EXCITATION STUDIES IN THE RARE GASES AND SIMPLE MOLECULES USING A HIGH RESOLUTION ELECTRON SPECTROMETER.

HENRICUS W. DASSEN
University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000 ext. 3208.
NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us a poor photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed:

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de mauvaise qualité.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RECUE
EXCITATION STUDIES
IN THE RARE GASES AND SIMPLE MOLECULES
USING A HIGH RESOLUTION ELECTRON SPECTROMETER

by

Henricus W. Dassen

A Dissertation
submitted to the Faculty of Graduate Studies
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

1983
ABSTRACT

A high resolution electron spectrometer has been used to perform electron scattering studies with both atomic and molecular targets. Work has been done on negative ion resonance production in the rare gases and on polarization correlation measurements in diatomic molecules.

High resolution metastable excitation function measurements have been made in the doubly excited state region for Ne, Ar and Kr targets. Comparison of the spectra obtained suggests that the gross features are due to negative ion resonances. Previous techniques which have proved successful in the identification and classification of resonances in the rare gases at energies below the first ionization threshold are shown to be applicable in this energy region also and assignments for a number of resonances are suggested. Where appropriate, comparisons have been made with data obtained by other techniques. The modified Rydberg formula has been used to predict energies for both doubly and triply excited configurations.

Polarization correlation measurements have been made with the target molecules N₂ and H₂. In H₂ the radiation resulting from excitation of the C₁Π_u v' = 0 band was studied. In N₂, excitation of the C₁Δ_u v' = 0 band was studied. Pseudo-threshold polarization measurements were made for these targets and comparisons with theoretical predictions were made. Systematic polarization correlation data for electron scattering angles up to 20 degrees have also been obtained.
and preliminary attempts have been made to analyze these.
ACKNOWLEDGMENTS

I would like to acknowledge my supervisor, Dr. J.W. McConkey for his guidance and encouragement throughout my career as a graduate student and in the course of the present work. I would also like to acknowledge Dr. G.C. King and his co-workers at the University of Manchester for graciously allowing us to use their design of the electron spectrometer and for his assistance and advice during the course of the work.

Thanks must also go to Dr. Kurt Becker for his invaluable contributions and assistance to this work, and to Dr. J.B. Westerveld for his contributions in the way of discussions and assistance.

The expert technical assistance of Mr. W. Grewe and his workshop staff in the construction of the spectrometer is also greatly appreciated, as is the assistance of Mr. B. Masse, our electronics technician.

The Son is the Radiance of God's glory and the exact representation of His being, sustaining all things by the word of His power.

Hebrews 1:3a
TABLE OF CONTENTS

ABSTRACT ........................................................................ iii

ACKNOWLEDGMENTS ....................................................... v

LIST OF TABLES ............................................................. ix

LIST OF FIGURES ........................................................... xi

1 INTRODUCTION ........................................................... 2

2 THE EXPERIMENTAL DETAILS ........................................ 7
  2.1 INTRODUCTION ...................................................... 7
  2.2 THE VACUUM SYSTEM ............................................ 8
    2.2.1 The Vacuum Chamber ........................................ 8
    2.2.2 The Pumping System ......................................... 13
  2.3 THE ELECTRON SPECTROMETER ............................... 16
    2.3.1 General Description .......................................... 16
    2.3.2 Design Criteria .............................................. 26
    2.3.3 Design of the Present Spectrometer .................... 43
    2.3.4 The Hemispherical Energy Selector ...................... 56
    2.3.5 Operation and Performance of the Spectrometer ..... 59
  2.4 APPENDIX ........................................................... 64

3 NEGATIVE ION RESONANCES IN THE RARE GASES ............ 70
  3.1 INTRODUCTION ...................................................... 71
  3.2 THEORETICAL BACKGROUND ..................................... 74
    3.2.1 Resonance Formation ....................................... 74
    3.2.2 Analysis Techniques Used .................................. 80
  3.3 DESCRIPTION OF THE EXPERIMENT ......................... 90
    3.3.1 The Interaction Region ..................................... 90

-vi-
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.2</td>
<td>Data Collection and Calibration</td>
<td>91</td>
</tr>
<tr>
<td>3.4</td>
<td>RESULTS AND DISCUSSION</td>
<td>93</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Introduction and Analysis</td>
<td>98</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Neon</td>
<td>118</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Argon</td>
<td>120</td>
</tr>
<tr>
<td>3.4.4</td>
<td>Krypton</td>
<td>125</td>
</tr>
<tr>
<td>3.4.5</td>
<td>Extension to Xe</td>
<td>130</td>
</tr>
<tr>
<td>3.4.6</td>
<td>Application of the Modified Rydberg Equation</td>
<td>134</td>
</tr>
<tr>
<td>3.5</td>
<td>CONCLUSIONS AND SUGGESTIONS</td>
<td>138</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Conclusions</td>
<td>138</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Suggestions for Future Research</td>
<td>140</td>
</tr>
<tr>
<td>3.6</td>
<td>APPENDICES</td>
<td>142</td>
</tr>
<tr>
<td>3.6.1</td>
<td>Ionization Potentials for the Rare Gases</td>
<td>142</td>
</tr>
<tr>
<td>3.6.2</td>
<td>Calculation of</td>
<td>143</td>
</tr>
<tr>
<td>3.6.3</td>
<td>Background Subtraction</td>
<td>145</td>
</tr>
<tr>
<td>4</td>
<td>POLARIZATION CORRELATION EXPERIMENTS WITH SIMPLE MOLECULES</td>
<td>146</td>
</tr>
<tr>
<td>4.1</td>
<td>INTRODUCTION</td>
<td>147</td>
</tr>
<tr>
<td>4.2</td>
<td>THE THEORETICAL FRAMEWORK</td>
<td>149</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Introduction</td>
<td>149</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Polarized Light and the Stokes' Parameters</td>
<td>149</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Coincidence Experiments With Atoms</td>
<td>155</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Coincidence Experiments With Molecules</td>
<td>171</td>
</tr>
<tr>
<td>4.2.5</td>
<td>Threshold and Pseudo-Threshold Polarization</td>
<td>181</td>
</tr>
<tr>
<td>4.3</td>
<td>DESCRIPTION OF THE EXPERIMENT</td>
<td>194</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Interaction Region and Detectors</td>
<td>194</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Data Collection and Analysis</td>
<td>202</td>
</tr>
<tr>
<td>4.4</td>
<td>RESULTS AND DISCUSSION</td>
<td>208</td>
</tr>
</tbody>
</table>
4.4.1 Nitrogen Data ...................................... 208
4.4.2 Hydrogen Data ........................................ 229
4.4.3 Discussion of the Results ......................... 240
4.5 CONCLUSIONS AND SUGGESTIONS ............... 247
4.5.1 Conclusions ..................................... 247
4.5.2 Suggestions for Future Research .......... 249
4.6 APPENDICES ........................................ 251
4.6.1 Hund’s Case (a) Coupling ...................... 251
4.6.2 The Momentum Transfer Direction ............ 251
REFERENCES ........................................... 253
VITA AUCTORIS ........................................ 258
<table>
<thead>
<tr>
<th>Table Number</th>
<th>Table Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Vacuum System Components</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>Spectrometer Electronics</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>Spectrometer Operating Conditions</td>
<td>61</td>
</tr>
<tr>
<td>3.1</td>
<td>Components - Metastable Detection Electronics</td>
<td>95</td>
</tr>
<tr>
<td>3.2</td>
<td>Neon Data</td>
<td>101</td>
</tr>
<tr>
<td>3.3</td>
<td>Argon Data</td>
<td>103</td>
</tr>
<tr>
<td>3.4</td>
<td>Krypton Data</td>
<td>105</td>
</tr>
<tr>
<td>3.5</td>
<td>Predicted and Observed Resonances in Xenon</td>
<td>131</td>
</tr>
<tr>
<td>3.6</td>
<td>Predicted and Observed Resonances in Xe: [5s^25p^4]^{++} Cores</td>
<td>133</td>
</tr>
<tr>
<td>3.7</td>
<td>Observed and Predicted Energies: (2S) Cores</td>
<td>135</td>
</tr>
<tr>
<td>3.8</td>
<td>Observed and Predicted Energies: Doubly Ionized Cores</td>
<td>136</td>
</tr>
<tr>
<td>4.1</td>
<td>Predicted Threshold Polarizations in H_2 and N_2</td>
<td>190</td>
</tr>
<tr>
<td>4.2</td>
<td>Coincidence Counting Electronics</td>
<td>201</td>
</tr>
<tr>
<td>4.3</td>
<td>P_C(0) vs Pressure: H_2</td>
<td>211</td>
</tr>
<tr>
<td>4.4</td>
<td>P_C(0) vs Incident Energy: N_2</td>
<td>215</td>
</tr>
<tr>
<td>4.5</td>
<td>Polarization Correlation Data vs Energy: N_2</td>
<td>218</td>
</tr>
</tbody>
</table>
4.6 Polarization Correlation Data vs Scattering Angle: \( n \) 223

4.7 \( P_c(0) \) vs Pressure and Energy: \( n \) 232

4.8 Polarization Correlation Data vs Scattering Angle: \( n \) 239
LIST OF FIGURES

2.1 The Vacuum System ........................................... 11
2.2 Aæstat Control Circuit ......................................... 12
2.3 (a) Selector ...................................................... 17
2.3 (b) Analyzer ...................................................... 18
2.4 Selector Control Circuit .......................................... 21
2.5 Analyzer Control Circuit .......................................... 22
2.6 (a) Typical Electron Optical System ......................... 27
2.6 (b) Defining Apertures ........................................... 29
2.6 (c) Energy Distribution of the Electron Beam .............. 32
2.7 Thick Lens Representation ....................................... 44
2.8 Characteristics of a 3 Element Lens ......................... 45
2.9 Lens Stack 1 Parameters ........................................ 46
2.10 Lens Stacks 2 and 3 Parameters ................................ 49
2.11 Zoom Lens Characteristics ..................................... 51
2.12 Lens Stack 4 Parameters ........................................ 52
2.13 (a) Fringe Field Correctors ................................... 54
2.13 (b) Performance of Field Correctors ......................... 55
2.14 The Hemispherical Energy Selector .......... 57
2.15 Metastable Spectrum in Neon ............... 60
3.1 Resonance Behaviour ......................... 78
3.2 (a) \(^{2}\text{S}\) (n\(\pm m\))\(_{p}\) States: I.P. vs Energy ........ 83
3.2 (b) \(^{2}\text{S}\) (n\(\pm m\))\(_{p}\) States: Binding Energy vs Energy ........ 84
3.3 Interaction Region: Metastable Detection .... 92
3.4 Metastable Counting Electronics ............ 93
3.5 \(^{3}\text{P}\) Calibration Spectrum ................. 94
3.6 (a) Metastable Excitation Spectrum - Neon ... 99
3.6 (b) Comparison of Neon Data With Other Work .... 100
3.7 Metastable Excitation Spectrum - Argon .... 102
3.8 Metastable Excitation Spectrum - Krypton .... 104
3.9 (a) \([\text{n}n\text{n}p^{6}]^{2}\text{S}\) \(\text{ml}m\)' I.P. vs Energy .... 107
3.9 (b) \([\text{n}n\text{n}p^{6}]^{2}\text{S}\) \(\text{ml}m\)' Binding Energy vs Energy .... 108
3.9 (c) Slope vs Principal Quantum Number - Singly Excited Cores .......... 113
3.10 (a) I.P. vs Resonance Energy: \(^{3}\text{P}\) Cores .... 114
3.10 (b) I.P. vs Resonance Energy: \(^{1}\text{D}\) and \(^{1}\text{S}\) Cores .... 115
3.10 (c) Binding Energy vs Resonance Energy: Doubly Excited Cores .......... 116
4.1 Polarized Light Source .................................................. 150

