J M \rangle \]
\[ = \sum_{M M} (-1)^{J' - M'} (2K + 1)^{1/2} \left( \begin{array}{c} J' \\ M' \\ -M \end{array} \right) \left( \begin{array}{c} J \\ M \\ -M \end{array} \right) \langle J M' | f'(M) | J M \rangle \] (2.66)
and this allows the density matrix to be rewritten as

\[ \rho = \sum_{J'KQ} \langle T(J')_{KQ} \rangle \langle T(J')_{KQ} \rangle. \tag{2.67} \]

For the case \( J' = J \) equation 2.66 can be written as

\[ \langle T(J)_{KQ} \rangle = \sum_{MM} (-1)^J M' (2K + 1)^{\frac{1}{2}} \begin{pmatrix} J & J & K \\ M' & -M & -Q \end{pmatrix} \langle f'(M') \rangle \langle f''(M) \rangle \]

and in particular, for the case \( Q = 0 \)

\[ \langle T(J)_{KQ} \rangle = \sum_{M} (-1)^J M' (2K + 1)^{\frac{1}{2}} \begin{pmatrix} J & J & K \\ M & -M & 0 \end{pmatrix} \langle f'(M') \rangle \langle f''(M) \rangle \tag{2.68a} \]

If the scattered electron is not detected then all scattering angles must be integrated over and the state multipoles are written as

\[ \langle T(J)_{KQ} \rangle = \sum_{MM} (-1)^J M' (2K + 1)^{\frac{1}{2}} \begin{pmatrix} J & J & K \\ M & -M & 0 \end{pmatrix} \langle \mathcal{F}(M') \rangle \langle \mathcal{F}''(M) \rangle \tag{2.69} \]

where \( \mathcal{F}(M) \) are the scattering amplitudes integrated over all scattering angles.

A property of the state multipole results from the hermiticity condition

\[ \langle JM' | \rho | JM \rangle = \langle JM | \rho | JM' \rangle^* \tag{2.70} \]

which results in the following relation

\[ \langle T(J)_{KQ} \rangle^* = (-1)^J J' Q \langle T(J')_{K'Q} \rangle. \tag{2.71} \]

For the case of sharp angular momentum (\( J' = J \))

\[ \langle T(J)_{KQ} \rangle^* = (-1)^Q \langle T(J')_{K'Q} \rangle. \tag{2.72} \]

which ensures that multipoles \( \langle T(J)_{KQ} \rangle \) are real.
For the present case there is reflection invariance in the scattering plane and thus it can be shown that

\[ \langle T(J)_{kQ} \rangle^* = (-1)^k \langle T(J)_{kQ} \rangle. \]

(2.73)

From equation 2.72 and 2.73 it can be seen that for the case \( J' = J = 1 \) five multipoles need to be determined of which \( \langle T(J)_0 \rangle \), \( \langle T(J)_1 \rangle \), \( \langle T(J)_2 \rangle \) and \( \langle T(J)_3 \rangle \) are real and \( \langle T(J)_4 \rangle \) is imaginary. From equations 2.72 and 2.73 it can also be seen that \( \langle T(J)_5 \rangle \) is zero.

In the present experiment the scattered electron is not detected and therefore there is axial symmetry. This means that the choice of \( X \) and \( Y \) axes perpendicular to the \( Z \) axis is arbitrary. Since the real and imaginary components of \( \langle T(J)_{kQ} \rangle \) are measurable quantities, their values must be the same independent of the orientation of the \( X \) and \( Y \) axes relative to the \( Z \) axis. It can be shown that the relation between \( \langle T(J)_{kQ} \rangle \) for the fixed \( XYZ \) and \( \langle T(J)_{kQ} \rangle_{rot} \) for the rotated \( xyZ \) system is

\[ \langle T(J)_{kQ} \rangle = \langle T(J)_{kQ} \rangle_{rot} \exp(-iQ\gamma) \]

(2.74)

where \( \gamma \) is the angle between the \( X \) and \( x \) axes. Since equation 2.74 must hold for any \( \gamma \), \( Q \) must therefore equal zero. This means that only two real multipoles are needed to describe an axial symmetric system with \( J' = J = 1 \) (i.e. \( \langle T(1)_0 \rangle \) and \( \langle T(1)_2 \rangle \)).

Up to this point the density matrix of the excited atom immediately after excitation \( (t=0) \) has been considered but due to apparatus and state lifetime limitations, the signal is collected over extended periods of time and therefore the time evolution of the atom must be taken into account. Effects which must be considered include the fine and hyperfine structure.

The evolution of the density matrix \( \rho(t=0) \) over time is described by

\[ \rho(t) = U(t)\rho(0)U(t)^* \]

(2.75)

where
\[ U(t) = \exp \left( \frac{-iHt}{\hbar} \right) \]

\[ H = H_0 + H' \]

\( H' \) is a perturbation coupling spin and angular momentum.

Fano and Macek [1973] have shown that the rank \( K \) and component \( Q \) of the initial multipole \((t=0)\) cannot change because of these time developments, due to total spin conservation, and therefore the time evolution of the state multipole under the influence of the fine structure is given by

\[ \langle \mathcal{T}(L_i; t)_{KQ} \rangle = G(L_i; t)_{K} \langle \mathcal{T}(L_i)_{KQ} \rangle \]

where the perturbation coefficient is given by

\[ G(L_i; t)_{K} = \frac{1}{2L_i + 1} \sum_{J'J} (2J'+1)(2J+1) \begin{vmatrix} L_i & J' & J \\ J & L_i & K \end{vmatrix}^2 \cos \left( \frac{(E_{J'} - E_J)\hbar}{\hbar} \right) \]

and where \( \langle \mathcal{T}(L_i)_{KQ} \rangle \) describes the state at \( t = 0 \).

The hyperfine structure can be treated using the same method as has been used for the fine structure and results in

\[ \langle \mathcal{T}(J; t)_{KQ} \rangle = G(J; t)_{K} \langle \mathcal{T}(J)_{KQ} \rangle \]

where the perturbation coefficient is

\[ G(J; t)_{K} = \frac{1}{2J + 1} \sum_{F'F} (2F'+1)(2F+1) \begin{vmatrix} J & F' & J \\ F & J & K \end{vmatrix}^2 \cos \left( \frac{(E_{F'} - E_F)\hbar}{\hbar} \right) \]

where \( J \) is the nuclear spin and \( F \) is the total angular momentum \((J + I = F)\).

If both the fine structure and hyperfine structure must be accounted for and the hyperfine interaction is smaller than the fine interaction then \( J \) remains a good quantum number and the perturbation coefficient becomes

\[ G(J)_{K} = \frac{1}{(2J + 1)(2L_i + 1) \sum_{F'F} (2J'+1)(2J+1)(2F'+1)(2F+1) \begin{vmatrix} L_i & J' & J \\ J & L_i & K \end{vmatrix}^2 \cos \left( \frac{(E_{F'} - E_F)\hbar}{\hbar} \right) } \]

\[ \times \begin{vmatrix} J & F' & J \\ F & J & K \end{vmatrix}^2 \cos \left( \frac{(E_{F'} - E_F)\hbar}{\hbar} \right) \]

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Note that $S_1$ and $I$ are assumed to be unaffected by the excitation and decay processes and that the energies $E_i$ refer to the excited states with angular momentum $J$ and $F$. The above equations are not valid if the fine and hyperfine splittings are comparable.

In steady state excitation experiments, time integrated quantities are observed and thus the perturbation coefficients must be integrated over the time resolution of the detector ($\tau_R$). Note that the lifetime of the states ($\gamma^{-1}$) has not been accounted for in the perturbation coefficients and therefore a factor $e^{\gamma t}$ must be included. If $\tau_R \gg \gamma$ then the upper time limit can be extended to infinity with minimal error. Performing the integration over the time dependent components in the perturbation coefficients yields

$$
\int_0^\infty e^{-\gamma t} \cos \omega t \, dt = \frac{\gamma}{\gamma^2 + \omega^2}, \quad \omega = \frac{E - E'}{\hbar}
$$

and results in

$$
G(t)_K = \frac{1}{(2I+1)(2S_1+1)} \sum_{F'F} \sum_{J'J} (2J'+1)(2J+1)(2F'+1)(2F+1) \left\{ \begin{array}{c} L_1 \\ J \\ L_1 \\ K \end{array} \right\}^2 \times \left[ \begin{array}{ccc} J & F' & I \\ F & J & K \end{array} \right]^2 \frac{\gamma}{\gamma^2 + \omega^2}
$$

Equation 2.83 must be used in general however if

1) $\gamma \gg \omega$ then

$$
\frac{\gamma}{\gamma^2 + \omega^2} \approx \frac{1}{\gamma}
$$

which results in

$$
G(t)_K = \frac{1}{\gamma}
$$

(2.84)

2) $\gamma \ll \omega$ then

$$
\frac{\gamma}{\gamma^2 + \omega^2} \ll \frac{1}{\gamma} \quad \text{for} \: J',F' \neq J,F
$$

which results in
\[ G(JL)_K = \int_0^\infty e^{-\gamma t} G(t)_K \, dt \]
\[ = \frac{1}{\gamma} \frac{1}{(2J+1)(2S+1)} \sum_{J', I'} (2J+1)(2F+1) \left[ \begin{array}{ccc} L_1 & J' & S_1 \\ J & J_1 & K \end{array} \right] \left[ \begin{array}{ccc} F' & I' \\ J & J_1 & K \end{array} \right] \] (2.85)

Similar results are found for \( G(L_i; t)_K \) and \( G(J; t)_K \).

The time integrated density matrix elements \( \rho(n)_{\chi, \lambda} \) are given by

\[
\rho(n)_{\chi, \lambda} = C(\omega) \sum_{\gamma} \left\langle J_2 \right| \left[ J_1 \times J_2 \right] \left| J_1 \right\rangle \gamma(-1)^{J_1+J_2} \sqrt{2K+1} \left( \begin{array}{ccc} 1 & 1 & K \\ -J_1 & -J_2 & 0 \end{array} \right) 
\times \left\{ 1 \begin{array}{ccc} 1 & 1 & K \\ J_1 & J_1 & J_2 \end{array} \right\} D(n)_{\chi, \lambda} G(JL)_K \left| \langle T(J)|_{\chi, \lambda} \rangle \right| (2.86)
\]

where \( D(n)_{\chi, \lambda} \) is a rotation matrix used to transform the state multipoles from the helicity representation to the \( XYZ \) representation. Using 2.86 in 2.45 and 2.47 and recalling that only \( \langle T(J, L)_{\chi, \lambda} \rangle_{\chi, \lambda} \) and \( \langle T(J, L)_{\chi, \lambda} \rangle_{2\chi} \) are non-zero, the following equations are obtained

\[ I(n) = C(\omega)(\langle J_2 \| J_1 \rangle)^2 \frac{2}{3\sqrt{2J_1 + 1}} G(JL)_K \left| \langle T(J)_{\chi, \omega} \rangle \right| (2.87) \]

\[ - C(\omega)(\langle J_2 \| J_1 \rangle)^2 \langle -1 \rangle^{J_1 + J_2} \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ J_1 & J_1 & J_2 \end{array} \right\} \sqrt{\frac{3\cos^2 \theta - 1}{6}} G(JL)_K \left| \langle T(J)_{\chi, 2\chi} \rangle \right| (2.88) \]

where \( n \) is the direction of the emitted photon which has polar angles \( (\theta, \phi) \). The linear polarization \( (\eta_3) \) observed at \( \theta = 90^\circ \) can be found by dividing equation 2.88 by 2.87 with the result

\[ \eta_3 = \frac{(-1)^{\lambda + \lambda} \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ J_1 & J_1 & J_2 \end{array} \right\} \sqrt{\frac{3}{2}} G(JL)_K \left| \langle T(J)_{\chi, 2\chi} \rangle \right|}{\sqrt{\frac{2}{3\sqrt{2J_1 + 1}} G(JL)_K \left| \langle T(J)_{\chi, \omega} \rangle \right| + (-1)^{\lambda + \lambda} \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ J_1 & J_1 & J_2 \end{array} \right\} \sqrt{\frac{1}{6}} G(JL)_K \left| \langle T(J)_{\chi, 2\chi} \rangle \right|} (2.89) \]
To determine the polarization function for the $^1P \rightarrow ^1S$ transition in helium equation 2.89 is used substituting $L_1$, $L_2$, $G(J_1)_k$, $\langle T(L_1)_k \rangle$, for $J_1$, $J_2$, $G(J_1)_k$, $\langle T(J_1)_k \rangle$. Using $L_1=1$ and $L_2=0$, equations 2.68a, 2.78 and 2.85 give

$$G(1)_0 = G(1)_2 = \frac{1}{\gamma} \cdot \langle T(1)_0 \rangle = \frac{(Q_0 + 2Q_1)}{\sqrt{3}} \cdot \langle T(1)_2 \rangle = \frac{2}{3}(Q_1 - Q_0). \tag{2.90}$$

Substituting these values into 2.89 and evaluating of 6-j symbols gives

$$\eta_3 = \frac{Q_0 - Q_1}{Q_0 + Q_1} \tag{2.91}$$

which agrees with the results given in section 2.3.

For the heavy rare gases the polarization function for the transition $J_1=1 \rightarrow J_2=0$ can be found using 2.89 directly if there is no hyperfine interaction ($I=0$) which is the case for neon and argon. The values for $G(J)_k$ and $\langle T(J)_k \rangle$ are the same as those given in 2.90 and therefore the polarization function is the same as 2.91 except that $Q_0$ ($Q_1$) represents the excitation of the sublevel $M_{j_1}=0$ (1).

For krypton and xenon which have isotopes with non-zero $I$ equation 2.89 must be used with $G(LJ)_k$ in place of $G(J)_k$. The values for $\langle T(LJ)_k \rangle$ are the same as those given in 2.90 but because the nuclear spin of the naturally occurring isotopes are not all the same a weighted average of the $G(LJ)_k$ factors based on their relative population must be used [Wolcke et al., 1983]. Table 2.4 lists all the isotopes present, their corresponding $G(LJ)_k$ factors and the weighted average. The resulting polarization function can be written in the form

$$\eta_3 = \frac{G(Q_0 - Q_1)}{h_0 Q_0 + h_1 Q_1}$$

where $G$, $h_0$ and $h_1$ are the same as those listed in Table 2.3.
<table>
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<th>Isotope</th>
<th>% Abundance</th>
<th>Nuclear Spin</th>
<th>$\gamma G(LJ)_K$</th>
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Chapter 3

Negative Ion Resonances

3.1 Introduction

Negative ion resonances have been studied by a variety of techniques such as laser photodetachment spectroscopy and negative-ion atom collisions. In this work collisions between electrons and atoms create the temporary negative ion resonance \((A^-\ast)\).

\[
e^- + A \rightarrow A^-\ast \rightarrow e^- + A^\ast
\]

The incoming electron interacts with the atomic target to form a relatively long-lived state (i.e. significantly longer than the transit time of the electron across the atom) which then decays via electron emission to a free electron and an excited atom. This process competes with the direct process

\[
e^- + A \rightarrow e^- + A^\ast
\]

and this interference leads to distinct spectral features at the location of the resonance.

Resonances are generally associated with the ground or an excited state of the neutral target atom (referred to as the "parent" state). If the parent state is an excited state (core-excited resonance) then the ion core is referred to as the grandparent state. For example, in the heavy rare gases some resonances are of the type \(\ldots np^{52}P_{3/2}n'ln'\) where \(\ldots np^{52}P_{3/2}n'ln'\) is the parent state and \(\ldots np^{52}P_{3/2}\) is the grandparent state.

Resonances are also classified into two types: Feshbach (Type I) and shape (Type II). The mechanism for the Feshbach resonance involves the incident electron interacting with the target (i.e. giving up some of its energy to an internal degree of freedom in the target) such that there is a potential well created which can temporarily capture the electron. The energy level of this resonance lies below that of the parent state and
therefore cannot decay via electron emission into the parent state due to energy conservation. This means the decay channel involves the parent state changing configurations (e.g. decaying to the ground state) which normally results in the resonance being long-lived and therefore showing up as a narrow feature.

Shape resonances involve the incident electron being trapped by a potential barrier. It remains trapped until it can tunnel out again. The barrier is a result of the \( l(l+1)/2\mu r^2 \) centrifugal term in the effective potential and therefore \( p-, d-, f-... \) wave resonances are expected but generally not \( s\)-wave \((l = 0)\). The lifetime of the resonance depends on the size of the barrier but since the barrier isn't an effective trap for electrons the lifetime is normally shorter than the Feshbach resonances which results in broader features in the energy spectrum. However, resonances near threshold experience a thicker barrier which results in a longer lifetime and therefore a relatively narrower feature.

### 3.2 Rare Gas Coupling Schemes

Before elaborating on a classification scheme for the negative ion resonances it will be instructive to give an overview of the coupling schemes for the neutral atoms and some of their properties.

#### 3.2.1 Neutral States

The helium atom is well described by the \( LS \) coupling scheme where \( l_i \) and \( s_i \) of the individual electrons are coupled separately to form \( L \) and \( S \) respectively. The singly excited states consist of an electron orbiting an ion core where the core has the properties of the inner electron such as zero orbital angular momentum and therefore even parity. Another important property is that the spin-orbit interaction is very weak which results in \( L \) and \( S \) being good quantum numbers (i.e. conserved). Also, when one of the electrons is excited the inner electron feels the full force of the nuclear charge and thus the wavefunction describing this electron is significantly altered. In order to describe this state, a technique referred to as Multi-Configuration Hartree-Fock (MCHF) is used to expand it in terms of the zeroth order wavefunctions. This method requires that the expansion
wavefunctions have the same parity and total angular momentum as the base wavefunction and that the configuration differs by no more than two electron orbitals.

The heavy rare gases have a spectrum which is significantly different than that of helium due to nature of the excited state's character. Unlike helium, which has as its neutral ground state an 1s$^2$ configuration, the heavy rare gases all have a np$^6$ outer shell for the neutral ground state ($n$ = 2, 3, 4 and 5 for neon, argon, krypton and xenon respectively). This results in the singly excited states having an ion core (...np$^5$) with different angular momentum and parity ($\pi = -1\uparrow$) from that of helium (Is). Also, the spin-orbit interaction causes the ion core to be split into two configurations, np$^5$ (2P$^0_{\frac{1}{2}}$) and np$^5$ (2P$^0_{\frac{3}{2}}$), which are separated by 97, 177, 666 and 1307 meV for neon, argon, krypton and xenon respectively and therefore a different coupling scheme to explain the excited states and negative-ion resonances of the heavy rare gases from that of the LS coupling used for helium.