4.2 Experimental Geometry .................................................. 157

4.3 Semiclassical Grazing Collisions ..................................... 164

4.4 (a) Double-Reflection Polarizer ..................................... 195

4.4 (b) Single-Reflection Polarizer ...................................... 196

4.5 Coincidence Counting Electronics ................................... 198

4.6 Polarizer Controller Logic ............................................ 199

4.7 Typical Coincidence Spectra ......................................... 205

4.8 Energy Loss Spectrum in \( N_2 \) ........................................ 209

4.9 \( P_C(0) \) vs Pressure: \( N_2 \) ........................................ 210

4.10 Pseudo-threshold Polarization Measurements: \( N_2 \) ........ 213

4.11 \( P_C(0), P_C(45) \) vs Energy: \( N_2, \theta_e = 5 \text{ deg.} \) ...... 217

4.12 Typical Radiation Pattern: \( N_2 \) ................................... 220

4.13 \( \theta_k, \theta_{\text{min}} \) and Phase vs Energy: \( N_2, \theta_e = 5 \text{ deg.} \) .. 221

4.14 \( P_C(0), P_C(45) \) vs Electron Scattering Angle: \( N_2 \) .... 222

4.15 \( \theta_k \) and \( \theta_{\text{min}} \) vs Electron Scattering Angle: \( N_2 \) .. 225

4.16 Phase Angle vs Electron Scattering Angle: \( N_2 \) ........... 227

4.17 Energy Loss Spectrum in \( H_2 \) ..................................... 230
4.16 $P_c(0)$ vs Pressure

4.19 $P_c(0), P_c(45)$ vs Electron Scattering Angle

4.20 Typical Radiation Pattern

4.21 $\theta_k, \theta_{\text{min}}$ vs Electron Scattering Angle

4.22 Phase Angle vs Electron Scattering Angle

231

235

236

237

238
CHAPTER 1

INTRODUCTION
Before the advent of high resolution electron spectrometers very little was known about the finer details of electron scattering processes in atoms and molecules. These details were smeared out by the poor energy resolution of simple electron sources. The resolution, or energy spread, inherent in the electron beams produced by these devices is on the order of 500 eV to several eV. Thus, atomic or molecular states separated in energy by say 50 or 100 meV could not be isolated and investigated.

With the introduction of high resolution electron sources and analyzers, this problem was significantly reduced. High resolution electron spectrometers are capable of producing and analyzing electron beams with resolutions on the order of 10 to 100 meV, enabling experimental physicists to study electron-atom and electron-molecule scattering in much more detail than was possible before. These devices quickly found applications in a variety of experiments, such as ejected electron spectra, differential elastic and inelastic scattering measurements, studies of excitation cross-sections, and most importantly, electron-photon coincidence experiments. In the latter type of experiment, it is essential that the target atom(s) or molecule(s) be prepared in a well-defined excited state, a task for which the spectrometer is much better suited than a simple electron gun. In addition to electrons, ions can also be used with these devices and this fact was exploited to the full in a variety of experiments. One other advantage of the electron spectrometer is its ability to simulate photo-excitation and photo-
ionization in energy regimes where photon sources are non-existent or simply not intense enough to work with. These properties make the high resolution electron spectrometer an ideal tool for the study of electron scattering using atomic and molecular targets.

In the present work, the electron spectrometer was used in two different ways. The first was as a high resolution source of electrons to study the production of metastable species of Ne, Ar and Kr in the doubly excited state region. The formation of negative ion resonances was examined in this phase of the work. The second way was as a combined high resolution source and analyzer for use in electron-photon polarization correlation studies in molecules. In the present work Ne and Ar were used as target gases.

This work is divided into three self-contained chapters. Chapter 2 describes the apparatus used in the experiments. A description of the vacuum system is given, and a detailed discussion of the electron spectrometer is also presented. Chapter 3 presents the work done on negative ion resonances in the rare gases. A discussion of resonance formation and the analysis techniques used is first given, followed by a description of the experiment itself, and then the results are presented and discussed. Chapter 4 describes the work done on polarization correlation measurements using simple molecules as targets. A review of the atomic case is presented first, and then the current theories for the molecular case are discussed. Polarization of molecular radiation
at the excitation threshold and the use of 'pseudo-threshold' techniques are discussed, as well as the framework used to analyze the data obtained. The experimental procedure is described in detail, followed by the results obtained with \( \text{N}_2 \) and \( \text{H}_2 \) as target gases.
CHAPTER 2
THE EXPERIMENTAL DETAILS
2.1 INTRODUCTION

This chapter is intended to provide a complete description of each component used in the present work. Note that it contains information relevant to both parts of this work.

The apparatus can be categorized into three sections:

(1) The Vacuum System
(2) The Electron Spectrometer
(3) The Detection Systems

Each of these categories will be discussed in detail, with diagrams and tables to illustrate the construction, performance and operation of each part, with the exception of the detection systems, which will be discussed in chapters 3 and 4.
2.2 THE VACUUM SYSTEM

The vacuum system is, of course, common to both experiments and is therefore discussed first. Each component of the system, with the exception of the chamber housing the spectrometer, is commercially available and Table 2.1 contains the relevant information about them. Figure 2.1 shows a schematic diagram of the vacuum system and its various components.

2.2.1 The Vacuum Chamber

The vacuum chamber consists of a 20" x 20" x 20" aluminum box with each of its six panels removable for easy access to the interior. Each panel is bolted into place to a welded aluminum framework, and vacuum sealing is done with O-ring seals. With the exception of the top and bottom panels, each one has provisions for three 4" accessory ports, also sealed with O-rings. As indicated in Figure 2.1, five of the 12 ports are used to attach the following:

(a) a roughing valve directly to the chamber so that it could be pumped out to the foreline pressure without having to go through the diffusion pumps.

(b) a gas inlet valve to leak a target gas into the collision region. This inlet system is also attached to the foreline so that it can also be pumped directly.

(c) an ionization gauge tube to monitor the pressure inside the chamber. The controller and
### Table 2.1

**Vacuum System Components**

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vacuum Pumps:</strong></td>
<td></td>
</tr>
<tr>
<td>Rotary</td>
<td>Edwards ED-660</td>
</tr>
<tr>
<td>Diffusion</td>
<td>(2) Edwards 633A (Mercury Vapour)</td>
</tr>
<tr>
<td><strong>Pressure Monitors:</strong></td>
<td></td>
</tr>
<tr>
<td>Foreline</td>
<td>Veeco TG-7 Controller/DW-1M</td>
</tr>
<tr>
<td></td>
<td>Thermocouple Gauge (0-1000 mTorr)</td>
</tr>
<tr>
<td>Gas Inlet</td>
<td>Veeco TG-27 Controller/DW-4AM</td>
</tr>
<tr>
<td></td>
<td>Thermocouple Gauge (0-20 Torr)</td>
</tr>
<tr>
<td>Chamber</td>
<td>Veeco HG-310 Controller/B3-75P</td>
</tr>
<tr>
<td></td>
<td>Ionization Gauge</td>
</tr>
<tr>
<td><strong>Isolation Valves:</strong></td>
<td></td>
</tr>
<tr>
<td>Foreline</td>
<td>(3) Edwards 1&quot; valves</td>
</tr>
<tr>
<td></td>
<td>(2) Edwards 1/2&quot; valves (to chamber)</td>
</tr>
<tr>
<td>High Vacuum</td>
<td>(1) Edwards 1&quot; Magnetic (Air Admittance)</td>
</tr>
<tr>
<td></td>
<td>(2) Vacuum Generators D1216 Valves</td>
</tr>
<tr>
<td></td>
<td>(2) Edwards 2346 6&quot; Butterfly Valves</td>
</tr>
<tr>
<td><strong>Gas Inlet Valve:</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vacuum Generators MD1871 Needle Valve</td>
</tr>
<tr>
<td><strong>Traps and Baffles:</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2) Edwards 8TM6 Liquid Nitrogen</td>
</tr>
<tr>
<td></td>
<td>Cold Traps</td>
</tr>
<tr>
<td></td>
<td>(2) Edwards DGH4 Thermoelectrically Cooled Baffles</td>
</tr>
</tbody>
</table>
The gauge tube used is indicated in Table 2.1. Typical chamber pressures (without a target gas) were on the order of 1 x 10^-6 torr.

(d) An electrical feedthrough to provide power to 2 quartz-halogen heating lamps, used to keep the interior of the chamber at a slightly elevated temperature. This was done primarily to reduce the formation of insulating layers on the electrodes in the spectrometer. It was found that operating the experiment with the lamps on improved the long-term stability of the apparatus.

(e) A small glass viewing port. The purpose of this was to be able to verify that the baking lamps were indeed operating.

The other 7 ports were simply blanked off and not used in the present set of experiments. The top flange has nine accessory ports which have electrical feedthroughs on them to connect the spectrometer to the outside world. It also has two rotary vacuum feedthroughs, one of which is used to rotate a polarizer, and the other to rotate the analyzer half of the electron spectrometer. The top flange was also used to hold the entire framework of the spectrometer and the magnetic shielding box. Using this arrangement it was possible to remove the entire spectrometer from the vacuum chamber without disturbing any electrical connections between the feedthroughs and the spectrometer. This was a distinct advantage when the spectrometer had to be removed for
FIG 21 THE VACUUM SYSTEM
cleaning or installation of major parts. It should be pointed out, however, that because of the foresight in the design of the chamber, it was rarely necessary to remove the spectrometer in order to work on it. Removal of one or two of the side panels allowed easy access to the spectrometer for most occasions.

It was essential to the operation of the spectrometer that stray magnetic fields be kept out of the interior of the vacuum chamber. This was accomplished by enclosing the entire spectrometer in a box constructed from u-metal shielding. This box was suspended from the top of the chamber, with four of its six sides removable. The shielding box was held together with self-tapping, non-magnetic stainless steel sheet metal screws. The bottom of the box was drilled out with an array of 0.5-inch diameter holes to allow the interior to be pumped efficiently. Measurements of the residual magnetic field inside the chamber indicated that it was fairly uniform throughout, with a field strength of about 10 milligauss.

2.2.2 The Pumping System

The essential elements used to pump the vacuum chamber are listed in Table 2.1 and shown in Fig. 2.1, so only the following points need to be noted:

1) Mercury vapour diffusion pumps were used to maintain the high vacuum for the simple reason that with an oil vapour pumping system the possibility exists that some residual oil
might reach the spectrometer and cause the formation of insulating layers. These layers could charge up when exposed to the electron beam and degrade the performance of the instrument. Mercury, being a conductor, would not cause this type of problem. To prevent mercury from getting into the collision region, a combination of thermoelectrically cooled baffles and liquid nitrogen cold traps were used on each diffusion pump. The baffles enabled the system to be kept on continuously for months at a time, unlike the situation which arises without them — the mercury vapour freezes on the cold surface of the traps until there is none left in the pumps. When this happens the entire system must be shut down to allow the mercury to thaw and fall back into the pumps. With the present system (and no baffling) this would happen on a weekly basis, making long term stability difficult to maintain.