The most successful coupling mechanism for the neutral excited states has been the jLS scheme where the orbital angular momentum (L) of the excited electron is first coupled to the ion core (J+L=K) and the resulting state (K) is coupled to the electron’s spin (S) to form the total angular momentum of the system (K+S=J). The notation for this state is expressed as \((2s^1l_j)^{2S+1}L[K]\), where \(l\) and \(s\) are the orbital and spin angular momentum quantum numbers for the positive ion core. This method results in the two VUV emitting levels of the first excited state being designated as \((2P_{\frac{3}{2}})^1S[\frac{1}{2}]\), and \((2P_{\frac{1}{2}})^1S[\frac{1}{2}]\), and the two metastable levels as \((2P_{\frac{3}{2}})^1S[\frac{3}{2}]\) and \((2P_{\frac{1}{2}})^1S[\frac{3}{2}]\). These states can be related to LS coupled states by the intermediate coupling scheme

\[
\begin{align*}
|S_{\frac{1}{2}}\rangle & = \alpha |P_{\frac{3}{2}}\rangle + \beta |P_{\frac{1}{2}}\rangle \\
|S_{\frac{3}{2}}\rangle & = -\beta |P_{\frac{3}{2}}\rangle + \alpha |P_{\frac{1}{2}}\rangle \\
|S_{\frac{5}{2}}\rangle & = \frac{1}{2} |P_{0}\rangle \\
|S_{\frac{7}{2}}\rangle & = \frac{1}{2} |P_{2}\rangle \\
\end{align*}
\]

(with $\alpha^2 + \beta^2 = 1$) (3.1)

where $\alpha$ and $\beta$ are given in Table 3.1 for each of the rare gases. Note that the metastable states can be represented by pure LS states while the VUV emitting states are admixtures. As pointed out by Andersen et al. [1988], the excited states of Ne and Ar can essentially
be considered singlet and triplet in character (see $\alpha^2$ and $\beta^2$ in Table 6.1), while this is not possible for Kr and Xe due to the nearly equal contributions of both states. The fine structure splitting of the $J=1$ states are 177 (Ne), 205 (Ar), 612 (Kr) and 1133 (Xe) meV. The negative ion resonances use a similar coupling scheme which will be discussed in the next section.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\alpha^2$</th>
<th>$\beta^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>0.964</td>
<td>0.266</td>
<td>0.929</td>
<td>0.071</td>
</tr>
<tr>
<td>Argon</td>
<td>0.893</td>
<td>-0.450</td>
<td>0.797</td>
<td>0.203</td>
</tr>
<tr>
<td>Krypton</td>
<td>-0.683</td>
<td>0.730</td>
<td>0.467</td>
<td>0.533</td>
</tr>
<tr>
<td>Xe-non</td>
<td>-0.645</td>
<td>0.764</td>
<td>0.416</td>
<td>0.584</td>
</tr>
</tbody>
</table>

3.2.2 Resonance Classification

The scheme used to describe the negative ion resonances for the heavy rare gases is referred to as the "Grandparent" model and was developed by Read et al. [1976]. Resonance pairs which have a separation in energy by an amount equal to the $^2P_{3/2}^0$ ion core splitting had been observed consistently in the experimental data prior to 1976. Note that the $^2P_{3/2}^0$ state lies energetically below the $^2P_{1/2}^0$ state. Spence [1974] had earlier concluded that the two excited electrons are in their most stable state when they have the same principle quantum number $n$ and similar angular momentum $l$. Read et al. [1976] then extended the description to give both a configuration and a coupling scheme. Their proposal treated the two outermost electrons as a correlated pair and therefore more strongly coupled to each other than either one is to the ion core. Since the interaction between the excited electrons is mostly electrostatic [Zetner, 1985], the orbital and spin angular momentum couple separately (i.e. $LS$ coupling): $l_1 + l_2 = L$ and $s_1 + s_2 = S$. By analogy with the $jLS$ coupling scheme for the neutral excited states of the rare gases, the
ion core angular momentum \( j \) is coupled with \( L \) to form the intermediate state \( K (j + L = K) \) which in turn is coupled with \( S \) to form the total angular momentum \( J (K + S = J) \).

The resonance is classified using a nomenclature which is also similar to that of the neutral excited states: \((j)^{2S+1}L[\ell K]\). Calculations by Noro et al. [1979], Ohja et al. [1982], and Clark and Taylor [1982] have shown that the \( jLS \) coupling is appropriate for neon and argon. Calculations for krypton and xenon are not known to have been made [Buckman and Clark, 1994].

The different classes of resonances observed were assigned to a particular configuration and each configuration was designated with an alphabetical letter. Using the designation of Read et al. [1976], the letters \( a-f \) correspond to the following configurations:

\[
\begin{align*}
  a_{1,2} & = np^{52}P_{3/2,1/2}^0 (n+1)s^{21}S \\
  b_{1,2} & = np^{52}P_{3/2,1/2}^0 (n+1)s(n+1)p^3P^0 \\
  c_{1,2} & = np^{52}P_{3/2,1/2}^0 (n+1)s(n+1)p^1P^0 \\
  d_{1,2} & = np^{52}P_{3/2,1/2}^0 (n+1)p^{21}S \\
  e_{1,2} & = np^{52}P_{3/2,1/2}^0 (n+1)p^{21}D \quad \text{or} \quad np^{52}P_{3/2,1/2}^0 (n+1)p^{23}P \\
  f_{1,2} & = np^{52}P_{3/2,1/2}^0 (n+2)s^{21}S.
\end{align*}
\]

Note that the final term only refers to the coupling of the outer electrons. For \( a, d \) and \( f \) the total angular momentum can be easily determined while for \( b, c \) and \( e \) a multiplet of states occurs.

The \( a \) resonances lie below their corresponding parent states which means they are Feshbach resonances and have sharp features. However, for krypton and xenon the \( a \) resonance associated with the \( ^2P_{1/2} \) core \((a_2)\) lies above the \( ^2P_{3/2} \) \( ^2S[\frac{3}{2}]_1 \) state and therefore can decay into this state, in particular to the \( j = 1 \) level, by emitting an \( s \)-wave electron and changing its core configuration. The \( a_2 \) resonance is broader than \( a_1 \) because of this additional decay channel which shortens its lifetime.

The \( b \) resonances lie just above the inelastic threshold of their parent states which, by the above definition, would classify them as shape resonances. However, there is
evidence that these resonances could be classified as Feshbach [Buckman and Clark, 1994]. In either case, the resonance feature is expected to be sharp.

The coupling of the \((n+1)s(n+1)p^3P\) electrons with \(j_c\) of the ion core produce considerable fine structure. The total number of states that can be produced is thirteen (eight when \(j_c = 3/2\) and five when \(j_c = 1/2\)), however several of these states will likely be undetectable. Since these states are of even parity they can be formed by the ground state atom interacting with \(s_{1/2}\) or \(d_{3/2,5/2}\) electrons (assuming no electrons with partial waves \(l \geq 4\)). This restricts the total angular momentum of the resonance to be \(\leq 5/2\) since the initial angular momentum of the target atom is 0 and therefore eliminates one of the eight states associated with \(j=3/2\) ion core. Also there are four resonances which are associated with the process

\[
ksnp \longrightarrow (n+1)s(n+1)p \longrightarrow ks(n+1)p
\]

which involves only a change in the principal quantum number. These resonances are expected to be short-lived and therefore produce broad features which are difficult to detect experimentally. This leaves the eight resonances which can be formed by \(d\)-wave excitation:

\[
np^5 \; ^2P_{1/2}(n+1)s(n+1)p \; ^3P[1/2]_{1/2}, \quad np^5 \; ^2P_{1/2}(n+1)s(n+1)p \; ^3P[3/2]_{3/2,5/2} \\
np^5 \; ^2P_{3/2}(n+1)s(n+1)p \; ^3P[1/2]_{1/2}, \quad np^5 \; ^2P_{3/2}(n+1)s(n+1)p \; ^3P[3/2]_{3/2,5/2} \\
np^5 \; ^2P_{3/2}(n+1)s(n+1)p \; ^3P[5/2]_{3/2,5/2}.
\]

All these states can decay through \(p\)-wave emission.

The \(3s3p\) electrons can also couple to form a \(^1P\) term (i.e. the \(c\) resonances) which is split into five states:

\[
np^{52}P_{1/2}(n+1)s(n+1)p \; ^1P[1/2]_{1/2}, \quad np^{52}P_{1/2}(n+1)s(n+1)p \; ^1P[3/2]_{3/2} \\
np^{52}P_{3/2}(n+1)s(n+1)p \; ^1P[1/2]_{1/2}, \quad np^{52}P_{3/2}(n+1)s(n+1)p \; ^1P[3/2]_{3/2} \\
np^{52}P_{3/2}(n+1)s(n+1)p \; ^1P[5/2]_{5/2}.
\]
Using the analogy with alkaline earth elements, these resonances are expected to lie higher than the $^3P (b)$ resonances. All these states can decay through $p$-wave emission to the $np^5(n+1)s$ manifold without rearrangement of the $(n+1)s$ electron being necessary and therefore the resonances are broad.

If the outer two electrons are both in $(n+1)p$ orbitals then they can couple to form the following states: $^1S$, $^1D$ and $^3P$. The resonances resulting from the $^1S$ state being coupled to the $j_e = 3/2$ and $j_e = 1/2$ core are designated as $d_1$ and $d_2$ respectively. The splitting of the $d_1$, $d_2$ pair is expected to be approximately the same as the ion core splitting if its interaction with the ion core is minimal. Also the relative heights of the resonances should be $d_1: d_2 = 1:2$ in accordance with their statistical weights. The $d$ resonances can be formed by an incident $p_{1/2,3/2}$ electron and can decay either 1) to the $np^5(n+1)s$ state by emitting an $s$-wave electron or 2) to the $np^5(n+1)p$ multiplet by $p$-wave emission. Path 1) involves both electrons changing configuration and therefore the resonance width will be limited in size (≤ 124 meV, Read et al., 1976) while path 2) is either energetically forbidden or the electron's excess energy is too small to effect the width.

The $^1D$ and $^3P$ configurations are labeled as $e$ resonances and can be formed by incident $p_{1/2,3/2}$ or $f_{3/2,5/2}$ electrons. In the case of the $^1D$ state six different resonances are possible while for the $^3P$ configuration, a total of thirteen resonances can be made. These resonances are expected to lie among the $d$ resonances with the $^3P$ states possibly being an unresolvable bump due to their large numbers. The $^1D$ state is expected to have a narrower width than the $d$ resonances because they cannot decay by $s$-wave emission into the $(n+1)s$ state due to angular momentum conservation. $d$-wave emission into the $(n+1)s$ state, which would require overcoming a large centrifugal barrier, and $p$-wave decay into the $(n+1)p$ manifold, which is either energetically forbidden or would have to little excess energy for the electron, would not be expected to alter the resonance width. The $^3P$ resonances can decay by $s$-wave emission and are therefore expected to have widths similar to the $d$ resonances.

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The $f$ resonances and other $np^3$ ml $^1S$ resonances are expected (and have been observed by Buckman et al., 1983) to have splittings and widths analogous to the $a$ and $d$ resonances discussed above.

For helium a similar classification can be used to describe the resonances. The orbital and spin angular momentum of the two excited electrons are added together, $l_1 + l_2 = l_{12}$ and $s_1 + s_2 = s_{12}$, and these sums are then added to the momenta of the ground state electron ($l_3 = 0, s_3 = 1/2$) to form $L', S'$. The nomenclature for the resonance is given as $2s+1l'\sqrt{2s+1}l_{12}^{2s+1}l'$. The term $2s+1l_3$ is often omitted when it is understood to be a $1s$ ($^3S$) electron. Note that because the ground state of neutral helium is $^1S$, $L'$ and $S'$ of the negative ion state is therefore determined by the incident electron ($s_0, l_0$) which results in only doublet states ($S' = s_0 = 1/2$) being created and $L' = l_0$.

3.3 Polarization Calculations

3.3.1 Preliminary Discussion (Mercury)

The polarization of light for mercury at the threshold of the $^3P_1$ state was measured by Hanne et al., [1981] using the pseudo-threshold technique (i.e. measuring photons resulting from forward scattered electrons so that $\Delta m = 0$). The values of $\eta_s$ approached a threshold value of -0.737 as predicted by theory [Bonham, 1982] for the case of exchange between the incident electron and an outer shell electron. However, Wolcke et al. [1983] measured the polarization near the threshold without monitoring the scattered electron and obtained a value of 0.2. They demonstrated that negative ion resonances could explain the observed result by calculating the scattering amplitudes for various negative ion states and concluded that $p$-wave emission of electrons from a $^4P_{3/2}$ negative ion resonance could explain this feature if the non-resonant background can be ignored. This result also showed that $s$-wave scattering was not necessarily the governing process at threshold if negative resonant states dominated the excitation.

The discrepancy in the threshold value can be explained by the fact that the resonance lies within 50 meV [Buckman and Clark, 1994] of the threshold and the beam resolution of Wolcke et al. was 140 meV which prevented the threshold region from being
studied independent of the resonance. Also, the best estimate for the resonance width is 50 meV and therefore threshold excitation will be perturbed by the resonance independent of the beam resolution.

In this work, the heavy rare gases show resonant features near the $np^5(3P_{3/2})(n+1)4[3/2]$ threshold and therefore a calculation of the effect of these resonances on $\eta_3$ would be helpful in determining which resonant states are relevant. Since the heavy rare gases have a different coupling scheme ($jLS$) than mercury (which uses $LS$ coupling), the direct use of Wolcke et al. formulas is not possible. However, their method can be used as a guide and therefore a summary of the relevant points of their technique will be presented below.

Their analysis involves calculating the scattering amplitude for a transition from the $^1S_0$ ground state to the neutral excited state $^2S^+L_J$

$$f(M,m_s,m_n) = \langle(LLS)JM,p,m_L|T|0,p,m_n\rangle$$  \hspace{2cm} (3.2)

where $L,S$ and $J$ are the orbital, spin and total angular momentum of the excited neutral atom

- $M$ is the $z$ component of $J$,
- $p_0, p_1$ are the incoming and outgoing momenta of the electron,
- $m_0, m_1$ are the spin components of the incoming and outgoing electron
- $|0\rangle$ represents the initial state of the atom and
- $T$ is the transition operator.

The spin $s_0$ ($s_1$) of the incoming (outgoing) electron has been suppressed and is equal to $\frac{1}{2}$. They expanded $p_0$ ($p_1$) in terms of partial waves with orbital angular momenta $l_0$ ($l_1$) which were then coupled with $s_0$ ($s_1$) to form the total electronic angular momenta $j_0$ ($j_1$). Finally, $j_1$ was coupled with $J$ to form the total angular momentum of the system $\bar{J}$ (which is equal to $j_0$).

$$f(M,m_s,m_n) = \sum_{l_{0,1},m_{0,1}} \langle l_0^m_{l_0} l_1^m_{l_1} |JM, j_0^m_{j_0} \bar{J} 0^1_{j_1} |0,0^1_{j_1} \rangle \langle j_0^m_{j_0} \bar{J} |T|0,0^1_{j_1}\rangle$$  \hspace{2cm} (3.3)

$$\times \langle (LS)J, J_{1/2} j_1, \bar{J} \bar{J}|(l_0^1_{j_1})\bar{J}\rangle C(p_1,m_{l_1},p_{0,0})$$
where \( m_l \) and \( m_h \) are the \( z \) components of \( l_1 \) and \( j_1 \), respectively. \( C(p_l m_l, p_h m_h) \) collects all other terms except Clebsch-Gordon coefficients. The derivation of equation 3.3 is based on the following two points: 1) the total angular momentum \( \vec{J} \) was conserved and 2) \( T \) does not depend on \( M_j \). The resonant states of mercury are classified using the Russell-Saunders scheme where \( L \) and \( l_1 \) are coupled to form \( \vec{L} \), \( S \) and \( s_1 \) are coupled to form \( \vec{S} \) and finally \( \vec{S} \) and \( \vec{L} \) are coupled to form \( \vec{J} \). The following recoupling transformation is required:

\[
\langle (LS)J, (l_1 \frac{1}{2})j_1, \vec{J}\mid (l_0 \frac{1}{2})\vec{J}\rangle = \sum_{LS} \langle (LS)J, (l_1 \frac{1}{2})j_1, \vec{J}\mid (L_1 \frac{1}{2})\vec{S}, \vec{L}\rangle \times \langle (L_1 \frac{1}{2})\vec{L}, (S_1 \frac{1}{2})\vec{S}, \vec{J}\mid (l_0 \frac{1}{2})\vec{J}\rangle
\] (3.4)

The summations in equations 3.3 and 3.4 can be reduced by using properties of the Clebsch-Gordon coefficients as well as the conservation laws for total angular momentum and parity. The total angular momentum must satisfy \( \vec{J} = |l_0 \pm \frac{J}{2}| \) and parity is given by \( \pi = (-1)^{l_0} \). This restricts \( l_0 \) to only one value for each resonance state. Since the excitation is near threshold the lowest value of \( l_1 \) allowed by parity and angular momentum conservation was only considered. The Clebsch-Gordon coefficients in equation 3.3 restrict \( j_1 \) to \( |l_1 \pm \frac{J}{2}| \) (see Table 3.2). \( \mathcal{M} \), \( m_l \) and \( m_h \) are fixed for each scattering amplitude and therefore \( m_l \) and \( m_h \) have specific values as determined by the Clebsch-Gordon coefficients. This means that the sum in equation 3.3 is only over \( j_1 \). The sum in equation is superfluous if the resonance has sharp \( \vec{L} \), \( \vec{S} \) and \( \vec{J} \). The \( T \)-matrix element can be ignored since it is independent of \( j_1 \), \( M \), \( m_l \) and \( m_h \) and therefore a common factor to all scattering amplitudes and will divide out in the \( \eta \) calculation. Similarly, after integrating over all electron scattering angles, \( C(p_l m_l, p_h m_h) \) can be neglected. This results in the scattering amplitude only depending on \( 3-j \), \( 6-j \) and \( 9-j \) symbols and can easily be calculated.
Table 3.2 Quantum numbers in partial wave expansion for a $6s^6p^{1^1P_1}6p^{2S+1}L_J$ resonance [Wolcke et al., 1981].

<table>
<thead>
<tr>
<th>Classification of the resonances</th>
<th>$l_0$</th>
<th>$j_0$</th>
<th>$l_1$</th>
<th>$j_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4P_{1/2}$</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>1/2, 3/2</td>
</tr>
<tr>
<td>$^4P_{3/2}$</td>
<td>2</td>
<td>3/2</td>
<td>1</td>
<td>1/2, 3/2</td>
</tr>
<tr>
<td>$^4P_{5/2}$</td>
<td>2</td>
<td>5/2</td>
<td>1</td>
<td>3/2</td>
</tr>
<tr>
<td>$^2D_{3/2}$</td>
<td>2</td>
<td>3/2</td>
<td>1</td>
<td>1/2, 3/2</td>
</tr>
<tr>
<td>$^2D_{5/2}$</td>
<td>2</td>
<td>5/2</td>
<td>1</td>
<td>3/2</td>
</tr>
</tbody>
</table>

3.3.2 Heavy Rare Gases

For the rare gases, a similar method can be used to determine the scattering amplitude in terms of only 3-\(j\) symbols. As in mercury, the ground state for all rare gases is \(^1S_0\) and is represented by the state vector \(\{0\}\). The quantization axis lies parallel to the electron momentum vector. The excited state is described by the grandparent scheme (i.e. \(jLS\) coupling); \((2\,^n\,l_e\,j_e\,)^{2S+1}L\{K\}_J\) where \(s_e\), \(l_e\) and \(j_e\) are the spin, orbital and total angular momentum respectively of the ion core, \(S\) and \(L\) are the spin and orbital angular momentum of the excited electron, \(K\) is the intermediate coupling of \(L\) with \(j_e\) and finally \(J\), which is the total angular momentum of the atom, is the result of \(K\) being coupled with \(S\). The incident (scattered) electron is described by momentum \(p_0(\vec{p}_i)\), spin \(s_e(\vec{s}_i)\) and spin \(z\)-component \(m_{s_e}(m_{s_i})\). The scattering amplitude is

\[
f(M_J,m_s,m_{s_e}) = \langle((s_{i} l_e, L) K S) J M_J; p_{0} s_{i} m_{s} | P 0; p_{0} s_{i} m_{s_e} \rangle.
\]  

(3.5)

The electron momentum vectors \((p_0, p_i)\) are now expanded in terms of partial waves with orbital angular momentum \((l_0, l_i)\). Unlike the mercury atom where \(l\) and \(s\) for each electron were coupled, the heavy rare gases couple \(l_i\) and \(L\) to form \(L'\), and \(s_i\) and \(S\) to form \(S'\). To do this we must first uncouple \(L\) and \(S\) from \(J\).
$$\sum_{LM_{L},SM_{S}} (KM_{S},SM_{S}|JM_{J})(j_{L}m_{J},LM_{L}|K) \times |(s_{L},j_{L},M_{L},S_{L},m_{S})>.$$  \tag{3.6}

Now $l_{1}$, $L$ and $s_{1}$, $S$ can be coupled to form $L'$ and $S'$ respectively:

$$\sum_{LM'_{L},SM'_{S}} (l_{1}m_{1},LM_{L}|LM'_{L})(\sigma m_{s},SM_{S}|SM'_{S}) \times |LM_{L},SM_{S}>.$$

$$\times |LM'_{L},SM'_{S}>.$$  \tag{3.7}

Finally, $L'$ is coupled to $j_{e}$ to form $K'$ which is then coupled to $S'$ to obtain the total angular momentum ($J'$) of the negative ion resonance.

$$\sum_{K'M'_{K'}} (K'M'_{K'},SM'_{S}|JM'_{J})(j_{e}m_{J},LM_{L}|K'M'_{K'}) \times |(j_{e}L',K'S)JM'_{J} >.$$  \tag{3.8}

The initial state of the electron-atom system before the collision can be described by

$$|\psi_{L}m_{L},s_{L}m_{S}> = \sum_{j_{e}m_{J}} (l_{0}m_{0},s_{0}m_{s},j_{e}m_{J},j_{e}m_{J})>.$$  \tag{3.9}

Substituting equations 3.6, 3.7, 3.8 and 3.9 into 3.5, the scattering amplitude for the negative ion state $(2^{J'}+1)^{2S+1}L'[K']_{J}$ becomes

$$f(M_{J},m_{J},m_{S}) = \langle(l_{0}L)K,S|JM_{J};l_{0}m_{L},s_{0}m_{S}|T0;l_{0}m_{L},s_{0}m_{S}\rangle$$

$$= \sum_{s_{0}} \langle(l_{0}m_{0},s_{0}m_{s},j_{e}m_{J})(KM_{S},SM_{S}|JM_{J})(j_{e}M_{J},LM_{L}|K'M'_{K'}) \times (LM_{L},l_{0}m_{L}|LM'_{L})(SM_{S},s_{0}m_{s}|SM'_{S})(j_{e}m_{J},LM'_{L}|K'M'_{K'}) \times (K'M'_{K'},SM'_{S}|JM'_{J});(l_{0}L)K,S)JM'_{J}|T(l_{0}m_{L})j_{e}m_{J}C(p_{0}l_{0},p_{0}m_{s}) \rangle.$$  \tag{3.10}

where $\ast$ represents $l_{0}$, $l$, $j_{e}$, $m_{J}$, $M_{K}$, $M_{S}$, $M_{L}$, $m_{L}$, $L'$, $M'_{L}$, $S'$, $M'_{S}$, $K'$, $M'_{K}$, $J'$, $M'_{J}$. $C(p_{0}l_{0},p_{0}m_{s})$ contains all terms from the partial wave expansion. Note that 1) $J' = j_{0}$ because the total angular momentum is conserved and 2) $M'_{J} = m_{J}$ because the $T$-matrix.
element is independent of \( M_J \) and 3) \( m_b = m_s \), because \( p_0 \) defines the quantization axis and therefore \( m_b = 0 \).

The properties of the Clebsch-Gordon coefficients restrict the values that the angular momenta \( z \)-components can have. The equations are

\[
\begin{align*}
ml + m_s &= m_j \\
M_K + M_S &= M_J \\
M_L + m_s &= M_L \\
ml + M_L &= M_K.
\end{align*}
\]

Since 1) \( m_b \), \( m_s \), and \( M_J \) are fixed for each scattering amplitude, 2) \( M_J = m_b \) and 3) \( m_b = 0 \), the number of independent variables in 3.11 can be reduced to 2 (in this case \( M_L \) and \( M_S \)).

\[
\begin{align*}
m_i &= a - b - c \\
M_K &= c - M_S \\
M_L &= M_L + a - b - c \\
M_S &= M_s + b \\
M_K &= a - b - M_S
\end{align*}
\]

where \( m_s \), \( m_s \), and \( M_J \) are represented by \( a \), \( b \), and \( c \) respectively. The negative ion states are specified by \(^{25+1}L'[K']\), which also reduces the number of terms to be summed in 3.10. Finally, angular momentum conservation and parity restrict \( l_s \) to only one possible value and since the excitation is close to threshold only the lowest values of \( l_s \) will be considered. The net result is that the summation in equation 3.10 has been reduced to 2 terms (\( M_L \) and \( M_S \)). As in the case of mercury, the \( T \)-matrix and \( C(p,l,m_i,p_0,l_0) \) can be neglected.

The above calculation does not allow for a change in the core angular momentum \( j_c \) which is needed to explain the decay of the \( \alpha_2 \) resonance state in krypton:

\[
^{2}P_{_1/2} \rightarrow ^{2}S_{_1/2} \rightarrow ^{2}P_{_3/2} 5s[\frac{3}{2}]_{1/2} + s_{1/2}e^{-}.
\]

If \( j_c \) is uncoupled after equation (3.6),

\[
\langle \alpha_s \sigma \rangle_{j_c m_i} = \sum_{m_s m_i} (s_s m_s \langle \alpha_s | j_c m_i \rangle \langle j_c m_i | s_s m_s \rangle),
\]
and then \( l_c \) and \( s_c \) are recoupled to form the new core state \( j'_c \),

\[
(s_c l_c j_{c n_c}) = \sum_{m_{j_c},m_{l_c}} (s_c m_{j_c}, l_c m_{l_c}, j_{c n_c}) (s_c m_{l_c}, l_c m_{j_c}, j_{c n_c}) \langle s_c l_c j_{c n_c} | j'_c \rangle \delta_{m_{j_c} m_{l_c}}, \tag{3.15}
\]

this leads to the scattering amplitude being zero for \( j_c \neq j'_c \) because of the following property for Clebsch-Gordon coefficients (Weissbluth, 1978).

\[
\sum_{m_{j_c}, m_{l_c}} (s_c m_{j_c}, l_c m_{l_c}, j_{c n_c}) (s_c m_{l_c}, l_c m_{j_c}, j_{c n_c}) = \delta_{j_c j'_c} \delta_{m_{j_c} m_{l_c}} \tag{3.16}
\]

Another approach to solving this problem is to include other configurations (i.e. configuration interaction) to more accurately describe the negative resonance and neutral excited state. Clark (1984) has used the MCHF approximation to solve for the energy level of the \( _{1s} \) resonance of Kr\(^-\) and Xe\(^-\). The addition of these configurations may allow for the transition to be calculated.

Finally, the VUV polarization fraction calculated using (3.10) above and equations (2.89), (2.69) and (2.56) for various negative ion resonances (where no change in \( _{1s} \) ion core angular momentum occurs) are shown in Table 3.3 (\( j_c = \frac{1}{2} \)) and 3.4 (\( j_c = \frac{3}{2} \)).

### 3.3.3 Helium

The scattering amplitude for electron impact on helium is represented by

\[
f(M_j m_{j_c}, m_{j_c}) = \langle SL | M_j; p_1 s_1 | \bar{s}_0 \rangle \langle p_0 s_0 | m_{j_c} \rangle \tag{3.5}\]

where \( p_0, p_1 \) are the momenta of the incident and scattered electron,
\( s_0, s_1 \) are the spins of the incident and scattered electron,
\( m_{j_c}, m_{l_c} \) are the spin components of the incident and scattered electrons,
\( J, L, S \) are the total, orbital and spin angular momenta of the excited neutral atom,
\( M_j \) are the \( z \)-components of \( J \),
\( |0\rangle \) represents the initial state of the atom and
\( T \) is the transition operator.
Table 3.3 VUV polarization fractions for the heavy rare gases resulting from the formation of the negative-ion resonance \((j_z = \frac{1}{2}) \text{s}^\text{n-1}[K]\), which decays to \((j_z = \frac{1}{2}) \text{S}[1/2]_1\).

<table>
<thead>
<tr>
<th>Resonant State ((j_z = \frac{1}{2}))</th>
<th>(K)</th>
<th>(J)</th>
<th>(l_0)</th>
<th>(l_1)</th>
<th>(\overline{G}_2 = 1) ((\text{Ne,Ar}))</th>
<th>(\overline{G}_2 = 0.909) ((\text{Kr}))</th>
<th>(\overline{G}_2 = 0.664) ((\text{Xe}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3^P(\text{&quot;b&quot;}))</td>
<td>1/2</td>
<td>1/2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>1/2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>3/2</td>
<td>2</td>
<td>1</td>
<td>-0.428</td>
<td>-0.385</td>
<td>-0.271</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>3/2</td>
<td>2</td>
<td>1</td>
<td>0.558</td>
<td>0.516</td>
<td>0.395</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>5/2</td>
<td>2</td>
<td>1</td>
<td>0.500</td>
<td>0.461</td>
<td>0.352</td>
</tr>
<tr>
<td>(1^P(\text{&quot;c&quot;}))</td>
<td>1/2</td>
<td>1/2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
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<td>3/2</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(1^S(\text{&quot;d&quot;}))</td>
<td>1/2</td>
<td>1/2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(1^D(\text{&quot;e&quot;}))</td>
<td>3/2</td>
<td>3/2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>5/2</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(3^P(\text{&quot;e&quot;}))</td>
<td>1/2</td>
<td>1/2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>1/2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>3/2</td>
<td>2</td>
<td>1</td>
<td>-0.428</td>
<td>-0.385</td>
<td>-0.271</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>3/2</td>
<td>2</td>
<td>1</td>
<td>0.558</td>
<td>0.516</td>
<td>0.395</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>5/2</td>
<td>2</td>
<td>1</td>
<td>0.500</td>
<td>0.461</td>
<td>0.352</td>
</tr>
<tr>
<td>(1^S(\text{&quot;f&quot;}))</td>
<td>1/2</td>
<td>1/2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

As in the previous cases the electron momentum vectors \((p_0, p_1)\) are expanded in terms of partial waves with orbital angular momentum \((l_0, l_1)\). Since spin and orbital angular momentum are separately conserved, the scattering matrix is diagonal not only in the \(J,M_J\) representation but also in the \(L, S, M_L, M_S\) representation \((\text{Baranger and Gerjuoy, 1958})\) and therefore the scattering amplitude can be written as

\[
f(M_J m_J, m_s) = \sum_{J M_J} (S L M_S M_L J M_J) (S L M_S M_L p_1 p_2 m_1 \bar{p}_0 \bar{p}_2 m_2).
\] (3.17)

Since the excited state is a singlet state \((S = 0)\), therefore \(J = L\) and \(M_J = M_L\) and the Clebsch-Gordon coefficient becomes \((0 LO M_L J M_L) = 1\) and the summation is superfluous.
Table 3.4 VUV polarization fractions for the heavy rare gases resulting from the formation of the negative-ion resonance \( j_i = \frac{1}{2} \) \(^{1+}\text{Li} [K]\), which decays to \( (j_i = \frac{3}{2}) \) \(^3\text{S}[3/2]\).

<table>
<thead>
<tr>
<th>Resonant State ((j_i = 3/2))</th>
<th>(K)</th>
<th>(J)</th>
<th>(l_0)</th>
<th>(l_i)</th>
<th>(\bar{G}_2 = 1) ((\text{Ne,Ar}))</th>
<th>(\bar{G}_2 = .909) ((\text{Kr}))</th>
<th>(\bar{G}_2 = .664) ((\text{Xe}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^3\text{P}(&quot;b&quot;))</td>
<td>1/2</td>
<td>1/2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>1/2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
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<td>3/2</td>
<td>1</td>
<td>1</td>
<td>-.428</td>
<td>-.385</td>
<td>-.271</td>
</tr>
<tr>
<td></td>
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<td>3/2</td>
<td>1</td>
<td>1</td>
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<td>-.622</td>
<td>-.430</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>3/2</td>
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<td>1</td>
<td>.447</td>
<td>.412</td>
<td>.312</td>
</tr>
<tr>
<td></td>
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<td>5/2</td>
<td>3</td>
<td>1</td>
<td>.500</td>
<td>.461</td>
<td>.352</td>
</tr>
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<td></td>
<td>5/2</td>
<td>5/2</td>
<td>3</td>
<td>1</td>
<td>.500</td>
<td>.461</td>
<td>.352</td>
</tr>
<tr>
<td>(^1\text{P}(&quot;c&quot;))</td>
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<td>1/2</td>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>1</td>
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<td>2</td>
<td>1</td>
<td>.500</td>
<td>.461</td>
<td>.352</td>
</tr>
<tr>
<td>(^1\text{S}(&quot;d&quot;))</td>
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<td>3/2</td>
<td>1</td>
<td>0</td>
<td>.600</td>
<td>.555</td>
<td>.427</td>
</tr>
<tr>
<td>(^1\text{D}(&quot;e&quot;))</td>
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<td>1/2</td>
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<td>2</td>
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</tr>
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<td>3/2</td>
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<td>-.473</td>
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<td>5/2</td>
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<td>2</td>
<td>-.088</td>
<td>-.080</td>
<td>-.058</td>
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<tr>
<td></td>
<td>7/2</td>
<td>7/2</td>
<td>3</td>
<td>2</td>
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<td>.418</td>
<td>.318</td>
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<tr>
<td>(^3\text{P}(&quot;e&quot;))</td>
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<td>1/2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>1/2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>3/2</td>
<td>1</td>
<td>1</td>
<td>-.428</td>
<td>-.385</td>
<td>-.271</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>3/2</td>
<td>1</td>
<td>1</td>
<td>-.698</td>
<td>-.622</td>
<td>-.430</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>7/2</td>
<td>1</td>
<td>1</td>
<td>.447</td>
<td>.412</td>
<td>.312</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>5/2</td>
<td>3</td>
<td>1</td>
<td>.500</td>
<td>.461</td>
<td>.352</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>5/2</td>
<td>3</td>
<td>1</td>
<td>.500</td>
<td>.461</td>
<td>.352</td>
</tr>
<tr>
<td>(^1\text{S}(&quot;f&quot;))</td>
<td>3/2</td>
<td>3/2</td>
<td>1</td>
<td>0</td>
<td>.600</td>
<td>.555</td>
<td>.427</td>
</tr>
</tbody>
</table>
The two electrons attached to the helium atom will be designated by the numbers 2 and 3 where electron 3 will be the one which remains in the ground state (1s) after impact. The negative ion resonance has electron 1 and 2 coupled together and the resultant is coupled to electron 3 to form the total angular momenta \( L' \) and \( S' \). To write equation 3.17 in terms of the negative ion state \( L \) and \( S \) must be uncoupled and then the electrons recoupled as stated previously. This leads to the following relation:

\[
\sum_{s_1} (s_{m_1}, s_{m_2}, s_{m_3}, s_{m_4} | S L_1, L_2, L \rangle \langle S L_3, L_4, L_L | S M_L, S M_L') \chi(L'M_L, L'M_L') C(m_1, m_2, m_3, m_4)
\]

where \( * \) represents \( L', S', l_2, s_2, m_2, m_3, m_4, l_3, s_3, m_3, m_4, l_4, s_4, m_4 \). The summation indices can be reduced by noting: 1) \( M_{L}, M_{S}, l_1, s_1 \) and \( m_{s_1} \) are fixed for each scattering amplitude, 2) \( l', s', l_2, s_2 \) are determined by the negative ion state be calculated, 3) \( M_{L}' = m_{s_1} \) and \( M_{S}' = m_{s_1} \) because the \( T \)-matrix doesn’t depend on these parameters and additionally \( M_{L}' \) equals zero because \( p_0 \) defines the quantization axis (i.e. \( m_{s_1} = 0 \)), 4) \( m_{s_1} = 0 \) because \( l_1 = 0 \) (1s electron), 5) \( m_{s_1} = 0 \) because \( S = 0 \) (singlet state) 6) \( m_{s_1} = m_{s_1} \) because we are dealing with excitation to a singlet state and 7) the restrictions on the z-components of the angular momenta due to the Clebsch-Gordon coefficients. The above results in the following relations

\[
\begin{align*}
m_{s_1} &= -m_{s_1} = a \\
m_{s_1} &= m_{s_1} = m_{s_1} = M_{L} = 0 \\
m_{s_1} &= -m_{s_1} \\
m_{s_1} &= M_{S} = 0 \\
m_{s_1} &= m_{s_1} = m_{s_1} = M_{L} = 0 \\
m_{s_1} &= M_{S}' = b \\
m_{s_1} &= b + m_{s_1}
\end{align*}
\]

where \( M_{L} = a, m_{s_1} = m_{s_1} = b \) and the summation is now reduced to one variable \( m_{s_1} \) (or \( m_{s_1} \) or \( m_{s_2} \)).

Now the VUV polarization fraction can be calculated using (3.18) above and equations (2.89), (2.69) and (2.56) for various negative ion resonances. The results for various negative ion resonances are shown in Table 3.5.
Table 3.5 VUV polarization fractions for helium resulting from the formation of the negative-ion resonance \( |l_2 \, ^{2+} l_{12} \, ^{2+} l' \) 

<table>
<thead>
<tr>
<th>Resonance State</th>
<th>( l_0 )</th>
<th>( l_1 )</th>
<th>Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>( sp^{1,3}p )</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( p^{2,1,3}S )</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>( p^{2,1,3}P )</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( p^{2,1,3}D )</td>
<td>2</td>
<td>1</td>
<td>0.600</td>
</tr>
<tr>
<td>( dp^{1,3}P )</td>
<td>1</td>
<td>2</td>
<td>0.143</td>
</tr>
<tr>
<td>( dp^{1,3}D )</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( dp^{1,3}F )</td>
<td>3</td>
<td>2</td>
<td>0.500</td>
</tr>
</tbody>
</table>

* not allowed due to parity conservation

3.3.4 Validity of Polarization Calculations

The preceding derivation of the polarization fractions due to negative ion resonances was based on the assumption that the resonance formation was the dominating channel. This assumption would be valid at threshold where the direct excitation cross-section is small. However when the direct excitation channel becomes comparable to the resonance channel then both scattering amplitudes must be considered which leads to interference effects between the two channels.

The preceding derived polarization fractions are therefore not expected to give true predictions for the polarization fraction above the threshold region where the direct excitation channel cannot be considered negligible but instead should be considered a first correction to the polarization function. If the resonance produces positively polarized radiation the parallel channel is expected to be enhanced relative to the perpendicular channel and vice versa for resonances which produces negatively polarized radiation. The shape of the resonance cannot be determined since the polarization fraction only gives a measure of the relative difference between the parallel and perpendicular channel.

It should also be noted that above threshold there are often several resonances and neutral states which lie in the same energy region and thus the polarization analysis
becomes very complicated. Earlier measurements of total electron impact excitation functions can be used to determine which channels are the dominant ones and thus simplify the analysis.
CHAPTER 4
Experimental Setup

4.1 Introduction

A schematic of the experimental set-up is shown in figure 4.1. The apparatus consists of an electron gun, a gas beam, a reflection analyzer for the emitted photons, a Faraday cup to collect the electron beam and a metastable detector used for calibration purposes. The remainder of this chapter will discuss each of these components as well as any relevant performance tests.

4.2 The Vacuum Chamber

The vacuum system consists of a 12" x 12" x 12" stainless steel chamber which was maintained under high vacuum by a turbomolecular pump (Edwards Model ETP 160/1000) and backed by a belt driven rotary pump. The roughing pump could also be connected directly to the vacuum chamber or to the gasline. A base pressure of \(2 \times 10^{-7}\) torr was obtained as monitored using an ionization gauge. Pressures stated in this work have not been corrected for the specific gas present.