(2) Oil vapour in the foreline was removed by a trap containing activated alumina (Zeolite). This prevented backstreaming of oil from the rotary pump into the diffusion pumps.

(3) The foreline pressures attained by the rotary pump were between 10 and 20 millitorr as measured by the thermocouple gauge unit.
(4) Butterfly valves were used to isolate the vacuum chamber from the pumping system when it became necessary to shut the system down and open it up. This also prevented the mercury in the diffusion pumps from slowly evaporating.

(5) To prevent the system from turning on again after a power failure of more than 10 secs duration, an Agastat power fail protection device was used to control power to the rotary pump and the diffusion pumps. The magnetic valve would then seal off the rotary pump from the foreline, thus preventing oil from being sucked into the line and then into the diffusion pumps. Figure 2.2 shows the schematic diagram of the Agastat control circuit.
2.1 THE ELECTRON SPECTROMETER

Since the electron spectrometer is the most important piece of equipment used in the present work, it is worthwhile to discuss the details of its design, construction and operation. The design of the spectrometer has already been discussed extensively in the literature\textsuperscript{1-3}, and the material presented here is an overview of these.

A general description of the spectrometer will be presented first, followed by a discussion of the criteria necessary to design the device, and lastly, the operation and performance of the spectrometer is discussed. Appendix 2.4 contains construction details other than what is discussed here.

2.2.1 General Description

The spectrometer consists of two independent halves: the selector, which produces an almost monoenergetic electron beam, and the analyzer, used to energy analyze scattered electrons. These are schematically illustrated in Figures 2.3(a) and 2.3(b), respectively. As can be seen from these diagrams the spectrometer consists of the following basic elements:

1. an electron source - filament, grid and anode. The filament is a heated tungsten wire bent into a hairpin shape, and is housed in a stainless steel holder which can be removed from Lens Stack 1 without having to dismantle.
the entire stack (see Appendix 2.4).

(2) seven 3 element aperture lenses (L1-L7), used to focus the electron beam within the spectrometer. Lenses L4 and L5 are focussed on the target region.

(3) pinhole apertures (A1-A8) used to define the electron beam. Apertures A1-A6 are also used to monitor the beam current at various points in the spectrometer.

(4) deflector assemblies (D1-D7) to steer the beam in the x and y directions, the z direction being defined by the beam itself (see Appendix 2.4).

(5) fringe field correctors at the entrance and exit planes of the hemispheres. These are used to match the fields of the final lens elements (L2C, L3A, L6C, L7A) to the hemisphere fields and to correct for the field distortion at the gaps in the hemispheres.

(6) double hemispheres (S1 and S2) which energy analyze the electron beam, resulting in an almost monoenergetic final beam.

(7) a channel electron multiplier, or Channeltron(*), to detect electrons scattered into the analyzer. Note that the Channeltron cone is at the potential on L7C.

(*) Trademark of Galileo Electro-Optics, Inc.
Figures 2.4 and 2.5 show schematic diagrams of the electronics used to control the selector and analyzer, respectively. Table 2.2 lists the components used in these circuits. These circuits are self-explanatory for the most part. Note the capacitors on the deflectors and on some of the lens elements; these are used to eliminate 'ripple' voltages and improve the stability of the electron beam. As will be discussed later, it is essential that the hemispheric voltages, the hoop voltages and the voltage on L2C (or L6C) be kept at a fixed ratio to each other. To ensure that this is the case, the scale power supply is used to adjust the potentials simultaneously. Not indicated on the diagrams are the jacks used to monitor the potentials on each element. Also, lens elements indicated on Fig.'s 2.3(a) and 2.3(b) which are not indicated in the schematics are internally connected to other lens elements at the spectrometer itself. The following table summarizes those internal connections:

<table>
<thead>
<tr>
<th>SELECTOR</th>
<th>ANALYZER</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1A - Anode</td>
<td>L5A - L4C(Target)</td>
</tr>
<tr>
<td>L2A - L1C</td>
<td>L6A' - L5C</td>
</tr>
<tr>
<td>L3A - L2C</td>
<td>L7A - L6C</td>
</tr>
<tr>
<td>L4A - L3C</td>
<td></td>
</tr>
</tbody>
</table>

A summary of the materials used in the construction of the spectrometer is in order at this point to give the reader an idea of what is involved.
Table 2.2
Spectrometer Electronics

| Potentiometers: | Pours 10 turn Helipots |
| Power Supplies: |
| Filament Supply: | Lambda LCS-2-02 (0-18 volts Reg.) |
| Contact Potential: | Lambda LCS-C-01 (0-7 VDC Reg.) |
| Scale Supply: | Lambda LCS-2-04 (0-60 VDC Reg.) |
| Lens Elements: | Lambda LPD-425A-PF (Dual 0-250 VDC Reg.) |
| Deflectors: | Power One HAA-24-6 (+24 VDC Reg.) |
| Target Energy: | Kepco ABC-100-0.2 K (0-100 VDC Prog., Reg.) |
| Energy Loss: | Kepco HE-2AD (0-325 VDC Reg.) |
| Needle Bias: | Power One E24-12 (0-24 VDC Reg.) |
| Voltage Monitor: | Hewlett-Packard 3439A Digital Voltmeter |
| Current Monitor: | Keithley 602 Solid State Electrometer |
(1) Molybdenum - used for components exposed to the electron beam: lens elements, deflectors, field correctors, and the hemispheres. The target region was also constructed out of this material. Molybdenum was chosen because it is non-magnetic, and is not subject to oxidation or corrosion.

(2) Non-magnetic stainless steel - for lens stack ends, support rods, filament holder, deflector assemblies, the baseplates (and associated hardware), channeltron mounting assemblies, as well as all screws, nuts and bolts.

(3) Ceramic - for the three lens stack alignment rods used in the 4 lens stacks.

(4) Macor, a machinable fiberglass - used to construct spacers of appropriate length to achieve the required element separation in the stacks. It was also used to insulate the screws holding the filament, deflectors, corrector hoops, and the hemispheres. The target region was also mounted on Macor to insulate it from the chamber. The channeltrons were insulated from their mounting assemblies by holders constructed out of this material.

(5) Aluminum - used to construct the supporting framework which holds the spectrometer to the top plate of the vacuum chamber. It was also used to construct the mounting bracket for the
target region assembly.

Electrical connections to the spectrometer were made by spot-welding wires from each element to pins mounted in insulating blocks attached to the selector and analyzer baseplates. From there, wires were spot-welded to the feedthroughs on the top plate of the chamber. Insulation of these connections was done by using teflon sleeving at the spectrometer, and glass fiber sleeving to the feedthroughs.

To minimize the amount of electron scattering from the lens elements and apertures, the area around the holes in these was coated with a fine layer of soot. The hemispheres (S1 — outer surface; S2 — inner surface) and the field corrector hoops were also coated with soot, as was the entire target region.

The analyzer half of the spectrometer could be rotated about the target region through about 95 degrees. This was accomplished by a rotary feedthrough placed on the axis of rotation on the top plate of the chamber. To allow for the placement of a detector immediately above the interaction region, the bracket connecting the analyzer to the rotary feedthrough was diverted through 90 degrees near the top of the chamber. To ensure that the rotation was smooth, small teflon pads were attached to the underside of the analyzer mounting assembly to reduce friction.

The detector was held above the interaction region by a framework attached to the supporting rods of the spectrometer assembly. To allow rotation of the detector needed for
a polarization sensitive one; another rotary feedthrough, offset from the axis of rotation, was placed on the top plate. A set of two gears were then used inside the chamber to couple the rotary feedthrough to the detector.

2.3.2 Design Criteria

There are many things which must be taken into account when designing any electron optical system, and these are especially important in the design of a high resolution electron spectrometer. Various effects present in electron optics put limitations on the available current and energy resolution, as well as beam definition, that a device is capable of achieving. The beauty of the present spectrometer lies in the fact that its designers (Mead and his co-workers at the University of Manchester) have expended a great deal of time and effort in the task of minimizing these effects and producing an optimized design. In doing so, they have accounted for effects which were not taken into consideration in previous designs, and thus have been able to achieve very high resolution electron beams (10–20 meV or better) with reasonable target currents (on the order of nanamps).

Figure 2.6(a) is a schematic diagram of a typical electron optical system. The system consists of 4 basic elements: an electron source (cathode); a combination of lenses and collimators to focus the source into an energy selector; the energy selector, which provides the high energy resolution; and another set of lenses and collimators to focus the
SCHEMATIC REPRESENTATION OF AN ELECTRON OPTICAL SYSTEM

FIG 2.6(a)
final beam into the target region. The goal in designing a working system is to produce the maximum current at the target for a given target energy and energy resolution. In addition the target beam must be spatially well defined, and the system should be able to keep these properties constant for a wide range of target energies. We shall first discuss the effects present in electron optical systems which place constraints on the design parameters and the 'quality' of the final electron beam. These are:

1. Removal of electrons by defining apertures and the energy selector.

2. Space charge repulsion and inter-electron interactions.


4. Lens, collimator and deflector aberrations.

5. Aberrations of energy selectors.

1. Removal of Electrons by Apertures and the Selector

A necessary part of any decent electron optical system is one or more sets of defining apertures or collimators which are used to spatially define the electron beam. Figure 2.6(b) shows a typical set of defining apertures. As can be seen, this set consists of a window to limit the diameter of the beam, and a pupil to define the beam angle $\theta_B$ and the pencil angle $\theta_P$. As we shall see later, these angles play important roles in the proper design of the system. The collimator will remove electrons from the beam, so that not all electrons emitted by the cathode will reach the selector. This happens in two ways. First, electrons which are
emitted too far from the beam axis will simply be screened out, and second, electrons which have a \textit{transverse momentum} which is too large will be stopped by the time they reach the collimator. Because of this second effect, the collimator will alter the energy distribution of electrons in the beam, a fact which was not considered in previous designs. Before discussing this aspect of collimators, we must examine the relationship between beam energy, beam radius and the beam pencil angle.

The above mentioned quantities are related to each other by the \textit{Helmholtz-Lagrange} equation:

\[ r^2 y^2 \sin \theta_p = \text{const.} \quad (2.3.1) \]

Thus, for the schematic diagram of Fig. 2.6(a), equation 2.3.1 gives:

\[ r_K^2 y^2 \sin \theta_K = r_S (r_K + e V_s)^2 \sin \theta_S = r_T (r_K + e V_T)^2 \sin \theta_T \]

where:

- \( r_K \) is the radius of that part of the electron source which is finally imaged at the target.
- \( E_K \) is the beam energy at the cathode.
- \( \theta_K \) is the beam pencil angle at the cathode.
- \( r_S \) is the beam radius at the selector entrance and exit.
- \( V_S \) is the potential of the selector region (with respect to the cathode).
- \( \theta_S \) is the pencil angle at the selector.
- \( r_T \) is the beam radius at the target.
- \( V_T \) is the target potential.
- \( \theta_T \) is the pencil angle at the target.
Note that equation 2.3.1 implies that the pencil angle can never be made arbitrarily small, and therefore the angular divergence of the beam, $\theta_B + \theta_p$, will always be non-zero. When using collimators, equation 2.3.1 must always be kept in mind.

Returning now to the effect that collimators have on the energy distribution of the electron beam, Fig. 2.6(c) shows this. Curve (a) on Fig. 2.6(c) is the (assumed) Maxwellian distribution of electrons emitted from the cathode at an effective temperature $T_K$. Curve (b) shows the distribution after passing through the collimator. This is obtained by defining a critical energy, $E_C$, given by:

$$E_C = \frac{eV_M^2 \sin^2 \theta_T}{1 - M_T^2 \sin^2 \theta_T} = eV_M^2 \sin^2 \theta_T$$

(2.3.2)

where $M_T = \frac{T}{T_K}$ is the linear magnification at the target. Electrons with energies less than $E_C$ will be transmitted by the collimator, whereas only a fraction of the electrons with energies greater than this will be transmitted. This fraction is given by:

$$f_{coll} = 1 - \frac{eV_T \exp(-E_C/kT_K)}{E_C + eV_T}$$

(2.3.3)

As can be seen from Fig. 2.6(c), the energy distribution is
altered significantly by the collimators.

Two additional points about collimators should be mentioned:

(1) If more than one set of defining apertures are used in the system, the energy distribution of the beam should be determined by only one set; the extra collimators and their image sizes should be larger than the primary collimator and its image. If this is not done, then the center of the beam will be 'brighter' than the edges (vignetting) and as a result there will be an unnecessary loss of current.

(2) It is desirable to place the primary collimator as soon after the cathode as possible, and definitely before the energy selector, to reduce the effects of too much current at the selector entrance. Also, placing the defining apertures early in the system has the advantage of starting with a well defined beam from the beginning, which will reduce the effects of aberrations later on in the system.

The energy selector also removes electrons from the beam, so that not all electrons entering it will reach the target. Electrons whose energies are too high or too low will not pass through the selector i.e., the selector will only pass an energy $E_0 \pm \Delta E$. Curve c on Fig. 2.6(c) shows the energy distribution on the electron beam after passing through the
hemispherical energy selector. In the past $E_0$ was taken to be $E = kT_K$, the energy of the maximum in the Maxwellian distribution. Clearly, the presence of the collimator changes this, especially when $E_0$ and $\Delta E$ are much less than $kT_K$. The mean energy transmitted by the selector is instead $E_C$, and the fraction of electrons transmitted by the selector is:

$$f_{sel} = \frac{(E_C/kT_K) \exp(-E_C/kT_K) \Delta E}{(1 - \exp(-E_C/kT_K)) kT_K} \quad (2.3.4)$$

The transmission of the entire system is the product of the collimator and selector transmissions, and is:

$$f_{trans} = \frac{E_C E \exp(-E_C/kT_K)}{(kT_K)^2} \quad (2.3.5)$$

for $\Delta E \ll E_C$. As indicated by equation 2.3.4, the fraction of current transmitted by the selector increases as $\Delta E$ increases. For $E_C \ll kT_K$, equation 2.3.4 can be written as:

$$f_{sel} = (1 - \frac{E_C \Delta E}{kT_K kT_K})$$

Thus a slight increase in transmission can be gained by decreasing $E_C$, but (shown later), $E_C$ and $\Delta E$ are proportional, so $E_C$ cannot be reduced too far.
(2) Space Charge Repulsion and Inter-Electron Interactions

The electrostatic repulsion between electrons in the beam has two effects: on the spatial distribution of the beam, and on the energies of individual electrons in the beam.

The repulsion between electrons means that a lens cannot focus the electron beam to a point on the 'optical' axis of the system (or anywhere, for that matter); i.e. the beam radius can never be zero anywhere in the system. The best that can be achieved is focussing the beam to some minimum radius, which depends in a complex way on the initial radius, the beam current, the distance from the lens, and the beam energy. Alternatively, this can be viewed as putting a constraint on the maximum amount of current that can be passed through a radius $r_1$ at a distance $z$ away from the lens for a given beam energy (determined by the beam voltage $v$) and initial beam radius $r_1$. This maximum current is given by:

$$I_{\text{max}} = \frac{38.5 \times 10^{-6}}{\ln(r_1/2r_2)} v^{3/2} \left( \frac{r_1}{r_2} \right)^2$$

(2.3.6a)

which is accurate to about 20% for $0.0035 \leq r_2/r_1 \leq 0.027$ and
\[ I_{\text{max}} = 38.5 \times 10^{-6} \left( 0.3 + 3.7 \frac{r_2}{r_1} \frac{v^{3/2}}{(r_1^2/x^2)} \right)^2 \] 

(2.3.6b)

which is accurate to about 20\% for \( 0.04 \leq r_2/r_1 \leq 1.0 \). The expression used in past designs is:

\[ I_{\text{max}} = 38.5 \times 10^{-6} v^{3/2} \left( 2r_1/x \right)^2 \]

which is the maximum amount of current that can be forced through a tube of length \( z \) and radius \( r_1 \). Read et al.\(^2\) pointed out that this is simply not accurate enough to account for all of the space charge repulsion, and does not agree with experimentally determined data. It should also be noted that the minimum radius of the beam is always subject to the constraints imposed by the Helmholtz-Lagrange equation (2.3.1).

The effect of inter-electron interactions can change the energies of individual electrons. This results in an anomalous energy spread in the beam, known as the Boersch effect. This energy spread is given by:

\[ \Delta E_B = \frac{1}{r_0^2} \chi(1r/v^{1/2}) \] 

(2.3.7)

where \( \chi(x) \) is a function which varies from about \( 10^{-10} \) for \( x = 10^{-15} \) (SI units) to about \( 3 \times 10^{-6} \) for \( x = 10^{-9} \) (SI units) (see graphs in ref 2). This effect can be neglected at the
selector entrance since it will be much smaller than the
'natural' energy spread in the electrons coming from the
cathode. After the beam leaves the selector, however, this
must be taken into account. For example, suppose that the
final set of lens elements is rather poorly designed, and
that the beam radius at the target is 0.5 mm, the pencil
angle is 0.025 radians, and \( I \) and \( V \) are such that \( X \) has the
value 10^-7. The Boersch energy spreading is then 8 meV,
which is certainly non-negligible if one desires final resolu-
tions of 10 or 20 meV. Thus the selector to target lens
system must be designed to keep this effect at a minimum (1
or 2 orders of magnitude lower than the above example would
do nicely).

(3) Gun Limitations

Space charge effects also put a limit on the maximum cur-
rent that can be obtained from a plane parallel diode
arrangement. This is given by:

\[
J_{K \text{max}} = 2.33 \times 10^{-6} \frac{d_{K}^{-2}}{V_{A}^{3/2}} \text{ (ampm}^{-2})
\]

where \( d_{K} \) is the distance between the cathode and anode and
\( V_{A} \) is the anode potential. This then also limits the avail-
able current at the target, given by the product of the
transmission of the system (equation 2.3.5) and equation
2.3.3, in the absence of other effects. There is not much
one can do to overcome this limitation. The maximum current
can be increased by making \( V_{A} \) large and \( d_{K} \) as small as pos-
sible, and the use of a triode arrangement will improve the situation to some degree. This limitation on the system, however, is less important than limitations from other causes.

(4) Lens, Deflector and Collimator Aberrations

Electrostatic lenses and associated elements introduce aberrations into the electron beam which have the effect of increasing the size, beam angle and pencil angle throughout the system. This results in a less well defined beam at the target, a loss of current, and an increase in the overall energy spread in the beam.

As in light optics, electron optics suffer from spherical aberration, coma, astigmatism, curvature of field, and other distortions as well. These aberrations are mainly due to non-uniformities in the lens fields near the edges of the elements, as well as the inability of the lens to focus the beam to a point. Thus it is desirable to keep the beam away from the edges of the lens elements, i.e., to make the lens diameter much larger than the beam diameter, and to make certain that the beam is on the optical axis.

Lens aberrations are usually discussed in terms of a quantity called the filling factor of the lens. This is defined to be the ratio of the beam diameter inside the lens to the lens diameter. The spherical aberration of a two-element cylinder lens, for example, due to the filling factor ($\eta$) is given by:
\[ \Delta r/D = 0.1 n^3 \]

where \( \Delta r \) is the radius of the image disc on the axis due to the aberration of a point source, and \( D \) is the lens diameter. For real objects, the aberration is generally much worse. The lenses used in the present spectrometer are all 3 element aperture lenses, and the aberrations of these are usually greater than those of 2 element lenses, particularly if the center element is at a lower potential than the other two. Thus the center element of a 3 element lens should always be operated at a higher potential than the outer elements. The aberrations of various types of lenses have been tabulated by Harting and Read\(^4\), and this reference can be used when designing an electron-optical system to determine the aberrations of lens elements that one could expect.

It is immediately clear that a defining aperture has a filling factor of 1.0 by definition. This has two important consequences: one, that a lens cannot also be used as a defining aperture without introducing severe aberrations into the image, and two, defining apertures must be placed in field-free regions lest they act as terribly aberrated lenses. It is also advisable to place defining apertures in regions of high potential, where the beam energy is large, to further minimize the effects of any aberrations that may occur.

Deflectors used to steer the beam within the system can also cause aberrations if the deflecting voltages used are too high. Thus the maximum deflector voltages should be
high enough to be able to push the electron beam around, but not so high as to distort the fields around them. Deflectors should also be placed in field-free regions, and to minimize any field distortion, the deflecting potentials should float on top of the potential within the region.

(5) Aberrations of Energy Selectors

Energy selectors suffer from what might be called 'chromatic' aberration, in that different energies are focussed at different points in the exit plane of the selector. Thus a finite energy spread will still remain in the final beam after passing through the selector. The base width of this energy spread is given by:

$$\Delta E_b = E_s \left( \frac{r_s}{L_s} + \beta \theta_s^n + \gamma \phi_s^2 \right)$$  \hspace{1cm} (2.3.9)

where:

- $E_s$ is the beam energy at the selector entrance (also called the analysis energy).
- $r_s$ is the beam radius in the selector.
- $L_s$ is the distance in a straight line between the selector entrance and exit positions.
- $\theta_s$, $\phi_s$ are the half angles of the beam in two perpendicular directions at the selector entrance.
- $\alpha$, $\beta$, $n$, and $\gamma$ are constants which depend on the selector geometry.

The following table lists the values of $L_s$, $\alpha$, $\beta$, $n$, and $\gamma$ for various types of selectors.
<table>
<thead>
<tr>
<th>SELECTOR TYPE</th>
<th>L</th>
<th>α</th>
<th>γ</th>
<th>μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 degree Hemispherical</td>
<td>2R</td>
<td>4.0</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>127 degree Cylindrical</td>
<td>1.75R</td>
<td>7.2</td>
<td>1.33</td>
<td>1.0</td>
</tr>
<tr>
<td>Parallel Plate Mirror</td>
<td>R*</td>
<td>4.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Cylindrical Mirror with 2nd order focus 3.39R*</td>
<td>6.5</td>
<td>5.54</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

R* is the mean radius of the orbit; R** is the maximum radius of the orbit.