A tungsten heating lamp (in a quartz bulb) was connected so that the chamber could be gently heated. Typically the heating lamp was operated at a power of 10-20W. The chamber was heated for the duration of the data accumulation since this enhanced the performance of the electron gun. Also, the cleanliness of the optical components was improved but sometimes at the cost of significantly altering some of their physical properties (e.g. transmission wavelength cut-off).

The experimental components were housed in a μ-metal cube shaped box to repel any stray magnetic fields. The magnetic field inside this box was reduced to less than 10 milligauss by attaching opposing corners of the box to a high current AC supply from a welding apparatus. By slowly reducing the current from a high value to zero, the material
of the box can be cycled through a progressively shrinking hysteresis loop. The bottom of
the \(\mu\)-metal box was separated from the turbomolecular pump by an optically opaque
baffle to prevent any debris from falling into the pump.

Ceramic feed-throughs were used to make electrical connections with the
components inside the chamber. Viton O-rings were used to seal the flanges.

4.3 Electron Optics

A diagram of the electron monochromator is shown in figure 4.2. The
monochromator consists of four 3-element lens stacks and a hemispherical energy analyzer.
The design of the monochromator [Zetner, 1985] was such as to allow a reasonable
output current (30-300 nA) at a resolution of \(~100\) meV. The design of the electron lenses
and energy analyzers are covered extensively in the literature [Read et. al. 1974, Harting
Figure 4.2 Schematic setup of the electron monochromator.
and Read, 1976, Paszkowski, 1968] and only a brief discussion of the components will be presented.

The electrons are produced by thermionic emission from a hairpin shaped 2% thoriated tungsten wire (.005" dia.). A triode arrangement of a grid and an anode was used to extract the free electrons which were then focused onto the entrance of the hemispherical analyzer by two electrostatic lenses. The beam is energy analyzed and focused by the two remaining lens stacks into the target region.

4.3.1 Beam Formation

The object to be focused is the charge cloud in front of the hairpin filament. The elimination of electrons with large perpendicular velocities and/or located too far from the beam axis was accomplished by using two apertures. The first aperture acts as a window to define the radial extent of the beam (r) while the second aperture acts as the pupil and defines the pencil angle (θₚ) and beam angle (θₜ) (see figure 4.3). Note that by locating the pupil at infinity, the beam angle can be made to zero. This is important in beam resolution because 1) the resolution of the hemispherical analyzer depends on the total beam angle (θₜ + θₚ) (see section 4.4.2) and 2) the magnitude of lens aberrations are also dependent on the total beam angle.

Figure 4.3 The beam and pencil angles (θₜ and θₚ) as defined for a beam passing through two apertures (window and pupil).
The design of the present monochromator used only one aperture which is located at the coincident foci of lenses L1 and L2. This arrangement produces a virtual aperture located at infinity so the beam angle is 0° at the analyzer entrance. A similar arrangement occurs after the analyzer so the beam angle at the target region is also 0°.

The pencil angle, beam energy (E) and beam radius are related to each other by the Helmholtz-Lagrange equation:

\[ r \sqrt{E} \sin \theta_p = \text{Constant} \quad (4.1) \]

Equation (4.1) yields the following relation for electrons at the source (K), analyzer entrance (S) and target (T):

\[ r_K \sqrt{E_K \sin \theta_K} = r_S \sqrt{E_S + eV_x \sin \theta_S} = r_T \sqrt{E_T + eV_T \sin \theta_T} \quad (4.2) \]

where \( V_x \) is the potential at \( x \) with respect to the cathode.

To determine the effect that the collimators and energy analyzer has on the electron current it is convenient to define a critical energy \( (E_c) \) [Langmuir, 1937]: by

\[ E_c = \frac{eV_T M_T^2 \sin^2 \theta_T}{1 - M_T^2 \sin^2 \theta_T} = eV_T M_T^2 \sin^2 \theta_T \quad (4.3) \]

where \( M_T = r_T / r_K \) is the linear magnification at the target. \( E_c \) defines the threshold for which all electrons with \( E_K \leq E_c \) will reach the target regardless of the angle at which they were emitted (\( \theta_K \)). Above the critical energy, only a fraction of the electrons are transmitted to the target (see figure 4.4).

The fraction of transmitted electrons \( (f_{\text{coll}}) \) is the ratio of the area under the curves and is given by [Langmuir, 1937]:

\[ f_{\text{coll}} = 1 - \frac{eV_T}{eV_T + E_c} \exp \left( -\frac{E_c}{kT_K} \right) \quad (4.4) \]

where \( T_K \) is the effective cathode temperature and a Maxwellian distribution for the emitted electrons from the cathode is assumed. Note that it has been assumed that only
two apertures are used to define the energy distribution and that all other apertures (and their images) are significantly larger. If this is not the case vignetting can occur.

The energy selector also limits the amount of current which can reach the target (see figure 4.4) by allowing only electrons with energy \( E_o \pm \Delta E_s / 2 \) (\( \Delta E_s \) is the Full Width at Half Maximum (FWHM) of the distribution of energies) to pass through. In the past \( E_o \) was assumed to be equal to \( E_K = kT_K \), but in low energy scattering experiments this is generally not the case. Here \( E_o = E_c \) and from figure 4.4 it can be seen that electrons with energy \( kT_K \) are not transmitted. The fraction (\( f^{\text{sp}} \)) of collimated electrons which are energy selected is given by

\[
 f^{\text{sp}} = \frac{(E_c / kT_K) \exp(-E_c / kT_K) \Delta E_s}{1 - \exp(-E_c / kT_K)}
\]

(4.4)
It can be seen from equation (4.5) that the current transmitted depends directly on $\Delta E_s$ and $E_c$. By reducing $E_c$ the transmission can be improved but since $\Delta E_s$ and $E_c$ are proportional to each other the effective range of $E_c$ is limited.

The total transmission of the system can be found by multiplying $f^\text{coll}$ and $f^\text{mil}$. This yields

$$f^\text{trans} = \frac{E_c \Delta E_s}{(kT_K)^2} \exp(-E_c/kT_K)$$

(4.6)

provided $\Delta E_s<<E_c$.

Space charge repulsion also affects the amount of current which can be obtained by the electron gun. This repulsion means that the focusing of the electron beam cannot be arbitrarily small but has a minimum radius. Note that the minimum radius is also subject to the Helmholtz-Lagrange equation (4.1) above. Space charge also limits the maximum amount of current ($J_k^\text{max}$) that can be obtained from a parallel diode arrangement

$$J_k^\text{max} = 2.33 \times 10^{-6} d_k^2 V_A^{-3/2} \text{ (amp m}^{-2}\text{)}$$

(4.7)

where $d_k$ is the distance between the anode and the cathode, and $V_A$ is the anode potential.

Electron optics suffer from the same aberrations as normal physical light optics, i.e. spherical aberration, coma, astigmatism, curvature of field, etc. These distortions are due to non-uniformities in the fields as well as to the inability to focus electron beams to a point. It is therefore advantageous to keep the beam away from the edges of the lens elements. A consequence of this is that beam defining apertures cannot be lens elements. Further, these apertures should be in high field regions (where the beam energy is large) to minimize the effects of any aberrations.
Deflectors which are used to steer the beam can also cause distortions if applied voltages are too large. Thus it is advisable to limit the range of deflector voltages, and to place them in a field free region. Deflector voltages are referenced to the potential of this region.

4.3.2 Hemispherical Analyzer

The analyzer consists of two concentric hemispheres of radius \( R_1 = \frac{10}{10} \) and \( R_2 = \frac{11}{10} \) with voltages \( V_1 \) and \( V_2 \) respectively. Due to spherical symmetry, the electric field depends only on \( r \) and is given by

\[
E(r) = E_0 \frac{R_0^2}{r^2} \quad (4.8)
\]

where \( R_0 = \frac{(R_1 + R_2)}{2} \) is the equilibrium orbit of the electron. By equating the centripetal and electrostatic forces at \( R_0 \) the following relation is obtained

\[
E_0 = \frac{2V_0}{R_0} \quad (4.9)
\]

where \( V_0 \) is the energy of the incoming electron. Integrating \( E(r) = -\frac{d\phi}{dr} \) yields

\[
\phi(r) = \phi(R_0) - \int_{R_0}^{r} E(r')dr' = \phi(R_0) - E_0R_0^2 \left( \frac{1}{r} - \frac{1}{R_0} \right) \quad (4.10)
\]

Setting the analyzing energy equal to the incident electron energy \( \phi(R_0) = V_0 \) and using equation (4.9) results in

\[
V(r) = V_0 \left( \frac{2R_0}{r} - 1 \right) \quad (4.11)
\]

from which the potentials on the hemispheres can be obtained.
Using equation (4.12), the voltages on the hemispheres can be determined for any incident electron energy.

The above derivation was made using spherical symmetry but since hemispheres were used, aberrations in the 1/r potential field occur in the gap of the analyzer (especially near the entrance and exit). To minimize the distortion of the field, correction hoops as discussed by Jost [1979] were incorporated at the entrance and exit to the hemispheres with appropriate potentials applied. Also, the matching of the entrance and exit aperture potentials with the analyzing energy (see step between 4.10 and 4.11) helped to reduce the fringing effect.

The resolution of the hemispherical analyzer is given by

\[ \frac{\Delta^B E_s}{E_s} = \alpha \frac{r_s}{L_s} + \beta \theta_s^2 + \gamma \phi_s^2 \]  

(4.13)

where: \( \Delta^B E_s \) is the base width of the energy spread
\( E_s \) is the beam energy at the selector
\( r_s \) is the beam radius at the selector entrance
\( L_s \) is a representative dimension of the selector (chosen to be 2\( R_o \))
\( \theta_s, \phi_s \) are the beam half angles in two orthogonal directions at the selector entrance
\( \alpha, \beta, \gamma \) and \( n \) are constants which depend on the selector geometry

For the 180° hemispherical analyzer, the values for \( \alpha, \beta, \gamma \) and \( n \) are 4.0, 1.0, 0 and 2 respectively. However, the quantity of interest is the FWHM of the beam (\( \Delta E_s \)) and therefore the values of \( \alpha \) and \( \beta \) are replaced by \( \alpha_{1/2} \) and \( \beta_{1/2} \), which are empirically determined parameters. It turns out that \( \alpha_{1/2} \approx \alpha / 2 \) and \( \beta_{1/2} < \beta / 2 \) and therefore equation (4.13) can be written as
Thus $\Delta E_s$ depends on $\theta_s$ for fixed $r_s$, $R_0$ and $E_s$. To minimize $\Delta E_s$, the beam and pencil angle need to be made as small as possible. This is accomplished using a real window and a virtual pupil (see section 4.3.1). With $r_s$ being limited by the Helmholtz-Lagrange equation (4.1) and not made arbitrarily small, it is advantageous to make $R_0 \gg r_s$.

For the present experiment, an estimation of the resolution can be determined using the following values

\[
\frac{\Delta E_s}{E_s} \leq \frac{r_s}{R_0} + \frac{\theta_s^2}{2}
\]

where $\theta_s$ was estimated by assuming the maximum trajectory was from the edge of the B element in the second lens stack. These values yield

\[
\frac{\Delta E_s}{E_s} \leq 0.04 + \frac{0.077}{2} = 0.044
\]

and one can immediately see that $\frac{r_s}{R_0}$ is the dominant term. In this experiment the value for $E_s$ was 3-5 eV and therefore $\Delta E_s \approx 0.130-0.220$ eV.

4.3.3 Monochromator Construction and Performance

The monochromator lens elements and apertures were made from molybdenum which is non-magnetic. These components were enclosed in a copper housing to prevent any stray electrons from the filament from reaching the interaction region. The hemispheres of the 180° analyzer were constructed from copper and coated with benzene soot to absorb any stray electrons incident upon them. The monochromator was gently heated using a quartz bulb (see section 4.1) to keep the elements relatively free from insulating oil layers which might charge up.

A schematic diagram of the experimental circuitry is shown in figure 4.5 with typical voltages applied to the monochromator displayed in Table 4.1. The voltages on the
Figure 4.5 Schematic diagram of the experimental circuitry.
Table 4.1 Monochromator Voltage Settings for high resolution measurements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Voltage (V)</th>
<th>Element</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid</td>
<td>-1.5</td>
<td>S1</td>
<td>11.55</td>
</tr>
<tr>
<td>Anode, L1A</td>
<td>101.8</td>
<td>S2</td>
<td>3.43</td>
</tr>
<tr>
<td>L1B</td>
<td>11.6</td>
<td>L3B</td>
<td>0.5</td>
</tr>
<tr>
<td>L1C, A1, L2A</td>
<td>21.4</td>
<td>L3C, A3, A4, L4A</td>
<td>20.0</td>
</tr>
<tr>
<td>L2B</td>
<td>12.0</td>
<td>L4B</td>
<td>3.3</td>
</tr>
<tr>
<td>L2C, L3A</td>
<td>5</td>
<td>L4C, Target</td>
<td>7-25</td>
</tr>
</tbody>
</table>

A and C lens stack elements were chosen such the voltage ratios (A/C) were the same (except for lens stack 4 where the C element varied as the target voltage).

The hemispheres were initially operated to pass electrons with a nominal incident energy of 5eV. To maximize currents the voltage on S2 was adjusted away from the theoretical value given by equation (4.12). This resulted in poorer resolution but much quicker data accumulation. To improve the resolution, S2 was set to the calculated value from equation (4.12), the potential upon which the filament power supply was floating was adjusted to maximize current and the filament heating current was lowered. The final tuning was then performed by adjusting the deflectors and the central lens elements.

4.4 The Gas Jet

The target gas was introduced into the system using a non-magnetic stainless steel tube with a capillary diameter of 0.5 mm. The end of the capillary tube was located ~2 mm from the beam axis.

The chamber pressure with no gas introduced was $2 \times 10^{-7}$ torr. To minimize the depolarizing effects due to radiation trapping, polarizations as a function of chamber pressure were measured (see figure 4.6). It was found that chamber pressures needed to be less than $2 \times 10^{-6}$ torr. Head pressures were monitored using a Baratron Gauge and ranged from 0.5 mtorr(He) to 0.27 mtorr (Xe).
The stated purity of the gas was at least 99.995% as supplied by Matheson or Linde.

4.5 Interaction Region

The interaction region was surrounded by a grounded mesh cage to prevent any electrical field penetration into this region. The mesh cage was movable so that alignment of the electron gun output, the gas needle and Faraday cup could be performed after any maintenance was performed on these components. Alignment pins were inserted in the electron gun and the Faraday cup to aid in their alignment.

4.6 Polarizer Details

The polarization analyzer consists of a single mirror and a channeltron (figure 4.7). The surface of the mirror was oriented at an angle $\theta$ to the incoming photons and the
Reflection analysis is the only method available for V.U.V. photons below 105nm due to a lack of transparent crystals. Because the reflecting material is opaque in the V.U.V. region, the material has a complex index of refraction \((n - ik)\) where \(n\) is the real index of refraction, \(k\) is the extinction factor and \(i = \sqrt{-1}\). A consequence of this is that it is impossible to find an angle of incidence such that the reflected light is completely polarized. The generalized Frensel equations for reflectance are [Samson, 1967]:

\[
R_\perp = \frac{a^2 + b^2 - 2a \cos \theta + \cos^2 \theta}{a^2 + b^2 + 2a \cos \theta + \cos^2 \theta}
\]

\[
R_\parallel = R_\perp \frac{a^2 + b^2 - 2a \sin \theta \tan \theta + \sin^2 \theta \tan^2 \theta}{a^2 + b^2 + 2a \sin \theta \tan \theta + \sin^2 \theta \tan^2 \theta}
\]

Figure 4.7  a) Schematic setup of a single reflection polarization analyzer and b) a triple mirror attachment used by Karras [1988] to obtain high accuracy polarization measurements.

The channeltron was positioned such that it receives the reflected photons. The channeltron and the mirror are held fixed on a stainless steel block which can be rotated 360° about the axis of the incoming photon vector.
where

\[ 2a^2 = [(n^2 - k^2 - \sin^2 \theta)^2 + 4n^2k^2]^{1/2} + (n^2 - k^2 - \sin^2 \theta) \]
\[ 2b^2 = [(n^2 - k^2 - \sin^2 \theta)^2 + 4n^2k^2]^{1/2} - (n^2 - k^2 - \sin^2 \theta) \]

\( \theta \) is the angle of incidence.

The measured intensities \((I_n^m, I_\perp^m)\) are related to the true values \((I_n, I_\perp)\) by

\[ I_n^m = D(R_{\parallel}I_n + R_{\perp}I_\perp) \]
\[ I_\perp^m = D(R_{\perp}I_n + R_{\parallel}I_\perp) \]

where \(D\) is the channeltron detection efficiency.

Using equations 4.17 in 2.1 yields

\[ p = \frac{(R_{\parallel} + R_{\perp})(I_n^m - I_\perp^m)}{(R_{\parallel} - R_{\perp})(I_n^m + I_\perp^m)} \]
\[ = \frac{1}{\eta} \frac{(I_n^m - I_\perp^m)}{(I_n^m + I_\perp^m)} \]

where \(\eta\) is the polarization efficiency.

By inverting equation 4.17 relations for the true intensities can be obtained.

\[ I_\perp = \frac{(\tau I_n^m - I_\perp^m)}{DR_\perp(\tau^2 - 1)} \]
\[ I_n = \frac{(\tau I_n^m - I_\perp^m)}{DR_\parallel(\tau^2 - 1)} \]

where

\[ \tau = \frac{R_{\parallel}}{R_\perp} \left( \frac{1 + \eta}{1 - \eta} \right) \]

If there are \(n\) mirrors present (i.e. \(n\) reflections) then the measured intensities are given by

\[ I_n^m = D \left( \sum_{i=1}^{n} R_{\parallel}I_n + \sum_{i=1}^{n} R_{\perp}I_\perp \right) \]
\[ I_\perp^m = D \left( \sum_{i=1}^{n} R_{\perp}I_n + \sum_{i=1}^{n} R_{\parallel}I_\perp \right) \]
which leads to

\[ P = \frac{\sum_{i=1}^{n} (R_{ii} + R_{i1})}{\sum_{i=1}^{n} (R_{ii} - R_{i1})} \left( \frac{1 - 1^{m}}{1 + 1^{m}} \right) \]  

(4.22)

If the mirrors are made of the same material then equation 4.22 can be written as

\[ P = \left( \frac{R_{ii}}{R_{i1}} \right)^{n} + 1 \left( \frac{1 - 1^{m}}{1 + 1^{m}} \right) \]  

(4.23)

Typically \( R_{ii}/R_{i1} \approx 5 \) [Hammond et al., 1989] and thus for the case of 4 mirrors

\[ \left( \frac{R_{ii}}{R_{i1}} \right)^{n} + 1 = \frac{626}{624} = 1.003 \approx 1 \]  

(4.24)

It can be seen from equation 4.24 that measurements made with multiple reflections are able to provide absolute polarization values directly from the measured data and therefore provide an excellent source for calibration.

There are several choices of materials to use as a reflector including LiF (which was first used to measure Lyman-alpha radiation [Ott, Kauppila and Fite, 1967] and Quartz (Chwirot et al., 1993). The mirror used in the present experiment was a 1" diameter, optically flat gold coated pyrex mirror. The choice of gold as a reflecting surface has many advantages [Westerveld et al., 1985] which include excellent long term stability and well known values for the optical constants \( n \) and \( k \) [Lynch and Hunter, 1985]. It also happens that the angle at which the mirror acts as a quarter wave retarder (\( \theta = 57.5^\circ \)) has very little variation over the wavelengths 30 to 200 nm, though this property is not significant in the present context.
Using the experimental values of $n$ and $k$ from Lynch and Hunter [1985] and equations (4.16) – (4.18), the inverse polarization efficiencies ($1/\eta$) were calculated over the wavelength range 45–170 nm (see figure 4.8) and specific values for the rare gases are shown in table 4.1. Note that the value of $1/\eta$ can vary rapidly and thus small errors in $n$ and $k$ can lead to significant changes in its value. The cleanliness of the mirror also will have an effect on $\eta$ and therefore calibration of the data to well known values is necessary.