From this table it is clear that the hemispherical analyzer is a good choice for an energy selector. The energy spread for this device is:

\[
\Delta E_b = E_S \left( 2 - \frac{r_s}{R} + \theta_s^2 \right) \tag{2.3.10}
\]

Thus, for a fixed \( r_s \), \( n \) and \( E_S \), it is desirable to make \( \theta_s \), the angular divergence of the beam, as small as possible. This can be done by arranging that the beam angle is zero; i.e. using a real window and a virtual (at infinity) pupil before the selector. Then \( \theta_s \) will be given by the pencil angle of the beam. Since \( \theta_s \), \( r_s \), and \( E_S \) are related by the Helmholtz-LaGrange equation, \( r_s \) cannot be made arbitrarily small, so it is also desirable to make \( R >> r_s \).

The quantity that is to be optimized at the target is not the base width of the final energy distribution, but the FWHM. This is not quite one-half of the base width, but is given by:
\[ \Delta E_{1/2} = E_S \left( \alpha_{1/2} \frac{r_S}{L_S} + \beta_{1/2} \theta_S^2 \right) \] (2.3.11)

where \( \alpha_{1/2} \) and \( \beta_{1/2} \) are empirically determined parameters which depend on the ratio of \( \theta_S^2 / (\alpha r_S / L_S) \). It turns out that \( \alpha_{1/2} \) is about equal to \( \alpha / 2 \), but \( \beta_{1/2} < \beta / 2 \).

The hemispherical energy selector also suffers from aberrations due to fringe fields in the gap between the hemispheres. This is due to the fact that half of each sphere is missing, and this must be corrected somehow so that the field in the gap has the proper \( 1/r \) dependence around the mean orbital radius of the beam. This is done by setting the potential of the last lens element to the mean energy of the beam in the selector and by introducing correction elements to modify the field in the gap. This will be discussed in greater detail in the next section.

(6) Optimization

Having discussed the various details of aberrations and limitations inherent in an electron optical system, it is clear that these effects are interrelated in some-complex fashion. Thus the effects cannot be considered and minimized independently, but some sort of optimization must be performed for a given set of specifications of the system. This has been very carefully and thoroughly done by the Manchester group, and has resulted in spectrometer systems such as the one used in this work. The focusing properties of various types of lenses have also been tabulated by Hart-
ing and Read* and these tables can be used in conjunction with the principles discussed above to design the optimum system to meet one's requirements.

2.3.3 Design of the Present Spectrometer

It is worthwhile to examine the design of spectrometer used in this work in the light of the previous section to see how it has been optimized. A complete discussion of this can be found in ref. 1 so only an overview will be given here.

Lens Elements

A brief discussion of thick lenses is included here to provide a basis for understanding the material that follows. Figure 2.7 shows a representation of a thick lens. As indicated, PP₁ and PP₂, are the first and second principal foci, F₁ and F₂, are the first and second principal planes, and h is the reference plane. p and q are the object and image distances, respectively. As in light optics, the relationship between these quantities is given by:

\[(p-F₁)(q-F₂) = f₁f₂\]  \hspace{1cm} (2.3.12)

and the linear magnification is given by:

\[M = -f₁/(p-F₁) = -(q-F₂)/f₂\]  \hspace{1cm} (2.3.13)

The behaviour of these lenses is determined by the voltage ratios between each lens element. Figure 2.8 (taken from Harting and Read*) illustrates this for a typical 3 element aperture lens.
Selector: Lens Stack 1

A schematic diagram of Lens Stack 1 is shown in Fig. 2.9. Indicated on this diagram are the voltages applied to each lens element (calculated for an analysis energy of 2.0 eV), the diameters of all apertures, the spacing between each element, and the calculated object and image distances for each lens. Several points should be noted about the design:

1. The electron source consists of a filament, grid and an anode, a triode configuration instead of a simple diode one. This enables one to extract somewhat more current from the cathode than would be possible with a diode. The presence of the grid, however, means that the effective position of the object is somewhat ill defined. For this reason, two oversize apertures are placed before lens L1 to limit the size of the beam and avoid problems caused by overfilling that lens.

2. Although a single lens could have been used to image the source onto the hemisphere's entrance plane, this would have meant that one of the defining apertures would not be in a field free region. Thus two lenses were used instead. Lens L1 focuses the source onto aperture A1, and L2 focuses A1 into the hemispheres. Aperture A2 is placed at the first focal point of L2, and is imaged at infinity. This ensures that the beam angle going into
the hemispheres is zero, as required.

(3) The center elements of lenses L1 and L2 were operated at higher potentials than their respective outer elements to minimize lens aberrations. The potentials on L1A, L1C and L2C were usually kept fixed, and focussing was done by varying L1B and L2B. This also provided some freedom of adjustment to correct for space charge effects, minor mechanical misalignment, and to minimize aberrations at the hemisphere entrance plane.

(4) With the diameter of the defining apertures fixed at 0.5 mm, the pencil angle of the beam at the energy selector was 0.037 rad for the lens potentials indicated on Fig. 2.9.

Selector: Lens Stack 2

A schematic diagram of Lens Stack 2 is shown in Fig. 2.10. As indicated on this diagram, Lens Stack 3 (on the analyzer) is the mirror image of Lens Stack 2; that is to say, Lens Stack 3 works the same way as Lens Stack 2, except in reverse. This can be done because electrostatic lenses are symmetric with respect to time reversal operations.

Lens Stack 2 is designed to provide a well defined beam at the target for a wide range of final energies. Again, two lenses are used to ensure that defining apertures are always placed in field free regions, and also eliminate the problems associated with placing a defining aperture too
close to the energy selector. It is also difficult to maintain the beam quality at the target with a single lens and still be able to 'zoom' the final energy. Note that the selector exit plane is imaged onto aperture A4, and aperture A3 is imaged at the target. Aperture A3 is placed at the second focal point of L3, and this guarantees that the beam angle at the target is close to zero. This arrangement in Lens Stack 3 also ensures that the beam angle going into the hemispheres is zero.

The last lens on the stack, L4, (first lens on stack 3 of the analyzer, L5) operates as a 'zoom' lens. It will operate over a wide range of target energies (up to 100 eV) while keeping the final beam properly focused at the target. Calculations have indicated that the lens properties remain constant for \( V(L4C)/V(L3C) > 1.5 \), provided \( V(L4B)/V(L3C) \) is chosen properly. This is shown in Fig. 2.11, taken from Ref. 1.

One additional point about Lens Stacks 2 and 3 is that they were designed to minimize the Boersch energy spreading at the target, making it negligible compared to the desired resolution. At a target energy of 50 eV and a beam current of 1 nA, the Boersch energy spreading is on the order of 0.01 meV for this spectrometer.

**Analyzer: Lens Stack 4**

Figure 2.12 shows a schematic diagram of Lens Stack 4, used to focus the exit plane of the hemispheres into the chaupeltron. A single lens is sufficient for this, since at
FIG 2.11
ZOOM LENS CHARACTERISTICS

M: Linear Magnification
D: Lens Diameter
V₁, V₂, V₃: Potentials Applied to L3C, L4B, Target
LENS STACK 4 PARAMETERS

L7A  L7B  L7C

Applied Voltage: 2 3.6 20

From Hemispheres

Aperture Diam. (mm): 6 4 4 .5 5 .5

Distances (mm): 11.5 14.3
9.5 2.2 6.3 4.4

Channeltron

FIG 212
this point one is more concerned about getting as much current to the channeltron as possible without overfilling the lens and accepting only those electrons from the hemispheres which have been properly energy selected than anything else. Thus one still requires defining apertures to limit the beam radius.

The Correcting Hoops

The correcting hoops are used to adjust the field in the gaps between the hemispheres so that it has the correct 1/r dependence throughout. Figure 2.13(a) shows the details of the correcting hoops, and Figure 2.13(b) shows how they modify the field in the gaps. The potentials indicated on Fig. 2.13(b) have been calculated for an analysis energy of 1.0 eV, by numerically solving Laplace's equation in the gaps with the shapes and potentials of the hoops as adjustable parameters.

The problem of field correction at the hemisphere gaps is an important one, and must be dealt with if the energy selector is to function properly. This is especially so in the present design, since the spacing between the hemispheres has been made rather large to minimize the effects of surface irregularities on the hemispheres (which would cause field distortion). The fringe field in the gap also becomes more of a problem, however, as the spacing increases. The use of 4 correcting hoops gives some freedom to obtain satisfactory field adjustment within the mechanical constraints of the hemispheres, and, since the potential
on each hoop can be varied independently, minor adjustments can be made to correct for various misalignments and deviations from the calculated operating conditions if necessary.

2.3.4 The Hemispherical Energy Selector

Since the 180 degree energy selector is at the heart of the spectrometer it is important to have some understanding of its principle of operation. Figure 2.14 shows a schematic diagram of the energy selector. Hemispheres $S_1$ and $S_2$ are kept at potentials $V_1$ and $V_2$, respectively. In the present spectrometer $R_2 = 2R_1$ and $R_0$, the radius of the 'equilibrium' orbit, is given by:

$$R_0 = \frac{(R_1 + R_2)}{2} = \frac{3R_1}{2}$$

In the following discussion we shall ignore the effects of the field in the gaps at the entrance and exit planes, as this is assumed to be corrected by the hoops.

The potential between the hemispheres is found by solving:

$$\nabla^2 \phi = 0$$

with the boundary conditions:

$$\phi(r=R_1) = V_1$$
$$\phi(r=R_2) = V_2$$
$$V_2 < V_1$$

Because of the spherical symmetry involved, the potential is a function of $r$ only, and is given by:
\[
\phi(r) = \frac{(V_2 - V_1) R_2 R_1}{r (R_2 - R_1)} + \frac{R_2 V_2 - R_1 V_1}{R_2 - R_1} \quad (2.3.4.1)
\]

The electric field is then given by:

\[
E(\hat{r}) = \frac{d\phi}{dr} = \frac{(V_2 - V_1)}{r^2} \frac{R_2 R_1}{(R_2 - R_1)} \quad (2.3.4.2)
\]

If the incoming beam has an energy \(E_0\) and enters at a radius \(R_0\), then for a circular orbit, equating the electrostatic force on the electrons to the centripetal force yields the transmitted energy:

\[
E_0 = \frac{(V_2 - V_1)}{2R_0} \frac{R_1 R_2}{(R_2 - R_1)} \quad (2.3.4.3)
\]

Expressing \(R_1\) and \(R_2\) in terms of \(R_0\), equation 2.3.4.3 becomes:

\[
E_0 = -2(V_2 - V_1)/3
\]

Thus, to transmit an energy of 2.0 eV, for example, requires a potential difference of 3 volts between the hemispheres. It is advisable to choose \(V_1\) and \(V_2\) close to the analysis energy to minimize the distortion of the field in the gaps, and so putting \(V_1 = 4\) volts and \(V_2 = 1\) volt will satisfy this condition.

Another property of the hemispherical energy selector is
that it will focus the entrance plane onto an exit plane which is 180 degrees 'away' (hence the name). To see this, one writes down the Lagrangian of the system and solves the equations of motion in the limit of small deviations from the equilibrium orbit. The results are equations of the form:

\[ \frac{d^2(\Delta X)}{dt^2} + \omega_0^2(\Delta X) = 0 \]

where

\[ \omega_0 = \left(\frac{2eE_0}{mR_0^2}\right)^{1/2} \]

is the angular frequency of the electrons inside the hemispherical region. Thus, when \( \omega_0 t = \pi \) rad, the electrons will have travelled through 180 degrees, and will be focussed on a plane at this point.