The scattered photons were counted using a Galileo Electro-Optics model 4039C channeltron. The cone of the channeltron was biased to $-200$ V to repel any stray electrons. The spiral end of the channeltron was maintained at 3-5 kV by a Bertan Associates Inc. high voltage supply (model PMT-50A/P). The electron cascade produced
Table 4.2 Calculated inverse polarization efficiencies for a gold mirror at 57.5° incidence angle

<table>
<thead>
<tr>
<th>Species</th>
<th>IS coupled State</th>
<th>λ (nm)</th>
<th>Energy (eV)</th>
<th>(\frac{1}{\eta})</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2^1P</td>
<td>58.4</td>
<td>21.22</td>
<td>1.536</td>
</tr>
<tr>
<td>Ne</td>
<td>3^1P</td>
<td>73.6</td>
<td>16.85</td>
<td>1.479</td>
</tr>
<tr>
<td></td>
<td>3^3P</td>
<td>74.4</td>
<td>16.67</td>
<td>1.487</td>
</tr>
<tr>
<td>Ar</td>
<td>4^1P</td>
<td>104.8</td>
<td>11.83</td>
<td>1.412</td>
</tr>
<tr>
<td></td>
<td>4^3P</td>
<td>106.7</td>
<td>11.62</td>
<td>1.419</td>
</tr>
<tr>
<td>Kr</td>
<td>5^1P</td>
<td>116.5</td>
<td>10.64</td>
<td>1.442</td>
</tr>
<tr>
<td></td>
<td>5^3P</td>
<td>123.6</td>
<td>10.03</td>
<td>1.451</td>
</tr>
<tr>
<td>Xe</td>
<td>6^1P</td>
<td>129.6</td>
<td>9.57</td>
<td>1.457</td>
</tr>
<tr>
<td></td>
<td>6^3P</td>
<td>147.0</td>
<td>8.44</td>
<td>1.458</td>
</tr>
</tbody>
</table>

by the incident photon yielded a 20mV, 20 nsec pulse which was directed to the counting electronics (see section 4.9).

The quantum efficiency of the channeltron is ~10% at 100 nm and decreases rapidly with increasing wavelength [Weller and Young, 1970]. The transitions being studied in Ar, Xe and Kr lie above 100 nm and thus the detection efficiency must be improved in this range. To do this the channeltron cone was coated with Cesium Iodide [Johnson, 1969] with the result that the detection efficiency was nearly 10% for the largest wavelengths being studied in this work (see figure 4.9).

In determining the polarization it has been assumed that the photons all travel on an axis (x-axis) oriented at 90° to the electron beam. However, in practice a cone of photons are observed due to the finite size of the detector. Humphrey [1994] has analyzed the variation in the polarization as a function of the size of the detector assuming circular symmetry about the x-axis and his results are shown in figure 4.10 where \(\theta_0\) is the angular extent of the observed light cone from the x-axis. His method involved numerically integrating \(I\eta_0(\theta,\phi)\) and \(I(\theta,\phi)\) over the solid angle subtended by the detector.

\[
I\eta_0(\theta,\phi) \propto \eta_0^0 \sin^2 \theta - \frac{\eta_0^0}{2} \sin 2\theta \cos \phi
\]

\[
I(\theta,\phi) \propto 1 - \eta_0^0 \cos^2 \theta
\]
where \( n_i^0, n_i^0 \) are the polarizations at \((\theta, \phi) = (\frac{\pi}{2}, \frac{\pi}{2})\). In the present experiment the acceptance angle \( \theta_0 \sim 2.2^\circ \) and from figure 4.10 it can be seen that the depolarization is less than 0.5%.

4.7 Metastable Detector

The metastable detector was also a channeltron which was located directly below the gas nozzle. The rare gas metastables all had internal energies in excess of the \( \sim 8 \) eV work function of the channeltron cone. Since the metastable detector and the photon detector were never operated at the same time, the power supplies and the counting electronics were shared between the two detectors.
The metastable yield was measured under the same operating conditions as the photon measurements (i.e. energy range, electron current etc.) before and after each polarization measurement. The metastable functions were compared to the high resolution data of Buckman et al. [1983a,b] to aid in determining the energy resolution of the photon data and for energy calibration.

4.8 System Checks

To ensure that the data accumulation was performed under optimum conditions the following measurements were performed in addition to polarization-pressure check (section 4.4):

1) The radiation intensity as a function of polarizer orientation (referred to as a polarization ellipse). The polarization ellipse can be shown to be described by the relation [Chiwirot et al., 1993]:

---

Figure 4.10  Depolari\zation of linear and circular polarization as a function of acceptance angle [Humphrey, 1994]. Note that 0.00 represents values nearly zero.
where \( \varphi \) is the orientation of the polarizer relative to the quantization (z) axis and \( P_1 \) is the polarization of the photons. From equation 4.26 it can be seen that \( I(\varphi) \) varies as \( \cos^2(\varphi) \) with maxima and minima occurring at \((0^\circ, 180^\circ)\) and \((90^\circ, 270^\circ)\) respectively or vice versa depending on the values of \( P_1, R_{\perp} \) and \( R_h \). This variation provides a convenient check for the alignment of the polarizer before a polarization measurement. In the present experiment the polarization ellipse was measured with \( \varphi \) incremented in steps of 1.8°. The location of the maxima and minima were determined and the polarizer was then realigned if necessary. Also, the intensities at \( 0^\circ \) and \( 180^\circ \) were compared (as well as \( 90^\circ \) and \( 270^\circ \)) since these values should be the same. A polarization ellipse is shown in figure 4.11.

2) The photon intensity as a function of source pressure (figures 4.12). This was done to ensure that only single collisions were occurring (i.e. photon intensity varied linearly).
4.9 Data Accumulation and Management

A schematic diagram of the counting system is shown in figure 4.13. The signal produced by the channeltron, a 20 mV pulse, was directed to a $\times10$ preamplifier (signal $\sim200$ mV) which in turn was connected to a Delay Line Amplifier (DLA, Ortec 460). The DLA was set to amplify the input signal by a factor of $\sim1400$ (signal $\sim3$V). The unipolar output was connected to an Integral Discriminator (Ortec 421) which was set to accept pulses in the range 0.2 - 10 V. The +5 V output of the discriminator was attached to 1) a ratemeter (Ortec 441) to give an indication of the count rate as well as 2) a multi-channel analyzer (MCA) (The Nucleus Quantum 8 Multichannel Pulse Height Analyzer).

The MCA had 1024 channels which were divided into 4 quadrants. For the metastable excitation measurements only one quadrant was used (256 channels) while for the polarization measurement all 4 quadrants were active (one for each orthogonal...
polarizer orientation). To ensure that the counts accumulated in each channel corresponded to a particular energy, the MCA was modified so that it could control the voltage ramp (Tracor Northern 1251) for the electron impact energy. For the metastable measurement, one of the MCA's internal programs was used to synchronize the energy ramp with the channel memory, but for the photon counting an IBM XT computer was used to coordinate the quadrants with the orientation of the polarizer. A stepping motor and four L.E.D. sensors were used to control the orientation of the polarizer. The dwell time for each channel (i.e. energy step) was 1000 msec.

The data stored in the MCA's memory was transferred via an RS232 output to a computer where it could be saved and analyzed. This was done periodically during the photon data accumulation to prevent against loss of data due to unexpected power interruptions during the 2-8 week runs which were needed.
The energy scan was usually over 5 V with the lower limit set approximately 1 eV below the onset value of the first excited state. This initial 1 eV range allowed the background to be determined and then extrapolated above the threshold. The background was then subtracted and the polarization calculated using equation 4.18. The value for $\eta$ was determined by measuring the polarization at a higher energy and normalizing this value to the previously measured accurate data of Karras [1988]. The energy at which the polarization was measured was located in a region of the spectrum where the polarization was approximately constant so that the energy resolution would not be a factor.

In calibrating the VUV spectrum it is beneficial to have sharp resonance features to fix the energy scale against. As shown in section 4.6 the measured parallel and perpendicular intensities are actually mixtures of the two polarizations and therefore equation 4.19 must be used to give the true values. Since only the shape and relative values of the excitation function are necessary in the present experiment $DR_1$ can be set to 1.
CHAPTER 5

HELIUM

5.1 Introduction

Helium is the most studied element of the rare gases due to the simplicity of its structure. It is also well described by LS coupling which results in the spin and orbital angular momentum being treated as independent quantities. Because of its differences with the other rare gases in areas such as coupling scheme and ion-core parity, helium will be treated separately. But first a discussion on the determination of the energy resolution will be presented.

5.2 Determination of Energy Resolution

In the present experiment there are two methods used to determine the energy resolution of the electron beam when applicable: 1) position of the onset of the VUV excitation function and 2) convolution of accurately measured metastable excitation functions.

In order to make an estimation of the energy resolution based on the observed position of the threshold, it is necessary to determine at what channel the excitation may be considered to have started. This problem has been addressed by Heddle et al. [1974] and their method is as follows: They considered a case where the data in the first $N$ channels was accumulated with no overlap between the electron energy distribution function and the excitation function but in the $(N+1)^{th}$ channel there was overlap. In the ideal case, the first $N$ channels would have the same value and the $(N+1)^{th}$ channel would be greater, however, since the background is statistical in nature, the first $N$ channels can be viewed as $N$ independent measurements of the same quantity. Now, if we consider the mean and standard deviation of the first $K$ channels ($K \leq N$) we should see the mean approach a constant value with the standard deviation steadily decreasing as $K$ approaches
When $K > N$ (i.e. when the excitation is said to have begun) the standard deviation should start to increase markedly.

For the case that the background can be represented by a straight line ($mx+b$), the average of the first $K$ points is given by

$$\frac{m(K+1)}{2} + b$$

with a standard deviation of

$$\sqrt{\frac{m}{2} \left(1 + \frac{2b}{Km}\right)^{1/2}}$$

where the approximation $K \pm 1 \approx K$ has been used. It can be seen that as $K$ increases the standard deviation smoothly approaches the constant $\sqrt{\frac{m}{2}}$. Thus the standard deviation should show a significant increase when $K > N$.

Once the onset has been determined, the energy resolution can be found by calculating the difference between the accepted threshold value and the measured onset.

A second method for determining the energy resolution is to convolute an accurate excitation function of the studied transition with various electron distribution profiles and compare these results with the measured data. In the present experiment, excitation functions for the metastable states from Buckman et al. [1983a,b] were convoluted with Gaussian profiles of various FWHM and compared with metastable measurements performed immediately before or after the VUV measurements.

5.3 Data Collection and Calibration

The measurement of the integrated VUV photons ($n^1P \rightarrow 1^1S$) as function of electron impact energy is presented in figure 5.1. A linear background has been subtracted from the data but no correction for fluctuations in the electron beam current or for the polarization sensitivity of the analyzer have been performed. The data accumulation took 220 hours to collect at a maximum rate of 33 Hz with head and chamber pressure set at 0.500 mtorr and $2 \times 10^{-6}$ torr respectively.
The data from the metastable measurement is presented in figure 5.2. This data has not been corrected for fluctuations in the electron current as a function of energy nor has any background subtraction been performed. The data took 8 hours to accumulate at a maximum count rate of 30 Hz. The head and chamber pressures were 0.500 mtorr and 2x10⁻⁶ torr respectively.

The VUV photon data was corrected for the polarization sensitivity of the analyzer using equation 4.19 and the results are shown in figure 5.3. The value used for 1/η was 1.95 (see below). It can be seen from this figure that the resonance features are enhanced using this technique which allows the effects on the polarization to be more clearly identified. To enhance the resonance features even more a linear function determined over the energy range 21.7 - 22.2 eV was subtracted from the corresponding data set and the results are displayed in figure 5.4.

Comparing the metastable data with various convoluted high resolution excitation functions [Buckman et al. 1983a] the resolution was determined to be 180 meV. The energy scale was calibrated against this data set.

The total photon emission spectrum (I₁ + I₉) is shown in figure 5.5. The energy scale of the spectrum was calibrated against the resonance feature located at 22.67 ± .015 eV [Brunt et al., 1977a]. The onset of the VUV data was determined using the technique described in section 5.2 and the energy resolution was determined to be 120 meV which is better than that obtained from the metastable data.

5.4 Results and Discussion

The polarization curve resulting from the VUV data shown in figure 5.1 and 5.3 is presented in figure 5.6. For sake of clarity data points below the threshold have been set to zero. The calibration of the polarization curve was done by comparing values measured at 24 eV (using the above data) and at 30 eV (from a separate measurement) with values obtained by Hammond et al. [1989]. A value of 1/η = 1.95 was obtained at both energies.
Figure 5.1 VUV excitation functions for helium with background subtracted.
Figure 5.2   Metastable excitaton function for helium
Figure 5.3 VUV excitation functions for helium corrected for the polarization sensitivity of the analyzer.
Figure 5.4 Corrected VUV excitation functions for helium with a linear function subtracted.
Figure 5.5 Total VUV emission spectrum for helium.
Figure 5.6  Polarization function for helium.
Table 5.1 Energies and widths for resonance features in helium

<table>
<thead>
<tr>
<th>Classification</th>
<th>Energy (eV)</th>
<th>Width (meV)</th>
<th>Comments</th>
</tr>
</thead>
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<tr>
<td>1s(3s-1S)S</td>
<td>22.47</td>
<td>35</td>
<td>1</td>
</tr>
<tr>
<td>1s(3s3p-3P)P</td>
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<td>42</td>
<td>1</td>
</tr>
<tr>
<td>1s(3s3d-1D)D</td>
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<td>47</td>
<td>1</td>
</tr>
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<td>1</td>
</tr>
<tr>
<td>2G</td>
<td>23.05</td>
<td>32</td>
<td>1</td>
</tr>
<tr>
<td>1s(4s21S)S</td>
<td>23.49</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>1s(4s4p-3P)P</td>
<td>23.53</td>
<td>40</td>
<td>3</td>
</tr>
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<td>3</td>
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<tr>
<td>1s(4p21S)S</td>
<td>23.67</td>
<td>18</td>
<td>3</td>
</tr>
</tbody>
</table>

* T denotes an l-electron bound in the polarization potential of a neutral state
(1) Buckman and Clark [1994]
(2) Brunt et al. [1977a]
(3) Brunt et al. [1977b]

Confidence in this value is given by the trend of the polarization function toward the theoretically predicted value +1 at threshold.

The positions of some of the neutral and negative-ion states are indicated on the figures and the resonance features are listed in Table 5.1. It can be seen that in the first eV above threshold (21.22 eV) there are no perturbing resonances present and thus the polarization function is entirely due to the 21P-11S transition (58.4 nm). This lack of structure in the polarization function near the threshold is in contrast to what is observed in the visible transitions of helium [Heddle et al., 1974, 1977] and, as will be seen in chapter 6, the heavy rare gases. This situation presents not only an excellent opportunity to test the threshold angular momentum arguments presented in section 2.2 but also allows one to see how the polarization of pure direct excitation varies with impact energy. The threshold polarization is predicted to be +1 from simple angular momentum arguments (see section 2.2) and from figure 5.6 it is clearly seen that the polarization function goes to unity. This effect can clearly be seen in the \( I_\parallel \) and \( I_\perp \) near threshold excitation functions (figure 5.7) where the signal in the parallel channel sharply increases at threshold (allowing for the energy resolution) while the signal in the perpendicular channel remains at zero for 0.15 eV above the threshold position observed in the parallel
channel. Using this result we can make predictions concerning the nature of the scattering process just above threshold.

![Figure 5.7 VUV excitation functions corrected for the polarization sensitivity of the analyzer at threshold](image)

We consider the following excitation schemes

\[
ks + 1s^2S \rightarrow kp + 1s2p^1P \quad (5.3a)
\]

\[
kp + 1s^2S \rightarrow ks + 1s2p^1P \quad (5.3b)
\]

Other excitation paths are not considered because they would require incident and/or scattered electrons with higher angular momentum. Above threshold both paths are allowed by parity and angular momentum conservation laws however path 5.3b has the additional requirement that only magnetic sublevels with quantum number equal to 0 are possible for the atomic state. This is because an s electron is scattered (the sum of the orbital angular momentum z-components must equal 0) while for path 5.3a atomic sublevels with quantum numbers equal to 0, ±1 are allowed since a p-wave electron is
scattered. Since the measured perpendicular intensity is zero above threshold this suggests
that path 5.3b is responsible for the scattering process. Also note that path 5.3b is more
probable for excitation since in path 5.3a two electrons are required to change their orbital
angular momentum quantum. Thus s-wave scattering is the dominant process in the
threshold region. Assuming this is the case, excitation of 2P close to threshold could have
significant possibilities in the area of calibration of the behaviour of electron spectrometers
used with very low energy electrons [Trajmar and McConkey, 1994]. In other polarization
experiments [Heddie et al. 1974,1977], the polarization was observed to change rapidly
within the first 100 meV which suggested that higher angular momentum electrons were
being scattered. However, the above comments coupled with the resonance calculations
and measurements by Wolcke et al. [1983](also see section 3.3.1) as well as the
measurements in chapter 6 indicate that negative ion resonances are most likely
responsible for these rapid changes.

The effect of the resonances first appear at approximately 22.4 eV where strong
broad features are evident. The polarization function appears to be leveling out at a value
of 0.8 before coming under the influence of the (3s2 1S)2S resonance and along with two
other resonances ((3s3p 3P)2P and (3p2 1D)2D) that have been observed at 22.60 and
22.66 eV respectively [Buckman and Clark, 1994], these resonances seem most likely
responsible for the oscillating shape of the polarization function in this region. After the
(3p2 1D)2D resonance one would expect the polarization function to return to the
background level which would presumably be between 0.7-0.8 based on an extrapolation
of the present unperturbed threshold values to the cascade-free values measured by Steph
and Golden [1980]. However the polarization has fallen to ~0.5 and this drop can be
attributed to the excitation of higher lying neutral states which cascade to the 2P state.
The 31S has only one M_l sublevel and therefore the 31S → 2P transition produces only
unpolarized radiation (i.e. it populates M_l = 0 and M_l = ±1 of the 1P state equally) which
causes a net depolarization in the radiation being emitted from 2P state. The next neutral
state is the 31D level which also decays to the 2P state. This state should favour the
population of the M_l = ±1 since the M_l = ±2 sublevels of 31D can only decay to the M_l = ±1 sublevels of 2P. Also in this region is the 31P level which can decay directly to the

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ground state \((1^1S)\). Its polarization curve should be identical to that of \(2^1P\) and therefore the polarization function should increase since these photons should have a large (~1) positive polarization and are not discriminated against by the photon detector. Heddle et al. [1974, 1977] have measured the excitation functions for the \(3^1S\), \(3^1P\) and \(3^1D\) levels and found that \(3^1S\) and \(3^1D\) are sharply enhanced very close to threshold and then level off while the \(3^1P\) level slowly rises from onset. Therefore the \(3^1S\) and \(3^1D\) states will have a strong effect on the polarization function near their thresholds and then become less important while the \(3^1P\) state should not significantly affect the polarization in this region but become more significant at higher energies.

At 23.5 eV there is evidence of similar structure on a smaller scale where the negative-ion resonances and neutral states associated with the \(n=4\) principal quantum number are located. Heddle et al. [1977] have studied the \(4^1S\) and \(4^1D\) excitation functions and have observed similar behaviour to those with \(n=3\).