2.3.5 Operation and Performance of the Spectrometer

Operating the spectrometer can be defined as transporting the electron beam from the cathode, through the selector, and into the target region. If scattered electrons are to be detected, then they must be transported from the target region, through the analyzer, and into the channeltron. All of this must be done in such a way as to achieve the optimum current and energy resolution for a given set of operating potentials, both at the target and at the channeltron.

The spectrometer can be 'tuned up' by monitoring the current on the apertures A1-A6. This can best be illustrated by way of an example. First, the potential on L2C is set to the desired analysis energy by adjusting the SCALE poten-
Table 2.3
Spectrometer Operating Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Theoretical Value</th>
<th>Actual Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pil</td>
<td>4.554</td>
<td></td>
</tr>
<tr>
<td>C.P.</td>
<td>+0.243</td>
<td></td>
</tr>
<tr>
<td>Grid</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>Anode</td>
<td>90.0</td>
<td>66.49</td>
</tr>
<tr>
<td>D1X</td>
<td>+24.27</td>
<td></td>
</tr>
<tr>
<td>D1Y</td>
<td>+11.58</td>
<td></td>
</tr>
<tr>
<td>L1B</td>
<td>210.0</td>
<td>158.6</td>
</tr>
<tr>
<td>L1C</td>
<td>15.00</td>
<td>15.87</td>
</tr>
<tr>
<td>D2X</td>
<td>+10.37</td>
<td></td>
</tr>
<tr>
<td>D2Y</td>
<td>-1.865</td>
<td></td>
</tr>
<tr>
<td>L2B</td>
<td>3.25</td>
<td>3.50</td>
</tr>
<tr>
<td>L2C</td>
<td>6.00</td>
<td>6.00</td>
</tr>
<tr>
<td>S1</td>
<td>1.250</td>
<td>1.250</td>
</tr>
<tr>
<td>S2</td>
<td>3.202</td>
<td>3.202</td>
</tr>
<tr>
<td>X1</td>
<td>2.849</td>
<td>2.849</td>
</tr>
<tr>
<td>X2</td>
<td>2.184</td>
<td>2.184</td>
</tr>
<tr>
<td>X4</td>
<td>1.901</td>
<td>1.901</td>
</tr>
<tr>
<td>L3B</td>
<td>32.35</td>
<td>32.35</td>
</tr>
<tr>
<td>D3X</td>
<td>+2.038</td>
<td></td>
</tr>
<tr>
<td>D3Y</td>
<td>+21.50</td>
<td></td>
</tr>
<tr>
<td>D4X</td>
<td>-23.19</td>
<td></td>
</tr>
<tr>
<td>D4Y</td>
<td>-4.864</td>
<td></td>
</tr>
<tr>
<td>h3C</td>
<td>25.00</td>
<td>24.31</td>
</tr>
<tr>
<td>L4B</td>
<td>82.5</td>
<td>124.0</td>
</tr>
<tr>
<td>Resolution</td>
<td>12.5 meV</td>
<td>20.0 meV</td>
</tr>
<tr>
<td>Peak Rate</td>
<td>35 kHz</td>
<td></td>
</tr>
</tbody>
</table>
tiometer. This determines the resolution of the final beam.
The rest of the lens elements are then set at or near the
calculated operating potentials. These potentials scale
linearly with the analysis energy; i.e., if the analysis
energy is changed from 2 volts to 4 volts, say, then the
potentials of the rest of the lens elements must be doubled
from the calculated values (at 2 eV analysis energy). The
filament is turned on and enough current is sent through it
to give a reasonable amount of emission (10 μA, for insta-
tance). One then adjusts the deflectors and lens elements
to maximize the current on A1 and then A2. The potential on
S1 is temporarily set to 0 to allow all the electrons enter-
ing the hemispheres to be collected on S2. The CONTACT
POTENTIAL is adjusted to maximize the current on S2, as are
the deflectors and lens elements. After this is done, S1 is
reset to the correct potential, and the current on A3 is
then maximized. The current reaching A4 is maximized, and
then one attempts to look for signal coming from the inter-
action region. Suppose that one desires to look for meta-
stable atoms in Neon, for example. With a suitable Ne gas
pressure, the electron beam is focused into the target
region at an energy where a known peak in the metastable
spectrum exists. Once a real signal is found, one then
tries to maximize the signal to noise ratio as well as
achieving the optimum energy resolution of the spectrometer.
This can be done by making small adjustments to the lens
element potentials and the deflector potentials until a
satisfactory compromise between resolution and signal-to-
noise is found. A typical metastable excitation spectrum in Ne (see Chapter 3 for one in Ar) is shown in Fig. 2.15, and Table 2.3 shows the operating characteristics of the spectrometer associated with this spectrum.

The spectrometer is also capable of energy analyzing scattered electrons. This is done by determining the amount of energy lost by electrons in collisions with target atoms. The energy loss power supply is used to add energy to the scattered electrons before entering the analyzer by floating the analyzer ground above the selector ground. The analyzer is tuned to accept only those electrons which have the correct energy, namely the energy set by the target potential. Electrons which have lost energy in collisions will reach the detector only if the amount of energy lost is equal to the potential difference between the analyzer and selector grounds. This energy loss can be varied by a ramp voltage from a multichannel analyzer, for instance, and an energy loss spectrum is obtained in this way. As with the selector, the analyzer half must be adjusted to maximize the signal-to-noise ratio, as well as achieving an optimum resolution. Energy loss spectra in N₂ and N₂ are shown in Chapter 4. These are by no means high resolution spectra; the estimated overall resolution is 100 meV. The spectrometer is certainly capable of much better resolutions; overall resolutions of about 30 meV were obtained routinely in initial testing of the device.
2.4 APPENDIX

This appendix contains additional construction details of the spectrometer in the form of scale diagrams. They are not necessary to the understanding of the device, and thus were not included earlier. It was felt, however, that it would be useful to include them for future reference purposes.
CHAPTER 3

NEGATIVE ION RESONANCES IN THE RARE GASES
3.1 INTRODUCTION

This chapter discusses the production of resonance structures in the metastable excitation spectra of the rare gases and the analysis and interpretation of these structures. The energy region of interest in the present work lies in the doubly excited state region (above the first ionization threshold). The region below the first ionization threshold has been extensively studied, and in the metastable channel the definitive work is that of Brunt et al. who were able to resolve a wealth of structure with the aid of a high resolution electron spectrometer. The doubly excited state region has also been the subject of intensive study using a variety of techniques and observation channels. In Ne, for example, measurements have been made on ion production, differential electron scattering, electron transmission, trapped electron production, broadband photon production and metastable production. In recent years many of these authors have applied their methods to the other rare gases as well. In many cases a large number of structures have been observed and accurate identification has proved difficult, particularly since the energy ranges covering the inner shell and doubly excited states exhibit much overlap. Two factors have emerged, however, which lead to a simplification of the situation. First, it appears that in certain observation channels the features are predominantly due to negative ion resonance formation rather than neutral auto-ionizing states, for example. Second, it has been found possible to unambiguously identify the resonances involved
in Se$_{10}$.

A comparison between the lower energy (i.e., below the first I.P.) data of Sanche and Schulz \cite{SancheSchulz54} and Brunt et al \cite{Brunt54} reveals that essentially every feature in the former data can be identified with a negative ion resonance. In the higher energy region, a comparison can also be made in Ne with the data of Spence \cite{Spence54} and again it is found that negative ion resonances dominate Sanche and Schulz's data. It is reasonable to suppose that this conclusion is valid for the other rare gases as well. In addition, it would appear that the differential inelastic scattering data \cite{Julian73,Julian74,Julian75} are also dominated by negative ion resonances and show an almost one-to-one correspondence with the data of Sanche and Schulz. In the light of all this, Spence's conclusion \cite{Spence54}, based on an analysis of possible resonance decay modes, that low-$n$ excitation functions should demonstrate structures preferentially due to negative ion resonances, would seem to be justified. High-$n$ excitation functions, on the other hand, are more likely to display auto-ionization features since these states are more closely coupled to this channel via post-collision-interaction (PCI) effects \cite{Spence55}.

Based on these ideas it was felt that a good channel to search for negative ion resonances in the rare gases in the doubly excited state region would be the metastable excitation channel. This possesses certain advantages and simplifications from an experimental point of view, and has been demonstrated to be very rich in resonance structures at
lower energies. Previous studies in this channel have been limited to some low resolution work in Ne\textsuperscript{12} and a much more extensive study in Ar\textsuperscript{17}.

The present work presents high resolution data for Ne, Ar and Kr, and a discussion of the analysis and identification of the observed structures is also undertaken. Two reports have already been presented previously\textsuperscript{18,19}.

The rest of this chapter is divided into four sections. Section 3.2 provides a theoretical framework for the understanding of resonance formation and the analysis of the resonance data. Section 3.3 describes the experimental details involved: the interaction region, energy calibration, and data collection. Section 3.4 presents the data and results of the analysis, and section 3.5 presents conclusions drawn and suggestions for further research.
3.2 THEORETICAL BACKGROUND

3.2.1 Resonance Formation

For reasons of simplicity this discussion of resonance formation will be limited to the metastable excitation channel only. Clearly the metastable channel is not the only one available in which to study resonances, but, as mentioned in the introduction, it is certainly rich in these structures.

Basically a negative ion resonance forms when an electron interacts with a target atom in such a way as to be captured by it for a short time, creating a temporary negative ion. The ion eventually decays, leaving the atom in some final state (not necessarily the same as the initial state) and releasing the captured electron. This phenomenon generally results in a rather pronounced change in the cross-section being measured, and is characterized by the shape and also the width of the feature, as well as the energy at which it occurs. The width of the feature is characteristic of the lifetime of the resonant state. The process involved in forming the resonance can either be elastic (no excitation of the atom) or inelastic (the atom undergoes excitation before the resonance is formed). The latter is the case in the present situation, where the process of interest is:

\[
e^{-} + X[ns^{2}np^{6}(1s_{0})] \rightarrow X[ns^{2}np^{5}(2s)]\text{mlm}^1 \rightarrow X[ns^{2}np^{5}(2p)(n+1)s(2s+1p_{2p})] + e^{-} (3.2.1a)
\]
and/or:

\[ e^- + X(\text{ns}^2\text{np}^6\{1S_0\}) \]
\[ X^- (\text{ns}^2\text{np}^5\{3P, 1D, 1S\} \text{ulmnl'nl''}) \]
\[ X(\text{ns}^2\text{np}^5\{2P\} (n+1)s\{2S+1P\}) + e^- \]

(3.2.1b)

where \(X(\text{ns}^2\text{np}^6\{1S_0\})\) denotes a rare gas atom in its ground state and \(X(\text{ns}^2\text{np}^5\{2P\} (n+1)s\{2S+1P\})\) is the metastable state which is finally detected. Note that equation (3.2.1a) denotes inner shell excitation and that equation (3.2.1b) denotes two electron excitation. Direct production of the metastable state is also possible and this will form a continuous background upon which resonance structures are superimposed. In addition to this, there is also the possibility of Rydberg metastable species contributing to the observed signal and producing structures which might erroneously be attributed to negative ion resonances. This results in at least six channels which can contribute to the observed metastable signal, not to mention additional channels (eq. auto-ionization) which may also be present. The overlapping of these channels leads to interference effects in the metastable cross-section, making identification and classification of features difficult and often ambiguous. This state of affairs is clearly reflected in the present state of the literature, as any survey of the problem will show.

To understand how resonance formation affects the behaviour of the metastable cross-section generally requires the use of multi-channel scattering theory. The large number of
available channels makes this a formidable problem to solve, but it is possible to greatly simplify the situation in some cases.

Consider the case of one resonance channel well separated from all other channels. This reduces the problem to essentially a single channel one, which is dealt with in most texts dealing with scattering theory (see, for example, Taylor, for a complete discussion).

By using a partial wave analysis, the scattering cross-section can be written as:

$$\sigma = \sum_{\ell} 4\pi(2\ell+1)|f_{\ell}(p)|^2$$  \hspace{1cm} (3.2.2)

where

$$f_{\ell}(p) = \frac{i\delta_{\ell}(p) \sin \delta_{\ell}(p)}{p}$$

is the scattering amplitude and $\delta_{\ell}(p)$ is the scattering phase shift for the $l$-th partial wave. Now a resonance usually has a well-defined orbital angular momentum associated with it, and so one partial wave in particular will dominate the scattering process near the resonance. Thus the scattering cross-section is:

$$\sigma_{\ell} = \frac{4\pi}{p^2} (2\ell+1)\sin^2 \delta_{\ell}(p)$$  \hspace{1cm} (3.2.3)

It is the behaviour of the scattering phase shift which det-
ermines the behaviour of the resonance; \( \delta \) is composed of two parts: a resonant part, \( \delta_{\text{res}} \), which varies rapidly with \( p \); and a background part, \( \delta_{\text{bg}} \), which varies slowly with \( p \). Figure 3.1 illustrates typical resonance profiles for different values of the background phase shift. Near the center of the resonance, the resonant phase shift is:

\[
\sin \delta_{\text{res}}(p) = \frac{\Gamma/2}{(E - E_R)^2 + (\Gamma/2)^2} \quad (3.2.4)
\]

where \( \Gamma \) is the width of the resonance and \( E_R \) is the resonance energy. Using the fact that the phase shift is composed of two parts, we can write:

\[
\sin \delta_{\text{res}}(p) = \sin(\delta_{\text{res}}(p) + \delta_{\text{bg}}(p))
\]

which is:

\[
\sin \delta_{\text{res}}(p) = \sin \delta_{\text{res}}(p) \sin \delta_{\text{bg}}(p) \left( \cot \delta_{\text{res}}(p) + \cot \delta_{\text{bg}}(p) \right)
\]

Define:

\[
q = \cot \delta_{\text{bg}}(p) \\
\varepsilon = \cot \delta_{\text{res}}(p) = 2(E - E_R) / \Gamma
\]

Then the scattering cross-section is given by:

\[
\sigma = \frac{4\pi}{p^2} \frac{(q + \varepsilon)^2}{(1 + \varepsilon)^2} \quad (3.2.5)
\]

This is the usual Fano formula for the behaviour of the cross-section near a resonance. If \( q = 0 \), then the result is the familiar Breit-Wigner formula.
Equation 3.2.5 is often parametrized and is then used to fit experimental data to obtain the various parameters. This parametrization is:

$$f(x; a) = a_1 \frac{(a_2 + c)^2}{(1 + c)^2} + a_3; c = \frac{2(x-a_2)}{a_4}$$  \hspace{1cm} (3.2.6)$$

where

- $a_1$ = amplitude of the feature
- $a_2$ = shape parameter (due to background)
- $a_3$ = resonance position
- $a_4$ = resonance width
- $a_5$ = amplitude away from resonance

In order to extract the values of these parameters from the experimental data it is first necessary to convolute equation 3.2.6 with the energy profile of the incident electron beam. The apparatus profile is written as a Gaussian distribution:

$$g(x) = \frac{1}{a_6 \sqrt{\pi}} \exp\left(-\frac{x^2}{2a_6^2}\right)$$  \hspace{1cm} (3.2.7)$$

where $a_6$ is the FWHM of the profile. A fitting routine which included the apparatus profile was developed and applied to some of the more isolated features in the spectra(*). The results of the fitting procedure are discussed

(*): Routine developed by William van Wijngaarden
in Section 3.4

3.2.2 Analysis Techniques Used

Once the sharp features in a metastable excitation cross-section have been positioned in energy, the task of deducing the identification of these features begins. As mentioned in the introduction, this is a rather complicated task, but there are some significant observations which simplify matters somewhat.

(1) The metastable channel is dominated by negative ion resonances thereby eliminating much of the complications due to neutral states.

(2) The negative ion resonances have been unambiguously identified in Ne.

(3) There is a systematic behaviour involved for equivalent resonances in the different rare gases. Much of this is due to the fact that the coupling between the excited electrons is the same for equivalent resonances, and that the influence of the core is not the dominant effect. Thus it is possible to establish simple relationships linking the energies of equivalent resonances in the different rare gases to the corresponding binding energies relative to the positive ion cores involved.

Two techniques which make use of the simple relationships are available at the present time. These give some insight into the nature and validity of the proposed relationships,
and are aids in classifying features in the metastable excitation spectra. The first approach is a graphical one due to Spence\textsuperscript{21}. This technique was previously found useful for classifying negative ion resonances in molecules. The second approach, suggested by Needle\textsuperscript{22}, and developed extensively by Read\textsuperscript{23}, who devised a "modified Rydberg" formula to predict the energies of resonances in different gases. These two techniques will be discussed in turn to illustrate how they can be used in the present situation.

The Graphical Approach

This technique has as its basis the idea that the energies of equivalent resonances in the heavy rare gases could be represented by an equation of the form:

\[ E = AI + B \]  \hspace{1cm} (3.2.8)

where \( I \) is the appropriate ionization potential (of the core), \( A \) is a constant close to unity, and \( B \) is another constant. To gain some insight into the significance of this it is instructive to apply such an analysis to the data of Cowling and co-workers\textsuperscript{24-27}. They measured photo-absorption cross-sections in the heavy rare gases using a synchrotron radiation source and observed a number of resonance (autoionizing) structures in their spectra. Let us examine the behaviour of the \([n\text{sn}p^6](2S) (n+k)p \cdot (z=1 \text{ to } 6)\) states in the different rare gases. Figure 3.2(a) shows a plot of ionization potential vs energy for this series, and it can be seen that very good straight lines can be drawn joining equivalent configurations. This illustrates the behaviour indicated by equation 3.2.8. Now, turning to Fig.
3.2(b), which is a plot of binding energy (or the resonance) vs energy for the same series, once again it can be seen that good straight lines join equivalent resonances (note that the data of Fig. 3.2(b) are equivalent to that of Fig. 3.2(a), but that the vertical scale is much finer, allowing one to see any deviations from a linear relationship). The notable exception to the linear relationship is $\Delta E$; the deviation increases as the outer electron gets closer to the core. The other bit of information apparent on Fig. 3.2(b) is the decrease in the slopes of the lines joining equivalent resonances as the value of $k$ increases. The numerical values of the slopes are indicated beside each line on Fig. 3.2(b). The slope is largest for the the $(n+1)p$ configuration and practically zero for the $(n+6)p$ configuration. This behavior has an immediate interpretation, namely, the slope of the line joining equivalent resonances must reflect the amount of interaction the outer electron has with the core, and that this interaction increases as one progresses from He to Ar. Thus, the energy of the $(n+m)p$ states could be written as:

$$E_{n} = E_{n} - \langle n|\tilde{V}|n+1 \rangle - \langle n|\tilde{V}|\text{core} \rangle$$

(3.2.9)

where $E_{n}$ is the ionization potential appropriate to each gas, $\langle n|\tilde{V}|n \rangle$ represents the interaction of the electron with the pure Coulomb field of the ion core, and $\langle n|\tilde{V}|\text{core} \rangle$ represents the other interactions the electron has with the core. It should be pointed out that equation 3.2.9 is simply another way of expressing the normal Rydberg-Szöke equation. The other interactions are contained in
FIG 3.2(a): I.P. vs Energy: \([n\text{snp}^6]^{(2S)}(n\cdot k)p\)
the quantum defect of the electron in this case. Equation
3.2.9 also sheds light on the deviation of Ar from this
"rule". The systematic behavior is "violated" because the
Ar+ core has a much greater influence on the outer electron
than the other gases do.

The other interactions between the electron and the core
would be dominated by the penetration of the electron into
the core (the essence of quantum defect theory), but the pec-
uliar behavior of Ar suggests that an additional term is
present. The nature of this additional term is probably
related to configuration interaction effects, which are
known to be strong in Ar. These effects are normally accom-
panied by a mutual repulsion of the states involved. Thus
the Ar term considered here could acquire a larger binding
energy.

The deviations from the linear relationship are not ap-
parent on Fig. 3.2(a) because the scale is too coarse to high-
light them. It would appear that this technique is good as
a first approximation to determine the energies, and to at
least identify the configuration of the features observed.

Having seen that the "graphical" approach is useful for
the simple case of one excited electron, the next question
to ask is, "How does it work for two excited electrons"? This
has been dealt with by Spence, who used the data of
Sanche and Schulz and Bruntet al to demonstrate the use-
fulness of equation 3.2.8. He did not plot binding energy
vs resonance energy for the data used, however, but did
demonstrate the applicability of the graphical approach.

Thus, it is proposed that a similar equation for the resonance energy can be written down for two electrons as was the case for a single electron, namely:

\[ E_{n''} = E_n - \langle n''|V|n''\rangle - \langle n''|V'|\text{core}\rangle \]  \hspace{1cm} (3.2.10)

where \( E_n \) is again the appropriate ionization potential, \( \langle n''|V|n''\rangle \) represents the interaction of two electrons with the core Coulomb field, and \( \langle n''|V'|\text{core}\rangle \) represents the other interactions of the electrons with the core. The normal Coulomb interaction term would presumably also include electron-electron interactions, and the strength of the other term is reflected in the slope of the line joining equivalent resonances.

When one considers the case of three excited electrons outside of a doubly ionized core, there is no data available to make an analysis of this type at the moment. However, having established the significance of the linear relationship and the deviations from it, it would seem to be a reasonable approach to use when attempting to analyze the present data. The success of this approach, then, remains to be seen for this case.

Thus, to analyze the data obtained in the present experiment, the graphical approach will be used as outlined above. It is reasonable to suppose that it will work above the first ionization threshold, as it did for resonances below the threshold. Even if the linear relationship is not strictly valid, the deviations from it are themselves signi-
significant and can be used to gain insight into the physics of resonance formation in this energy region. Also, the fact that the graphical approach works as a first approximation means that it can be used to identify major features or at least put limits on the possible classifications.

The Modified Rydberg Formula

This is an intuitive extension (proposed by dead^{23}) of the familiar Rydberg-Ritz equation:

\[ E_{nl} = \frac{I_n - RZ^2}{(n - \delta_{nl})^2} \tag{3.2.11} \]

where:

- \( I \) is the ionization potential
- \( R \) is the Rydberg constant (13.606 eV)
- \( Z \) is the charge of the core
- \( n, l \) are the radial and angular momentum quantum numbers
- \( \delta_{nl} \) is the quantum defect

For the case of two excited electrons, the modified Rydberg equation is:

\[ E_{n_1n_1'} = I_n - R(Z-\sigma)²((n-\delta_{n_1})^{-2}+(n-\delta_{n_1'})^{-2}) \tag{3.2.12} \]

The assumptions involved in this extension are:

1. The two outer electrons will screen each other to some extent from the core, and that both electrons experience the same amount of screening, independent of the value of \( l \) (i.e.
the screening is the same for nl and nl' electrons). Thus each electron experiences an effective charge \( Z - \sigma \), where \( \sigma \) is the screening constant.