The effects of the resonances and cascade can clearly be seen in the corrected excitation functions. Referring to figure 5.3 it can be seen that the resonances are effecting the \(I_p\) and \(I_\perp\) excitation functions differently. In the parallel channel the signal is observed to rise linearly after the threshold region until the first resonance at 22.47 eV where it drops in value but does not recover back to the level that would be expected based on a linear extrapolation of the data at energies below the resonance. This effect is more clearly shown in figure 5.4 where the linear extrapolation has been subtracted from the data. Also in this figure the effect of the resonances at 23.5 eV can be seen to cause another smaller downward displacement. The perpendicular channel shows a slight enhancement of the signal before showing the dip. After the resonances the perpendicular channel has a steeper slope indicating enhancement of the population of this state due to cascade most probably from the \(3^1D\) state. Also at 23.5 eV the effect of resonances associated with the \(n=4\) principal quantum number can be seen to produce the same effect with the corresponding increase in the slope. Thus the net effect of the resonances and cascading states is to enhance the population of the perpendicular channel and decrease the population of the parallel channel successively at the \(n=3\) and \(n=4\) thresholds.
Finally, the theoretical predictions of section 3.3.3 can be used to analyze the data. The first resonance identified in figure 5.6 has a $1s(3s^2 \, ^1S)_2^S$ configuration. The analysis of section 3.3.3 does not allow for this state directly because the technique involves recoupling the final states and therefore the negative ion state must consist of the orbital angular momenta of these individual electrons. A way around this dilemma is to assume that configuration interaction allows the $1s(3s^2 \, ^1S)_2^S$ to evolve into the $1s(3p^2 \, ^1S)_2^S$ state and then decay. This results in a polarization of 0 for this state and from figure 5.6 it can be seen that the polarization does indeed drop toward smaller values. The next two resonances, $1s(3s3p \, ^3P)_2^P$ and $1s(3p^2 \, ^1D)_2^D$, lie near each other has and thus it is not possible to clearly distinguish the effect that each resonance has on the polarization curve. The $1s(3s3p \, ^3P)_2^P$ resonance has a predicted value of +1 and the polarization curve could be reflecting this by increasing back to 0.8 since the $1s(3p^2 \, ^1D)_2^D$ resonance has a predicted value is 0.6 and thus it should not significantly affect the polarization curve since it is already near this value.

In summary the shape of the polarization curve (figure 5.6) can be understood as follows:

1) the threshold is governed by angular momentum conservation and is dominated by $s$-wave scattering,

2) above threshold the polarization falls from unity due to electrons being able to possess higher $l$ partial waves,

3) $nlnl'$ family of resonances cause perturbations in the polarization around 22.6 eV ($n=3$) and 23.6 eV ($n=4$) and

4) cascading from $n=3$ and $n=4$ neutral states at approximately 23 eV and 23.8 eV respectively cause the polarization to decrease from the pure direct excitation.

Note: After submission of this work for examination, theoretical calculations of the polarization of the radiation resulting from the direct excitation (no cascade) of the $2^1P \rightarrow 1^1S$ transition have been reported by Bartschat (private communication) which are in very good agreement with the present results below 22.8 eV.
Chapter 6

Heavy Rare Gases

6.1 Introduction

The heavy rare gases will be grouped together in a single chapter because of their similarities in coupling scheme and ion core parity which suggests that common features may be observed. Note, however, that for the excited states ($J=1$), the more massive rare gases (Kr and Xe) can be viewed as nearly equally mixed $^3P$ and $^1P$ states while the lighter rare gases (Ne and Ar) can be viewed as nearly "pure" $^3P$ or $^1P$ (see Table 3.1). This feature along with the increasing ion core splitting (section 3.1.1) as one progresses up the periodic table suggests we should see systematic changes in the polarization as we progress toward more massive gases since the position of resonances and cascading states associated with each ion core ($j_c = 1/2, 3/2$) will shift relative to each other due to the ion core splitting.

6.2 Neon

6.2.1 Data Collection and Calibration

The measurements of the VUV photons and the metastable data are presented in figures 6.1 and 6.2 respectively. Note that the data has not been corrected for the polarization sensitivity of the detector nor for any fluctuations in the electron current as a function of energy but a linear background subtraction has been performed. The VUV data took approx. 1500 hours to accumulate at a maximum count rate of 4.5 Hz. The metastable data had a 67 hour accumulation time with a 58 Hz count rate in the largest channel. The head pressure and chamber pressure were 0.171 and $5.8 \times 10^{-7}$ torr respectively for all data accumulation.
Figure 6.1 VUV excitation functions for neon with background subtracted
Figure 6.2 Metastable excitation function for neon
The VUV photon data were corrected for the polarization sensitivity of the analyzer ($1/\eta = 1.9$, see below) using Equation 4.19 and the results are shown in figure 6.3. As in helium, one can see that some of the resonance structures are significantly enhanced, most noticeably in the perpendicular channel near the $d_1$ and $d_2$ resonances.

The total photon emission spectrum ($I_\parallel + I_\perp$) is shown in figure 6.4. The location of the prominent resonance features labeled $b$, $d_1$, and $d_2$ in Brunt et al. [1977c] were compared to the positions of similar features observed in figure 6.4 and since the $d_1$ and $d_2$ resonance features were not resolved from each other in the present data, a weighted average of their measured positions based on their observed height [Brunt et al. 1977c] was used. The metastable data (figure 6.2) were also compared to the data of Buckman et al. [1983b] to check the energy calibration.

The onset of the combined VUV data was determined to be 16.59 eV by observing the variation of the standard deviation of successively added data points (see section 5.2). This leads to an estimate of 80 meV for the resolution of the electron beam. Also, the onset of the $np^4 3s[1/2]_1$ state is evident in figure 6.4 where there is a change in slope at 16.68 eV, 80 meV below its spectroscopic location. This resolution estimate is consistent with the energy resolution predictions at the end of section 4.3.2 and with the poorer energy resolution determined for the other data (He, Ar, Kr and Xe) since the analyzing energy was set to a lower value of 3 eV and the hemisphere potentials were adjusted to the theoretically predicted values (equation 4.12; see section 4.3.3)

6.2.2 Results and Discussion

The polarization curve resulting from the VUV data shown in figure 6.1 and 6.3 is presented in figure 6.5. The data points below the threshold have been set to zero for sake of clarity. In a separate measurement, the polarization was determined at 40 eV and a value of 1.9 was calculated for $1/\eta$ from a comparison with Karras’s [1988] value. Confidence in this result is given by the overall good agreement of the present data with the other polarization measurements shown in figure 6.5.

The polarization function (figure 6.5) clearly shows that resonances and cascading from higher lying states are perturbing the excitation of neon. Near threshold, where
cascade from higher excited states is not a factor, it can be seen that the \( b \) resonances, observed in both the VUV and metastable spectra are having a perturbing effect. This is in contrast to helium where the polarization was smoothly varying and no resonances were observed in the threshold region.

Following the polarization toward lower energy from the \( b \) resonance it is observed that it falls off rapidly toward a large negative value indicating that the exchange process is dominating at threshold (see equation 2.6). This result is not unexpected since the lower state, \( np^3 3s[3/2] \), is predominantly \( ^3P \) in character and therefore requires exchange for excitation. Within the first 0.5 eV, the polarization quickly increases to a peak value of \( \sim 0.13 \) and then drops down to -0.15. The dominating presence of the \( b \) resonance clearly causes the rapid change in polarization. This assertion is supported by the polarization calculations presented in section 3.3.2 (see Table 3.3 and 3.4) which show the polarization that would have been measured if the excitation of the \( b \) resonance was dominating. The possible \( b \) states are \( ^2P_{3/2} \), \( ^3P[3/2]_{3/2} \), \( ^2P_{5/2} \), \( ^3P[3/2]_{5/2} \), \( ^2P[5/2]_{3/2} \), \( ^2P[3/2]_{5/2} \), \( ^2P[5/2]_{5/2} \) which have predicted polarization of 0.558, 0.500, 0.447, 0.500 and 0.500 respectively. The fact that the observed peak polarization is \( \sim 0.13 \) rather than \( \sim 0.5 \) as predicted can be explained by 1) the energy resolution of the beam and/or 2) the presence to several resonance states. If the energy resolution was poor enough to significantly convolute the resonance signal with the signal of the direct excitation then a decrease in polarization would be observed since the polarization of the direct excitation has been shown to be negative in this region. Earlier measurements with a poorer energy resolution have shown the peak polarization to have a value closer to 0 and therefore an even better energy resolved electron beam may bring the peak value closer to the predicted values. There could also be several resonances present of which some have polarizations of zero or negative values (see Table 3.3 and 3.4) and therefore the averaged polarization would be less than the predicted values above. Note that an accurate calculation of the combined polarization of these resonances would require determining the interference effects between the different scattering amplitudes (c.f. section 3.3.4)
Figure 6.3 Excitation functions for neon corrected for polarization sensitivity of the analyzer.
Figure 6.5 Polarization function for neon
The $b$ resonance located at 16.95 eV has an estimated FWHM of 180 meV \cite{brunt1977} and with an electron beam resolution of 80 meV, it is clear that the effects of the $b$ resonance can extend near the threshold of np$^5$ 3s[$3/2$], state and therefore cause the rapid rise observed just after threshold.

The np$^5$ 3s[$1/2$], state, which lies 177 meV above threshold, is predominantly $^1$P in nature and thus excited by direct excitation which has a threshold polarization value of +1 (c.f. helium). Since the present experiment cannot discriminate against VUV radiation emitted from this state, any contribution to the polarization from its decay would be expected to bias its value toward +1. Since the observed polarization drops back to negative values as the impact energy increases past the region where the $b$ resonance influences the data, this is an indication that the $^3$P component of the admixture is still dominating the excitation mechanism at energies between 17 and 18 eV.

After the $b$ resonance, the polarization decreases to a value of -0.15 at 17.25 eV and remains relatively flat up to 17.5 eV. At this point the polarization starts to rise again. To see the changes in the perpendicular and parallel channels more clearly, a straight line was determined from the corrected data over the energy range of 17.5 to 17.86 eV for each spectrum (see figure 6.3) and was subtracted from the respective data sets (see figure 6.6).

Measurements by Phelps et al. \cite{phelps1983} on the excitation cross-sections for the np$^5$3s[$1/2$], and the np$^5$3s[$3/2$], states at 18.2 eV show that the np$^5$3s[$1/2$], level is responsible for 81% of the total signal and therefore one could expect that resonances based on this state ($j_c = 1/2$) should dominate (Table 3.3). From Table 3.3 it can be seen that the polarization of the $c$, $d$ and $e$ resonances are predominately 0 indicating that the resonance structure should enhance both the perpendicular and parallel channel equally. In the perpendicular channel a broad dip is evident in the neighbourhood of the $c$ resonance (18.3 eV) which is not observed in the parallel channel suggesting that this decays predominantly into the parallel channel. This behaviour is not expected from resonances with a $j_c = 1/2$ ion core but could be expected from the calculations for resonances based on a $j_c = 3/2$ (Table 3.4). Thus it appears that either resonances based on the $j_c = 3/2$ ion core are significant even though excitation to the corresponding neutral state is diminished.
Counts (arb. units)

Figure 6.6  Perpendicular and Parallel Excitation Functions with a linear function subtracted
or else the interference effects which have been considered negligible as a first approximation are in fact significant. Clearly it would be beneficial to have more detailed calculations performed. Note that the dip around 18.3 eV was also observed in the metastable channel and was designated a Wigner downstep by Buckman et al. [1983b].

Following the broad minimum a strong peak is observed in the perpendicular channel, most likely due to the effects of the \( e \) and/or \( d \) resonances in this region. We note from Table 3.3 and 3.4 that \( e \) resonances should greatly enhance the perpendicular channel leading to a dip in the observed polarization as is in fact observed. Because of the significance of the effect and the dominance of the \( j_e = 1/2 \) ion core noted above, one might infer that the predominant resonance is the \( \text{^2P}_{{1/2}} \text{^3P}[1/2]_{{3/2}} \) with a predicted polarization of -0.428. Here the incoming and outgoing partial waves are \( d \)-wave and \( p \)-wave respectively. However there are resonances with a \( j_e = 3/2 \) ion core which also could cause the above effect (Table 3.4).

### Table 6.1 Energies and widths of features for neon (figures 6.1-6.7)

<table>
<thead>
<tr>
<th>Feature</th>
<th>Classification</th>
<th>Energy (eV)</th>
<th>Width (meV)</th>
<th>Source</th>
</tr>
</thead>
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<td>( 2p^2(\text{^2P}_{{3/2}})3s[3/2]_1 )</td>
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<td>1</td>
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<tr>
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<td>1</td>
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<td>1</td>
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<td>b₁</td>
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<td></td>
<td>2</td>
</tr>
<tr>
<td>e</td>
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<td>18.464</td>
<td></td>
<td>3</td>
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<td>f₂</td>
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<td>19.778</td>
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<td>3</td>
</tr>
</tbody>
</table>

1) Moore (NBS Atomic Energy Levels, 1949)
2) Brunt et al. (1977c)
3) Buckman et al. (1983b)

96
In the parallel channel a broad feature is observed with an onset occurring at 18.16 eV. This is probably due to the combined effect of the \( c \) and \( d \) resonance both of which should preferentially enhance the parallel channel (Table 3.4) if the \( j_c = 3/2 \) core resonances are strong. This observation is supported by the argon data (see section 6.3) which again shows the \( c \) resonance having a strong effect. It has been suggested [Brunt et al., 1977c] that unresolved \( e \) resonances are present based on the observation that the \( d_1 \) to \( d_2 \) ratio is not the predicted 2:1 value. As noted in section 3.2 the \( e \) resonances with \( ^3P \) character are expected to form an unresolved bump in the region of the \( d \) resonances and could explain this feature. The \( d \) resonances could also contribute to this feature but their presence cannot be clearly identified (see below). A higher resolution study would be beneficial since it would help determine if this feature consists of the two \( d \) resonances or if it is a single resonance, presumably an \( e \) resonance.

Finally between 19.45 and 20 eV another broad feature is observed in the parallel channel. In this region there are four resonances (\( n_1, n_2, f_1 \) and \( f_2 \)) which were observed in the metastable spectrum [Buckman et al., 1983b] and four excited states (4s(\( j=2,1 \)) and 4s'(\( j=0,1 \))). We note that both \( f \) and \( n \) (also a \(^1S\) state) resonances based on the \( j=3/2 \) core are expected to enhance the polarization and hence the parallel channel (see Table 3.4).

The effects of the above resonances on the polarization can plainly be seen in figure 6.5. After the \( b \) resonance, the polarization curve falls to a minimum of -0.15 and then begins to rise toward zero over the energy range 17.5-18.15. The onset of the broad resonance at 18.16 eV in the parallel channel causes the polarization function to rise to a maximum of 0.2. The strong enhancement of the perpendicular channel appears as a dip superimposed on the broad resonance from the parallel channel (this effect is also seen in argon) and therefore it seems unlikely that the \( d \) resonances are enhancing the parallel channel. The polarization resulting from the \( d \) resonances decaying directly to the \( 2p^53s \) state are given in Table 3.3 and 3.4 but Sharpton et al. [1970] observed a sharp peak at 18.6 eV in the excitation function of the lowest lying \( 2p^53p \) (\( J=1 \)) state (\( 2p_{10} \) in Paschen notation) which was attributed to the negative ion resonances and therefore it appears that the \( d \) resonances are instead decaying through the \( 2p_{10} \) state to the \( 2p^53s \) state. After the
$d_2$ resonance, the polarization curve returns to its background value of 0.2 followed by a drop to a value of 0.1 as the electron energy is further increased. This could well be due to the depolarizing effect of the cascade feeding the $3s$ levels from the $3p$ states which are known to be strongly excited in this region. As mentioned earlier in the discussion of $I_n$, there are indications of resonance perturbations of the polarization near 19.5 eV due probably mainly to $f$ resonances. The polarization then slowly rises to a value of 0.2 at 20.66 eV.

The observed polarization function agrees well with previous measurements by Karras [1988] and Uhrig et al. [1994a]. The only discrepancy is at threshold where Karras observes a value of 0.065, Uhrig et al. observe the polarization rise toward +1 as the electron impact energy decreases (suggesting that direct excitation is predominant) and the present results show the polarization drop towards -1 as the impact energy decreases very close to threshold. The value obtained by Karras is consistent with the present results since his energy resolution (500 meV) would not permit the observation of the rapid decrease in polarization (a drop from 0 to -1 in 80 meV). Uhrig’s sharp increase in polarization starts 300 meV above threshold and therefore Karras should have observed a larger polarization value than he measured at threshold if this effect was real.

As observed above, the exchange excitation mechanism is dominant at threshold but at higher energies direct excitation is expected to dominate. It is of interest to determine how the exchange excitation varies with respect to the direct excitation as a function of energy. To do this we start with the following definitions for the cross-section

$$
\sigma^e = \frac{2}{3} (l_n^e + 2l_n^e) = \frac{1}{3} (3 - P^e)(l_n^e + l_n^e)
$$

$$
\sigma^d = \frac{1}{3} (3 - P^d)(l_n^d + l_n^d)
$$

where the superscripts $e$ and $d$ refer to exchange and direct respectively. The measured polarization ($P^m$) can be written as

$$
P^m = \frac{(l_n^e + l_n^e) - (l_n^e + I_n^e)}{(l_n^e + I_n^e) + (l_n^d + I_n^d)}
$$

$$
= \frac{P^d(l_n^e + I_n^e) + P^e(l_n^e + I_n^e)}{(l_n^e + I_n^e) + (l_n^d + I_n^d)}
$$

(6.19)
and substituting equation 6.18 results in

\[
p^m = \frac{P^d (3\sigma^d)(3 - P^d)^{-1} + P^e (3\sigma^e)(3 - P^e)^{-1}}{(3\sigma^d)(3 - P^d)^{-1} + (3\sigma^e)(3 - P^e)^{-1}} \tag{6.20}
\]

Rearranging terms yields

\[
\frac{\sigma^e}{\sigma^d} = \frac{3 - p^e}{3 - p^d} \left( \frac{p^d - p^m}{p^m - p^e} \right) \tag{6.21}
\]

Using the relation \( \sigma = \sigma^e + \sigma^d \) results in

\[
\frac{\sigma^d}{\sigma} = \frac{1}{(3 - p^e) (3 - p^d)} + 1 \tag{6.22}
\]

To proceed further the following assumptions are made:

1) \( P^e = -P^d \). This seems reasonable because, neglecting resonances and other perturbing effects, \( P^d \) is known (e.g. helium) to fall from +1 at threshold to smaller positive values as the energy is increased whereas \( P^e \) is known to be -1 at threshold (e.g. mercury) and presumably also falling toward zero as \( E \) increases.

2) The polarization of the “directly” excited components was assumed to follow that of He(\(^1\)P\(_1\)) excitation measured in chapter 5. Note that because the first eV above threshold is resonance and cascade free, it therefore provides a true “direct” polarization function. To determine the shape of the direct polarization function after the first eV, we must consider how it would look in the absence of cascade which always leads to a depolarizing effect and thus the data of Steph and Golden (1982), whose coincidence measurements are cascade-free, are taken and a cubic spline technique was used to fit the near threshold data (chapter 5) to theirs at 25.5 eV. The energy scale of the helium data was shifted so that the onset coincided with that of neon and the resultant curve is shown in figure 6.7a.
Figure 6.7  a) Direct excitation polarization curve determined from helium data,  
b) Exchange excitation polarization curve determined from the neon data and  
c) Direct and exchange excitation functions relative to the total excitation function
3) The measured polarization ($P_m$) is determined from the parts of the neon polarization data which are considered free from resonances and assuming a threshold value of -1. Note that no attempt has been made to correct for cascade but considerable weight is put on the region between 17 and 18 eV which is free of resonances and lies below the threshold for cascade.

In order to apply equations 6.21 and 6.22 to obtain the relative contributions of the direct and exchange excitation, the measured polarization ($P_m$) must be determined. This was done by picking data points in resonance free regions and performing a polynomial fit. Figure 6.7b shows the measured data with the polynomial line running from threshold ($P=-1$) through the 17-18 eV region and then to higher energies. Note that the resonance effects just above threshold have been neglected.

With the assumptions noted above the ratios $\sigma^d/\sigma$ and $\sigma^e/\sigma$ have been calculated and are plotted in figure 6.7c. As noted above the effect of cascade on the measured polarization has not been accounted for and would start becoming significant around 18 eV where a "knee" shape is observed in the relative cross-sections (figure 6.7c). It can be seen that the exchange mechanism (3P excitation) dominates only in the first 1 eV and then the direct mechanism (1P excitation) quickly becomes the predominant mode of excitation. As far as the excitation of the VUV emitting states is concerned, the excitation of the $np^5 3s[1/2]_i$ should quickly rise from zero to dominate the excitation process since it is predominantly $1P$ in character (see section 3.1) while the excitation of the $np^5 3s[3/2]_i$ state should rapidly decrease above threshold. This behavior is supported by the excitation measurements Phelps et al. [1983] and Phillips et al. [1985] (collectively referred to as the "Wisconsin Group"). Their measurements involved exciting the neon atom by electron impact and then probing the excited states using a laser. Phelps et al. [1983] used 18.2 eV electrons to excite neon so that they would not have to correct for cascade and from their data the ratio of the apparent excitation cross-section of the $np^5 3s[1/2]_i$ (i.e. $1P$) state to the total apparent excitation cross-section ($np^5 3s[1/2]_i + np^5 3s[3/2]_i$) is 0.81. Phillips et al. [1985] performed measurements at 40 eV and above.
which required corrections for cascade from the higher lying states. Using the measurements of Sharpton et al. [1970] to correct for cascade they obtained at ratio of \( \sim 0.92 \) for the energy range 40-300 eV. Our prediction, from figure 5.7c, is that at 18 eV about 30% of the excitation of the \( J=1 \) states is direct and about 70% is via exchange.

Given the uncertainties in our procedure the agreement with the Wisconsin Group is acceptable. It is not possible to make more detailed comparisons between our measurements and those of the Wisconsin Group because of a number of factors. In our case we have measured the integrated emission from the two \( J=1 \) states whereas they considered the two states separately. The Phelps et al. data were taken at 18.2 ± 0.5 eV where cross-sections are changing rapidly and thus the accuracy of the energy calibration becomes an important factor. Their work also involved the use of relatively high target pressures where radiation trapping was complete and where, presumably, considerable collisional transfer effects must be occurring. We worked at very low pressures to insure that no radiation trapping occurred.

Hanme et al. [1981] have the polarization of the \( 6^3P_1-6^1S_0 \) resonance line in coincidence with a forward scattered electron for mercury. The \( 6^3P_1 \) state is not a pure state but contains an \( 6^3P_1 \) admixture (17.1%) which is similar to neon and argon. Because the forward scattered electron is measured, the selection rule \( \Delta M_L=0 \) is in effect. Using equation 2.6 one can immediately see that for \( M_J = \pm 1 \) to be excited exchange \( (\Delta M_S = \pm 1) \) must occur and therefore a measurement of the polarization will determine whether exchange or direct excitation is occurring. Their results show that at threshold exchange excitation is dominating (i.e. the polarization is approaching the theoretical limit for pure exchange at threshold) and quickly rises over 2-3 eV above threshold toward the polarization limit for direct excitation. This result is in agreement with the present measurement that exchange excitation is dominant in the near threshold region. Theoretical calculations by McConnell and Moiseiwitsch [1968] (electrons scattered in all directions) and Bonham [1982] (electrons scattered in forward direction) also show this trend.
6.3 Argon

6.3.1 Data Collection and Calibration

The data collected for the VUV photons and the metastables are presented in figures 6.8 and 6.9. The data has had a linear background subtracted from it but variations in the electron beam current and the sensitivity of the polarizer have not been corrected for. The data presented represents 265 hours of accumulation at a maximum count rate of 35 Hz for the VUV photons and an accumulation time of 10.5 hours at a maximum rate of 130 Hz for the metastables. The head pressure and the chamber pressure were .092 and $1.15 \times 10^{-6}$ torr respectively.

The polarization sensitivity of the VUV photon analyzer was corrected for in the VUV data and the results are presented in figure 6.10. As in the neon data the resonant structures are enhanced, in particular the $c$ and $d$ resonances in the perpendicular channel and the $e$ resonance in the parallel channel.

The total photon emission spectrum ($I_\perp + I_\parallel$) is shown in figure 6.11 and it can be seen that the resonant features are not well defined. As noted above, the corrected perpendicular and parallel data have better defined resonant features and therefore calibration of the VUV data will be done with these data sets.

As in the case of neon, the $b$-resonances at the threshold and the $d$-resonances are dominant features in the energy spectrum and provide the best points for calibration. The metastable data (figure 6.9) were also compared to the data of Buckman et al. [1983b] where many features are observed. The $p$ resonance has been classified as a "nonvalence" resonance formed by the incident electron being captured in the polarization potential associated with the neutral state $3p^5(^2P_{3/2})4p$ ($J = 0$) (which lies 5 meV above $p$). The $d_1$ and $d_2$ resonances are nearly resolved which gives the best evidence for the energy resolution of the electron beam. The $d$ resonances are separated by 160 meV and therefore the FWHM of the electron beam is expected to be of the same magnitude. The approximately 2:1 height ratio of $d_1:d_2$ is also evident in the present data, indicating that the two peaks are being resolved, and therefore the actual value for $d_1$ is used to calibrate the spectrum. The resolution of the electron beam was estimated by convoluting Buckman
Figure 6.8 VUV excitation functions for argon with background subtracted. The statistical errors are less than or equal to the size of the symbols.
Figure 6.9 Metastable excitation function for argon
Figure 6.10 VUV excitation functions corrected for the polarization sensitivity of the analyzer.
Figure 6.11 Total VUV photon emission spectrum for argon.
et al.'s [1983b] metastable data with various Gaussian functions. A comparison of the convoluted spectrum with the present measured one results in a beam with an energy resolution of 160 meV (FWHM) providing the best fit. The measured onset of the metastable channel is located 160 meV below the accepted value of 11.548 eV which supports the estimate made from the $d$ resonances.

6.3.2 Results and Discussion

The polarization function resulting from the VUV data shown in figure 6.8 is presented in figure 6.12. The data points below the threshold have been set to zero for sake of clarity. The polarization curve was calibrated to Karras's data point at 16 eV since this is a linear region in the polarization function and value of 2.09 was determined for $1/\eta$. The data of Karras [1988] and Dassen et al. [1977] are also presented for comparison. Note that Dassen et al. used an LiF filter to suppress the 104.7 nm line and therefore their data reflects the polarization of the 106.8 nm line only. Karras performed measurements with and without an LiF filter.

From the corrected VUV data (figure 6.10), the effects of the negative ion resonances on each channel is very clear. In the perpendicular channel, the $b$, $c$ and $d$ resonances are prominent while in the parallel channel the $e_1$ resonance observed by Brunt et al. [1977c] is evident as well as a broad feature at 14.15 eV. Note that in the total emission spectra, figure 6.11, the $c$ resonance is not clearly observable as was the case in Brunt et al.'s [1977c] measurement.

The polarization function reflects the predominance of the resonances in one channel or the other. Near threshold, the presence of the $b$ resonances make it difficult to determine the trend of the polarization with the present energy resolution but it appears to be going toward negative values. Since the $^{3}\Pi$ character is dominant (see Table 6.1) the exchange mechanism is expected to dominate as it did in neon and therefore the polarization should tend toward $-1$. However the polarization is clearly strongly perturbed by the existence of the $b$ resonances (Table 6.2). For example, the $b_1$ resonance is observed in the metastable channel at 11.631 meV, just 8 meV above the threshold of the
Figure 6.12  Polarization function for argon
Table 6.2 Energies and widths of features for argon (figures 6.8-6.12)

<table>
<thead>
<tr>
<th>Feature</th>
<th>Classification</th>
<th>Energy (eV)</th>
<th>Width (meV)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁</td>
<td>3p⁺(^3P^o)4s[^3/2]</td>
<td>11.548</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B₂</td>
<td>3p⁺(^3P^o)4s[^3/2]</td>
<td>11.624</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>b₁</td>
<td>3p⁺(^3P^o)4s[^3/2]</td>
<td>11.631</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>b₂</td>
<td>3p⁺(^3P^o)4s[^3/2]</td>
<td>11.675</td>
<td>75</td>
<td>2</td>
</tr>
<tr>
<td>B₃</td>
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<td>11.723</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>b₃</td>
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<td>11.785</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>B₄</td>
<td>3p⁺(^3P^o)4s[^1/2]₀</td>
<td>11.828</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>b₄</td>
<td>4p⁺(^3P^o)4s[^3]ₗ</td>
<td>11.845</td>
<td>70</td>
<td>2</td>
</tr>
<tr>
<td>c₁</td>
<td>3p⁺(^3P^o)4s[^3]ₗ</td>
<td>12.7</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>c₁</td>
<td>3p⁺(^3P^o)4s[^3]ₗ</td>
<td>12.926</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>e</td>
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<td>3</td>
<td>3</td>
</tr>
<tr>
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<td>3p⁺(^3P^o)4s[^3]ₗ</td>
<td>12.99</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>d₁</td>
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<td>2</td>
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<tr>
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<td>2</td>
</tr>
<tr>
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<td>13.190</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
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<td>13.204</td>
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<td>2</td>
</tr>
<tr>
<td>n₁</td>
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<td>2</td>
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<tr>
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<td>13.864</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
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<td>14.006</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>f₁</td>
<td>3p⁺(^3P^o)4s[^3]ₗ</td>
<td>14.054</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>f₂</td>
<td>3p⁺(^3P^o)4s[^3]ₗ</td>
<td>14.209</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

* not shown in figures 6.8-6.12
1) Moore (NBS Atomic Energy Levels, 1949)
2) Brunt et al. (1977c)
3) Bucknian et al. (1983b)

first VUV emitting state with the b₂ resonance 44 meV higher in energy. Ohja et al. [1982] have calculated excitation cross-sections for argon assuming an LS configuration and their results show that the b resonances perturb the excitation of the 4p²4s^3P^o state.

Before the onset of the second VUV emitting state the polarization begins to rise sharply toward the value of 0.30. Since the cross-section of the 2P₃/₂ 4s[^3/2] state should be significantly larger than 2P₁/₂ 4s[^1/2] in this region, the effect of the 2P₁/₂ 4s[^1/2] state on the polarization should be minimal unless it is strongly polarized near threshold. In support of this are the measurements of Karras [1988] who has measured VUV polarization with and without an LiF filter and has found that each data set showed a different trend at threshold. The LiF filter suppresses the 104.8 nm line and therefore only
the 106.7 nm line is observed. His LiF data shows the polarization dropping to 0 which is consistent with the present data since the threshold only contains the 106.7 nm line. The polarization data collected without the LiF filter is seen to rise to 0.146 which could be attributed to the presence of the 104.8 nm line emanating from the $^2P_{1/2}4s[1/2]$ state (predominantly $^1P$ in character) and therefore having a +1 threshold value (from threshold angular momentum arguments). This would suggest that the excitation of the $^2P_{1/2}4s[1/2]$ state is significant near threshold. However, Ajello et al. (1990) show that at 12 eV, direct excitation to the $^2P_{3/2}4s[3/2]$ state is 74% of the total VUV emission. The deviation of the polarization function in the non-resonant region after threshold from that observed in neon may be a result of the its larger deviation from an LS coupling scheme. Dassen et al.'s measurements using an LiF filter are in agreement with the measurements of Karras [1988].

In the region between 12.0 and 12.5 eV, where the polarization should be unaffected by resonance excitation, it is noted that the polarization is significantly positive. This is in contrast to the situation in neon where negative polarization values were observed at energies above the threshold resonance region. One might conclude that the exchange excitation is not as significant in argon as in neon or at least that the exchange mechanism drops off more rapidly than in the case of neon.

After the maximum observed at 12.2 eV the polarization then experiences the effects of the $c$ resonance and drops to 0. The width of the $c$ resonance has not been determined experimentally but it can be seen to be very broad in the metastable data as well as in the corrected perpendicular data. This drop to 0 is supported by the present calculations shown in tables 3.3 and 3.4. Note that the designation of the $c$ resonance is not agreed upon. The grandparent model predicts these should be $^1P$ resonances but the theoretical calculations of Ojha et al. [1982] indicate that this resonance should be a $^1D$ configuration. Buckman and Clark [1994] suggest that this state may in fact be a mixture of both. The present data, based on table 3.4, suggests that some $^1D$ admixture is possible due to the fact that this resonance could enhance the perpendicular channel as observed.

The analysis of the polarization function becomes more difficult after the center of the $c$ resonance because of the overlap of numerous resonances. Note that the overlap of
the c resonance with the e and d resonances is not due to lack of experimental resolution but results from the natural widths of the resonances. After the center of the c resonance the e resonance appears and causes the polarization function to rise sharply. A maximum value of 0.25 is reached, followed by a drop to 0 which can be explained by the presence of the d resonances which are located here. After the d2 resonance the polarization rises to a maximum value of 0.20 and then falls to a value of 0.05. This shape in the polarization curve was also observed in neon where the d resonances appeared as a dip in the midst of a broader “bump” and therefore this broad “bump” may be due to e resonances of \(^3\text{P}\) character. Alternatively, the positive excursion of the polarization at energies higher than the d resonances may reflect the fact that the so called “singlet” transition is beginning to dominate the excitation process. In support of this is the fact that the polarization data taken with an LiF filter (triplet line only) lies lower on average than the integrated data (see figure 5.12). The influence of cascade from the 4p levels in this region should not be overlooked also.

The polarization function shows a slight bump centered at 14.15 eV which lies within the range of the \(n_1, n_2, f_1\) and \(f_2\) resonances as well as the 3d and 5s excited states. Table 3.4 indicates that the \(f_1\) resonance should lead to positive polarization values as seems to be observed. The small perturbation to the polarization may reflect the fact that the resonance structure is relatively small compared to the background. From 14.4 to 16 eV the polarization has a slight linear increase. It is interesting to note that by 15 eV, it is estimated from data presented by Ajello et al. [1990] that cascade to both \(3p^4s, 4s'\) (J=1) VUV emitting states represent more than half of the signal. Measurements by Ballou et al. [1973] on the cascading states did not observe the emissions to be significantly polarized. However, it is difficult to estimate the effect of cascade because no measurements of polarization have been reported for the cascading features.
6.4 Krypton

6.4.1 Data Collection and Calibration

The data collected for the VUV photons are presented in figure 6.13. Metastable data was not collected due to the metastable detector malfunctioning. The data has had a linear background subtracted from it but variations in the electron beam current and the sensitivity of the polarizer have not been corrected for. The data represents approximately 100 hours of acquisition time at a maximum count rate of 23 Hz. The head pressure and chamber pressure were 1.3 and 1.7x10^6 torr respectively.

The calibration of the VUV data was done by comparing the position of the prominent feature $a_2$ of the total emission spectrum $I_{\parallel} + I_{\perp}$ (figure 6.14) with that measured by Brunt et al. [1977c]. The onset of the VUV data was determined to be 160 meV below the threshold of the $^2\!P_{3/2}^o 5s[3/2]_1$ by noting the change in the standard deviation of successively added data. The FWHM of the $a_2$ resonance was estimated to be 160 meV in the present data which yields an energy resolution of 155 meV, since the FWHM measured by Brunt et al. [1977c] is 42 meV. This energy resolution is consistent with the threshold data.

The polarization sensitivity of the polarizer was corrected for using a value of 1.542 for $1/\eta$ and the results are shown in figure 6.15. The polarization fractions are presented in figure 6.16 where the data points below the threshold have been set to zero for clarity. The polarization curve was calibrated to Karras's data at 14 eV resulting in the value of $\eta$ shown above. Also presented with the present polarization data are the results of Karras [1988], Uhrig et al. [1994] and Al-Shamma and Kleinpoppen [1978].

6.4.2 Results and Discussion

Krypton has a large spin-orbit splitting (666 meV) which results in the negative ion resonance pairs being well separated. Also, $jj$ coupling becomes more appropriate in describing the excited states of the noble gases as the mass increases. Thus krypton presents an opportunity to evaluate the effectiveness of the coupling schemes used to describe the various excited states. Another feature of krypton is the nearly equal
Figure 6.13 VUV excitation functions for krypton with background subtracted
Figure 6.14 Total VUV photon emission spectrum for krypton
Figure 6.15  VUV excitation functions corrected for the polarization sensitivity of the analyzer
Figure 6.16 Polarization function for krypton.
contributions of $^3P$ and $^1P$ to both $4p^5s(J=1)$ VUV emitting levels and therefore the overall configuration cannot be approximated by singlet or triplet states like neon and argon. Finally, the nuclear spin of the isotopes are not all 0 as with helium, neon and argon so the threshold polarization will be altered. Since naturally occurring krypton gas contains 11.5% Kr$^{83}$, which has nuclear spin 9/2, the threshold polarization for direct excitation becomes 0.937 while for exchange excitation the threshold polarization is -0.882.

The VUV spectrum shows the presence of an $a_2$ resonance which lies 86 meV above the $^2P_{3/2},5s[3/2]$, threshold. In argon and neon this structure lay below the $3p^44s$ and $2p^33s$ states respectively and was therefore not observed in either the VUV or metastable spectrum. The $a_2$ resonance dominates the spectrum near threshold which is quite surprising since the decay of this state to the $^2P_{3/2},5s[3/2]$, state requires a change in the ion core angular momentum. Decay of the $a_2$ resonance to the metastable state is also observed [Buckman et al., 1983b] but it has a significantly reduced signal. Note that in the present data the center of the resonance is not the same in both channels but differ by 20 meV, the parallel channel being lower. This may be a result of the presence of an unresolved $b$ resonance which was observed in the metastable spectrum at 10.039 eV (6 meV above the $^2P_{3/2},5s[3/2]$, threshold) and has a FWHM of 130 meV.

At energies higher than the $a_2$ resonance, the spectrum does not have the prominent features observed in neon and argon. This is due to the resonances being small and narrow [see data of Brunt et al., 1977c] and the resolution of the electron beam of the present experiment being relatively large. The corrected parallel data does show the presence of the broad $c_2$ resonance and the $d_1$ and $d_2$ resonances appear as dips as was the case with argon.

While the integrated VUV data does not show well defined resonant structure, apart from the threshold $a_2$ resonance, the polarization function (figure 6.16) clearly indicates their presence. At threshold it can be seen that the polarization curve is tending toward -1 indicating that exchange is taking place. The polarization quickly rises to a value of 0.08 and then falls to -0.38. Note that the position of the resonance does not line up with the center of the dip in polarization which reflects the non-alignment of the
Table 6.3 Energies and widths of features for krypton (figures 6.13-6.16)

<table>
<thead>
<tr>
<th>Feature</th>
<th>Classification</th>
<th>Energy (eV)</th>
<th>Width (meV)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁</td>
<td>4p²(P₃/₂)5s[3/2]</td>
<td>9.915</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>B₂</td>
<td>4p²(P₃/₂)5s[3/2]</td>
<td>10.033</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>b₁</td>
<td>4p²(P₃/₂)5s5p²(P₃)</td>
<td>10.039</td>
<td>130</td>
<td>3</td>
</tr>
<tr>
<td>a₂</td>
<td>4p²(P₃/₁)5s²(S)</td>
<td>10.128</td>
<td>42</td>
<td>2</td>
</tr>
<tr>
<td>B₃</td>
<td>4p²(P₃/₁)5s¹(1/₂)</td>
<td>10.563</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>b₂</td>
<td>4p²(P₃/₁)5s5p²(P₃)</td>
<td>10.60</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>B₄</td>
<td>4p²(P₃/₁)5s¹(1/₂)</td>
<td>10.644</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>b₃</td>
<td>4p²(P₃/₁)5s5p²(P₃)</td>
<td>10.671</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>c₁</td>
<td>4p²(P₃/₂)5s5p²(P₃)</td>
<td>11.12</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>c₁</td>
<td>4p²(P₃/₂)5s5p²(D)</td>
<td>11.276</td>
<td>21</td>
<td>2</td>
</tr>
<tr>
<td>c₂</td>
<td>4p²(P₃/₂)5s5p²(D)</td>
<td>11.310</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>d₁</td>
<td>4p²(P₃/₁)5p²(S)</td>
<td>11.397</td>
<td>55</td>
<td>2</td>
</tr>
<tr>
<td>c</td>
<td>4p²(P₃/₂)5p²(D)</td>
<td>11.49</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>c₂</td>
<td>4p²(P₃/₁)5s5p²(P₃)</td>
<td>11.7</td>
<td>400</td>
<td>2</td>
</tr>
<tr>
<td>c</td>
<td>4p²(P₃/₂)5p²(D)</td>
<td>11.996</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>d₂</td>
<td>4p²(P₃/₁)5p²(S)</td>
<td>12.034</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>c</td>
<td>4p²(P₃/₂)5p²(D)</td>
<td>12.137</td>
<td>80</td>
<td>2</td>
</tr>
<tr>
<td>p</td>
<td>4p²(P₃/₁)5p₁₀+c₁</td>
<td>12.262</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>f₁</td>
<td>4p²(P₃/₂)6s²(S)</td>
<td>12.378</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

* not shown in figures 6.13-6.16

1) Moore (NBS Atomic Energy Levels, 1949)
2) Brunt et al. (1977c)
3) Buckman et al. (1983b)

centers of the peaks observed in the parallel and perpendicular channels (figure 6.15). This may be partly due to the different background contributions to the two channels in this energy region. The quick rise to 0.08 at threshold is consistent with polarizations measured for the b resonances in neon. It appears as if the two resonances are competing for dominance in this region very close to threshold.

After reaching a minimum at 10.2 eV, the polarization function rises to a maximum value of 0.25 at 10.6 eV where the b₃ resonance and the ²P₁/₂,5s[1/2]₁ state are located. Since the direct excitation of the ²P₁/₂,5s[1/2]₁ state is not expected to contribute significantly near threshold, the rise in polarization is likely due to the b₃ resonance. After the b₃ resonance the polarization falls to ~0 at 11 eV which is in the vicinity of the c₁ resonance. The polarization remains level until the location of the d₁ resonance where it drops below 0. The effect of the e₁ and e₂ resonances is not clear due to the statistical
scatter in the data. The polarization rises to a value of 0.10 after the $d_1$ resonance and then declines to 0 under the successive influences of the $e_2$ and $d_2$ resonances. After the $d_2$ resonance, the polarization curve exhibits a broad bump in the location of the 6s levels and the $f_1$ resonance. This is very similar to the behaviour found with argon.

The measurements of Karras [1988] and Uhrig et al. [1994] agree with the present data. The same cannot be said for the data of Al-Shamma and Kleinpopen whose data are significantly lower in value. However, these authors now believe their data to be in error [Kleinpopen, 1994].

6.5 Xenon

The VUV spectrum of xenon was measured with and without a BaF$_2$ filter. The BaF$_2$ filter has a cut-off (which is temperature dependent) which lies between the 129.6 nm line ($\left( ^3\!P_{1/2}\right)6s[1/2]_1$) and the 147.0 nm line ($\left( ^3\!P_{3/2}\right)6s[3/2]_1$). The transmission of the 147.0 nm line fortunately increases with temperature (allowing the chamber to be heated for maximum current production (see section 3.2)) and is roughly 20% [Samson, 1967, pp.182].

6.5.1.1 Data Collected with BaF$_2$ filter.

The VUV spectrum measured with the BaF$_2$ filter is shown in figure 6.17. Metastable data were not obtained due to the detector malfunctioning. Background subtraction was performed on the data set but variations in electron current with beam energy and in polarization sensitivity with time of the photon analyzer were not corrected for. The accumulation time was 400 hours at a maximum count rate of 4 Hz. with the head and chamber pressure at 0.137 and $2.1\times10^4$ torr respectively.

The polarization sensitivity of the photon analyzer was accounted for by comparing the polarization data in the region before the onset of the $^2\!P_{1/2}\,6s[1/2]_1$ state with data in the same region measured without the BaF$_2$ filter (see section 6.5.2). This was done since polarization measurements of only the $^2\!P_{3/2}\,6s[3/2]_1$ state have not been performed to the author's knowledge. It was found that $1/\eta$ equal to 1.505 (the same value as the case without the BaF$_2$ filter) produced the same polarization curve (see figure 120.)

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Figure 6.17 VUV excitation functions for Xenon (using BaF₂ window) with background subtracted
6.25) in this energy range. The fact that 1/\eta was the same for both xenon data sets demonstrates the reproducibility of the system.

The corrected perpendicular and parallel data are presented in figure 6.18 and The energy calibration of xenon was performed by comparing the position of the c1 resonance in the corrected perpendicular spectrum with the position observed by Buckman et al. [1983b]. This point was chosen since the feature is very prominent in the spectrum. Note the very good agreement in position for the n1 resonance, as compared with the Buckman et al. [1983b] data, highlighting the accuracy of the calibration. The onset of the VUV channel in the combined spectrum (figure 6.19) indicates a resolution of 160 meV which is consistent with the measurements on krypton which were performed immediately after the xenon runs.

The corresponding polarization curve is shown in figure 6.20 where the data points below the threshold have been set to zero for sake of clarity. The data of Karras [1988], Uhrig et al. [1994b] and Al-Shamma and Kleinpappen [1977] are shown for comparison.

6.5.1.2 Results and Discussion

The spin-orbit splitting of the ion core is the largest (1307 meV) of the rare gases studied in the present work and therefore the resonance structures based on the two different cores will be well separated. Like krypton, the VUV emitting states cannot be classified as 3P or 1P (see table 3.1) but are roughly a 60-40 mixture of the two. An a2 resonance, observed near threshold in krypton, now lies approximately 740 meV above the first VUV emitting state [Buckman and Clark, 1994] which results in it being a much broader and weaker resonance which is difficult to distinguish due to the presence of the c1 resonance. Finally, only VUV emissions from the 2  P3/2 6s[3/2], state are being monitored because of the BaF2 window placed in front of the photon detector.

The corrected VUV spectrum clearly shows the effect that the resonances have on populating the magnetic sub-levels of the 2  P3/2 6s[3/2], state. In the threshold region, a pronounced shoulder appears in the perpendicular channel near the location of the b2 resonance. In the metastable measurements of Buckman et al. [1983b] a b resonance was observed 100 meV below the threshold for the 2  P3/2 6s[3/2], which could have a minor
Figure 6.18  VUV excitation functions for Xenon (BaF₂ window) corrected for polarization sensitivity of the analyzer.
Figure 6.19  Total VUV photon emission spectrum for xenon (BaF$_2$ window)
Figure 6.20  Polarization function for xenon (BaF₂ window). Errors are not shown when smaller than the data symbol.
influence on the relative populations at threshold if its width exceeds 100 meV. Observations in the other heavy rare gases indicate that this is possible.

The effect of the $c_1$ resonance in populating the perpendicular channel is visible at 9.08 eV. After the $c_1$ resonance there are several resonances clustered together including another $c$ resonance labeled $c'_1$ (see Table 6.4). Due to the energy resolution and statistical scatter the effects of each resonance are not clear however there does appear a dip in the parallel channel where the $d_1$ resonance is located. Note that the onset for the $^2P_{3/2} 6s[3/2]_1 (B_4)$ as well as the $6p$ neutral states is in this region as well. Also there should be $b$ resonances associated with the $^2P_{3/2} 6s[3/2]_1$ state present. However these have not been positively identified, probably being obscured by the many $e$ resonances observed by Buckman et al. [1983b]. The opening of these channels could also be responsible for the small drop in signal observed.

Table 6.4 Energies and widths of features for xenon (figures 6.17-6.24)

<table>
<thead>
<tr>
<th>Feature</th>
<th>Classification</th>
<th>Energy (eV)</th>
<th>Width (meV)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1^*$</td>
<td>$5p^5(2P^{3/2})6s[3/2]_2$</td>
<td>8.315</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$b_1$</td>
<td>$5p^5(2P^{3/2})6s6p(2P^o)$</td>
<td>8.338</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$B_2$</td>
<td>$5p^5(2P^{3/2})6s[3/2]_1$</td>
<td>8.437</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>$b_2$</td>
<td>$5p^5(2P^{3/2})6s6p(3P^o)$</td>
<td>8.48</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>$c_1$</td>
<td>$5p^5(2P^{3/2})6s6p(3P^o)$</td>
<td>9.08</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$c'_1$</td>
<td>$5p^5(2P^{3/2})6s6p(4P^o)$</td>
<td>9.36</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$B_3$</td>
<td>$5p^5(2P^o)6s[1/2]_1$</td>
<td>9.447</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$B_4$</td>
<td>$5p^5(2P^o)6s[1/2]_2$</td>
<td>9.570</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$e_1$</td>
<td>$5p^5(2P^{3/2})6p^2(3D)$</td>
<td>9.505</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>$e$</td>
<td>$5p^5(2P^{3/2})6p^2(3D)$</td>
<td>9.551</td>
<td>3</td>
<td></td>
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<tr>
<td>$d_1$</td>
<td>$5p^5(2P^{3/2})6p^2(3S)$</td>
<td>9.612</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>$e^*$</td>
<td>9.644</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e$</td>
<td>9.686</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e'$</td>
<td>9.743</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e$</td>
<td>9.831</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_1$</td>
<td>$5p^5(2P^{3/2})5d^2(3S)$</td>
<td>9.896</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$c_2$</td>
<td>$5p^5(2P^{1/2})6s6p(2P^o)$</td>
<td>10.48</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$c'_2$</td>
<td>$5p^5(2P^{1/2})6s6p(2P^o)$</td>
<td>10.71</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$d_2$</td>
<td>$5p^5(2P^{1/2})6p^2(3S)$</td>
<td>10.901</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$n_2$</td>
<td>$5p^5(2P^{1/2})5d^2(3S)$</td>
<td>11.14</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

*not shown in figures 6.17-6.24
1) Moore (NBS Atomic Energy Levels, 1949)
2) Brunt et al. (1977c)
3) Buckman et al. (1983b)
The effects of the $n_1$ resonance are seen at 9.9 eV as well as the broad feature of the $c_2$ resonance. Again statistical scatter prevents the clear indication of resonances after $c_2$ but there is a hint of structure in the parallel channel at the location of the $d_2$ and $n_2$ resonances.

The polarization function shows many of the features discussed above. As in the case of krypton the theoretical threshold polarization value for direct (exchange) excitation is less than +1 (-1) due to the non-zero nuclear spin (I) of its naturally occurring isotopes $\text{Xe}^{129}$ ($I=1/2$, 26.4%) and $\text{Xe}^{131}$ ($I=3/2$, 21.2%). The predicted threshold polarizations are 0.748 and -0.597 for direct and exchange excitation respectively using the analysis of Percival and Seaton [1958]. At threshold the polarization appears to be heading toward the pure exchange threshold value of -0.597.

After the threshold region, the polarization rises to a maximum of .25 and then drops to zero. The effect of the $c_1$ resonance is seen to lower the polarization function to a value of -0.10. It then rises to 0 possibly under the influence of the $c'_1$ resonance. After the $c'_1$ the polarization drops again below zero under the influence of the $e$, $d_1$ and the postulated $b$ resonances. A broad feature in the polarization curve is observed in the region of the 6p and 5d neutral states indicating that cascade may be significantly polarized. Also located in this region is the $n_1$ resonance. No other features are distinguishable in the VUV spectrum after the $n_1$ resonance due to the statistical scatter.

Other polarization measurements are shown and as in the case of krypton the data of Al-Shamma and Kleinpoppen significantly differ with the present results. These authors now believe their data to be suspect [Kleinpoppen, 1994]. The results of Karras and Uhrig et al. are seen to be in very good agreement with the present data. The data of Uhrig et al. does not show the dip centered on the $c_1$ resonance but this is probably a result of their poorer resolution (300 meV).
6.5.2.1 Data Collection without BaF₂ filter

The VUV photon data collected under these conditions are presented in figure 6.21. Metastable data were not obtained due to the detector malfunctioning. The data presented in figure 6.21 has had the background subtracted but no correction for variation in the electron current or the polarizer sensitivity has been performed. The accumulation time for the data was 220 hours with a maximum count rate of 3 Hz. The head pressure and chamber pressure were 0.13 and 2×10⁻⁶ torr respectively.

The energy calibration was performed by comparing the position of the \( c_1 \) resonance in the perpendicular channel with that measured by Buckman et al. [1983b]. The onset of the summed VUV data (figure 6.22) was determined to be 160 meV below the threshold of the \( ^2P_{3/2} 6s[3/2] \), which yields a resolution consistent with the measurements of krypton which were performed immediately after this run.

The polarization sensitivity of the analyzer was corrected for using a value of 1.505 for \( 1/\eta \) and the adjusted VUV spectrum is shown in figure 6.23 and the corresponding polarization curve is displayed in figure 6.24. The data points below the threshold in figure 6.24 have been set to zero for sake of clarity. The value for \( 1/\eta \) was obtained by comparing the polarization observed at 30 eV with the value determined by Karras [1988]. The data of Karras [1988], Uhrig et al. [1994] and Al-Shamma and Kleinpoppen [1977] are shown for comparison.

6.5.2.2 Results and Discussion

The shape of the polarization curve is similar to measurements made with the BaF₂ filter. The polarization functions (with and without BaF₂ window) are compared in figure 6.25. Note the very good agreement between the two data sets within the statistical errors. This reflects the dominance of the \( ^2P_{3/2} 6s[3/2] \) in this energy range and for that matter at higher energies [Suzuki et al., 1991]. Because of the similarities only the deviation between the two polarization curves at threshold will be discussed.

At threshold, the non-BaF₂ data set shows the polarization suddenly increasing toward large positive values while the BaF₂ data clearly shows a trend toward negative
Figure 6.21  VUV excitation functions for xenon (no BaF₂ window) with background subtracted.
Figure 6.22 Total VUV emission spectrum for xenon (without BaF₂)
Figure 6.23 VUV excitation function for xenon (no BaF) corrected for the polarization sensitivity of the analyzer.

Electron Impact Energy (eV)

Counts (arb. units)

Parallel
Perpendicular
Figure 6.24 Polarization function for xenon (no BaF). Errors are not shown when smaller than the data symbol.
Figure 6.25 Comparison of xenon polarizations made with and without a BaF$_2$ filter

values. This discrepancy is believed to be a spurious fluctuation in the non BaF$_2$ data since the energy resolution would not permit such a narrow structure to be observed. Also note that the statistics are not as good (4× less counts) as the BaF$_2$ data and therefore does not carry the same weight.

6.6 Negative Ion Systematics

As suggested in the introduction there are some similarities in the data between the heavy rare gases, most noticeably in the threshold region. The threshold polarization for all the gases show a trend toward negative values indicating that exchange excitation is the dominant channel. This finding is in agreement with measurements by Hanne et al. [1981] for Hg where they also observed exchange excitation dominating at threshold.

Above threshold the $b$ resonances cause the polarization to rise to large positive values. Note that these states associated with these resonances have total angular momentum ($J$) = 3/2,5/2 and are created by incident electrons with partial waves ($l_o$) ≥ 1.
The fact that $s$-wave scattering is not responsible for the near threshold resonances has also been observed by Wolcke et al. [1983] in their analysis of polarized and unpolarized electrons impacting ground state mercury. Their results show that electrons with $l_0 = 2$ are responsible for the formation of a negative ion resonance with $J = 5/2$.

The effect of the $c$ resonance is not consistent throughout the elements which may reflect the changing nature of this resonance as mass increases. Recall that there is some discussion on the designation of this state in argon (section 6.3.2) since theoretical calculations suggest its configuration differs from that of neon (Ohja et al., 1985).

The $d_1$ resonances ($j_c = 3/2$) however appear as dips in all the polarization functions. These decreases in the polarization are not consistent with the resonance polarization calculations of Table 3.4 ($j_c = 3/2$) since the polarization is predicted to be large and positive and thus would not act to depolarize the observed radiation. Therefore it seems clear that either the Grandparent model does not adequately describe the resonance or more likely the resonance polarization calculation needs to consider interference between the various states and alternate decay channels (i.e. changes in ion core configuration). The $d_2$ resonances are also observed to have a depolarizing effect.

The $e$ resonances are much more difficult to quantify due to their large numbers. However, it appears that those which lie between the $c$ and the $d$ resonances cause the polarization to increase in the positive direction. This feature is clearly seen in argon and neon.
7.1 Conclusions

The polarization functions for the integrated VUV radiation resulting from electron impact on the rare gases (He, Ne, Ar, Kr and Xe) have been measured in the threshold region. The polarization data clearly displayed the effects of negative-ion resonance formation, which have been observed in other electron impact experiments, and cascading from higher lying neutral states. Additionally, a BaF$_2$ window was also used to isolate the 1469.6Å line of xenon.

At threshold, the polarization function for helium was observed to go to unity which is in agreement with simple conservation of angular momentum arguments as well as the more detailed theories outlined in Chapter 2. The heavy rare gases however showed trends toward negative values indicating that exchange excitation was dominating in the near threshold region. Using the polarization functions of He and Ne, an estimate of the energy range that exchange excitation dominates was made and it was found to be on the order of 2-3 eV above threshold.

Just above threshold, resonances are clearly seen to perturb the polarization functions of the heavy rare gases in contrast to helium which is resonance free for the first eV. Using a modified Baranger-Gerjuoy theory (chapter 3) and assuming that resonance formation is dominating the excitation process, polarization calculations were made for different intermediate resonant states. It was concluded that the $b$ resonances with $J \geq 3/2$ were most likely responsible for the observed features indicating that $s$-wave scattering are not the dominating process here. In the case where there is no resonances at threshold (i.e. helium), the analysis of the magnetic sublevel excitation cross-sections suggested that $s$-wave excitation is the dominant process.
At higher energies (1 eV+) above threshold, resonances were seen to influence the polarization of all the rare gases. Systematic trends in the polarization function of the heavy rare gases, which are similar in atomic structure such as ion-core parity and angular momentum coupling, were observed as a function of the resonance structure.

7.2 Future Directions

Future directions for this experiment would be:

1) use of LiF and CaF₂ filters to isolate the Ar 4s[3/2] and Kr 5s[3/2] states respectively. Since this state for argon is predominantly (~80%) \(^3\)P in nature, it would provide the opportunity to observe the effects of exchange excitation.

2) use of a better energy resolved electron beam would allow individual resonances to be isolated so their effect on the polarization curve could be more clearly identified.

As noted in earlier chapters, there is a lack of theoretical calculations which can be used to analyze polarization data in the threshold region and thus it would be extremely beneficial for this avenue to be pursued.
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VITA AUCTORIS

I was born on September 13, 1961 in Westmount, Quebec. At the age of two my family moved to Welland, Ontario where I remained until entering the University of Western Ontario in 1980. I received my honours B.Sc. in 1985 and chose to remain to pursue my Master’s degree in experimental physics studying electron-ion recombination under the supervision of Dr. J.B.A. Mitchell. Upon completion of my Master’s degree in 1989, I came to the University of Windsor to study under Dr. J.W. McConkey which has resulted in this work.


**IN PREPARATION**


CONFERENCES