(2) The presence of the second electron does not influence the penetration of the first electron into the core. Thus, the quantum defects for the nl and nl' electrons are the same as they would be for a single nl (or nl') electron outside of the same core. The quantum defects can then be obtained from the [core]nl energies using equation 3.2.11, after taking into account the level splittings due to exchange and magnetic interactions.

The screening constant is related to the amount of correlation between the two electrons (see Appendix 3.6.2). For completely correlated electrons, the screening constant has the value of 0.25, and for completely uncorrelated electrons, it has the value of 0.5. The recent work of Lin on electron correlations indicates that the two electrons would tend to stay on opposite sides of the core, and thus, a high degree of correlation is to be expected in this case. In fact, Wood found that the average value of the screening constant was 0.254 for two excited electrons in a variety of gases using his analysis.

For the case of three excited electrons outside the core, with the configuration [core]nlnl'nl'', the extension pro-
posed by acad is:

\[ E_{n'l'n'l''} = I_n - R(Z-2\sigma)^2((n-\delta_{n'l'})^{-2} + (n-\delta_{n'l''})^{-2}) \]

(3.2.13)

For completely correlated electrons (on the vertices of an equilateral triangle), the screening constant has the value of 0.269.

To use the modified Rydberg formula in the present case, one first determines the quantum defects for each electron in each gas using the normal Rydberg-Ritz equation. Then the screening constants for each configuration in Ne are deduced from the resonance data, and these are used to predict the energies of equivalent resonances in the other gases. The results of this are discussed in section 3.4.
3.2.1 The Interaction Region

Figure 3.3 shows a scale diagram of the interaction region used to detect metastable atoms. Note that the gas beam enters the interaction region from below the electron beam and drifts up into the detector. Only metastable atoms (and in principle, VUV protons) are detected in this arrangement. All non-metastable excited atoms decay long before they reach the channeltron and charged particles are kept out of the detector by suitably biased grids - positive ions are discriminated against by a grid kept at a potential of about +20 volts, and negative ions/electrons are kept out by biasing the channeltron cone at -250 volts.

The gas beam itself was produced by a single capillary needle made from platinum-iridium alloy (non-magnetic), and gas simply effused out or the capillary under pressure (1 to 5 torr) into the interaction region. A single capillary was used instead of a multi-channel array for the gas source to minimize the total gas load on the vacuum system. The electron beam passed through the gas just above the end of the needle, through the region of highest density, thus ensuring high signal rates.

The interaction region was kept field free by the use of a molybdenum shielding arrangement kept at the same potential as L4C and L5A. The needle, although the facility to bias it with respect to the target region was available, was
also kept at the same potential as the target.

3.3.2 Data Collection and Calibration

Figure 3.4 shows a block diagram of the electronics used in the collection of the data, and Table 3.1 lists the relevant components. The TN-1710 multichannel analyzer was used in conjunction with the TN-1251 ramp generator to vary the incident electron energy to obtain a metastable excitation spectrum.

As mentioned above, the possibility of detecting VUV photons exists, but solid angle limitations and the lower quantum efficiency of the channeltron for photons restricted this to less than 0.1 percent, whereas the detection efficiency for metastable atoms approached 100 percent. In addition to this, a comparison of the present Ar data to that of Marchand and Cardinal reveals an almost one-to-one correspondence between the two sets of data. These authors used a pulsed excitation technique to discriminate against photons, so this comparison suggests that photons contributions to our observed signal were indeed negligible. Thus, no attempts were made to discriminate against photons in the present work.

The absence of any structure near the ionization threshold in the present data and that of Brunt et al suggests that high-n Rydberg species represented only a minor contribution to the observed signal.
INTERACTION REGION: METASTABLE DETECTION

FIG 3.3
FIG 34
METASTABLE DETECTOR ELECTRONICS
FIG 3.5 Ar Calibration Spectrum

(a)

(b)
### Table 3.1
Components - Metastable Detection - Electronics

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kepco HE2AM Power Supply</td>
<td>Grid Bias</td>
</tr>
<tr>
<td>Power-One 250 VDC Supply</td>
<td>Channeltron Cone Bias</td>
</tr>
<tr>
<td>Tennelec AEC-5000 Power Supply</td>
<td>Channeltron High Voltage Supply</td>
</tr>
<tr>
<td>Ortec 460 NIM Module</td>
<td>Delay Line Amplifier</td>
</tr>
<tr>
<td>Ortec 421 NIM Module</td>
<td>Integral Discriminator</td>
</tr>
<tr>
<td>Ortec 441 NIM Module</td>
<td>Proportioner</td>
</tr>
<tr>
<td>Tracor Northern TN-1710</td>
<td>Multi-Channel Analyzer</td>
</tr>
<tr>
<td>Tracor Northern TN-1251</td>
<td>Ramp Generator (0-10 v)</td>
</tr>
</tbody>
</table>
Typical counting rates approaching $100\text{kHz}$ were readily obtainable in the present set-up and the energy resolution of the incident electron beam was estimated to be 20-30 meV at the most. This value was arrived at by examining the initial fast rise in the metastable spectrum of Fig. 3.5 (see inset a). Also shown in Fig. 3.5 is a similar spectrum (inset b) taken from Brunt et al., using a similar spectrometer but operated at a much higher resolution. Since the features of interest represented a small fraction (about $10^{-4}$) of the total signal, data collection times were 2 to 3 days in order to gain statistical significance. The data was then transferred to a PDP-8/E computer for analysis and plotting. In order to highlight the features present in the spectra the large background was removed. In some cases a constant or linear background was removed, while in others a subtraction routine which removed the low frequency oscillations from the data was used (see Appendix 3.6.3).

Accurate energy calibration of the spectra was achieved by using the known positions of the sharp features below the first ionization threshold. A calibration spectrum was taken before the data was acquired and also after data collection was stopped. This allowed the energy per channel to be determined as well as the 'contact potential' or difference between the starting value of the incident energy (measured as target potential) and the actual value. The positions of the sharp features could then be determined.
to 25 meV or better in this way. The energies given in the tables of the next section are averages obtained from a number of spectra for each gas. A typical calibration spectrum is shown in Fig. 3.5, taken with Ar as the target gas.
3.4 RESULTS AND DISCUSSION

3.4.1 Introduction and Analysis

The data obtained are displayed in figures 3.6(a), 3.7 and 3.8, which show reestable excitation spectra for Ne, Ar and Kr, respectively. As can be seen a large number of features are evident, and the most prominent of these are listed in tables 3.2, 3.3 and 3.4. These tables also include data from other authors for comparison purposes, and also some widths for the more isolated features (where a reasonable curve fitting procedure (see section 3.2.1) could be applied). It should be stressed at this point that the current analysis seeks to provide a framework for the major features observed; no attempt was made to discuss the fine detail superimposed on the larger features, as has been done by other authors.

As a first step in the analysis consider the Ne spectrum of Fig 3.6(a), where the features are all fairly distinct and well separated. A comparison of this data with that of Spence reveals the following significant facts:

1. An exact one to one correspondence occurs in the position of each feature (see Table 3.2).
2. Good correspondence is obtained if a visual comparison of the respective profiles in both sets of data is made. Such a comparison is justified since something close to a total cross-section is being measured in both cases.
3. Although this is probably not as significant
<table>
<thead>
<tr>
<th>Feature</th>
<th>Present Data (eV)</th>
<th>Energy</th>
<th>Spence (10) Config.</th>
<th>Width (a) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>42.11</td>
<td>42.98</td>
<td>[3p]^{++}3s^{2}3p</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>43.10</td>
<td>43.06</td>
<td>[2S]^{2}3s^{2}(2S)</td>
<td>0.070±0.028</td>
</tr>
<tr>
<td>c</td>
<td>43.67</td>
<td>43.69</td>
<td>[2S]^{+}3s3p</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>43.86</td>
<td>44.05</td>
<td>[3p]^{++}3s3p^{2}</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>44.07</td>
<td>44.37</td>
<td>[3p]^{++}3s3p^{2}</td>
<td>0.050±0.020</td>
</tr>
<tr>
<td>f</td>
<td>44.36</td>
<td>45.17</td>
<td>[3p]^{++}3s3p^{2}</td>
<td></td>
</tr>
<tr>
<td>q</td>
<td>45.25</td>
<td>45.42</td>
<td>[2S]^{+}3p^{2}</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>45.45</td>
<td>46.52</td>
<td>[2S]^{+}4s^{2}(2S)</td>
<td>0.035±0.010</td>
</tr>
<tr>
<td>i</td>
<td>46.53</td>
<td>46.88</td>
<td>[2S]^{+}4s4p</td>
<td></td>
</tr>
<tr>
<td>j</td>
<td>46.97</td>
<td>47.60</td>
<td>[2S]^{+}5s5p</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>47.38</td>
<td>49.04</td>
<td>[1S]^{+}3s^{2}3p^{2}</td>
<td></td>
</tr>
<tr>
<td>l</td>
<td>47.64</td>
<td>49.04</td>
<td>[1S]^{+}3s^{2}3p^{2}</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>49.02</td>
<td>49.04</td>
<td>[1S]^{+}3s^{2}3p^{2}</td>
<td></td>
</tr>
</tbody>
</table>

(a) These widths were obtained by fitting a Fano profile to the observed data (see text).
<table>
<thead>
<tr>
<th>Present Value</th>
<th>Predicted Value (see text)</th>
<th>Tentative Classification</th>
<th>Sancho &amp; Schulte'6</th>
<th>Ray and Eecotte'13</th>
<th>Merchan'd &amp; Cardinal'17</th>
<th>Bolduc et al.'06</th>
<th>Lefalvred &amp; Barret'44</th>
<th>Width (in 0) (o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>24.54</td>
<td>[3s3p^6]1^2S^1s^2(5S)</td>
<td>24.49-24.50</td>
<td>24.49-24.51</td>
<td>24.55</td>
<td>-</td>
<td>-</td>
<td>59±15</td>
</tr>
<tr>
<td>b</td>
<td>24.99</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>25.03</td>
<td>[24.95/25.20]</td>
<td>[24.96/25.25]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>c</td>
<td>26.54</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>26.55</td>
<td>26.50</td>
<td>[26.65]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>d</td>
<td>27.08</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>26.84-26.90/27.07</td>
<td>[26.92/27.15]</td>
<td>[26.95]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>e</td>
<td>27.30</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>27.08</td>
<td>27.09-27.09</td>
<td>[27.05]</td>
<td>[27.05]</td>
<td>[27.05]</td>
<td>75±10</td>
</tr>
<tr>
<td>f</td>
<td>28.00</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>28.00</td>
<td>28.00</td>
<td>[28.00]</td>
<td>[28.00]</td>
<td>[28.00]</td>
<td>75±10</td>
</tr>
<tr>
<td>g</td>
<td>28.44</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>28.44</td>
<td>28.44</td>
<td>[28.44]</td>
<td>[28.44]</td>
<td>[28.44]</td>
<td>75±10</td>
</tr>
<tr>
<td>h</td>
<td>28.98</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>28.98</td>
<td>28.98</td>
<td>[28.98]</td>
<td>[28.98]</td>
<td>[28.98]</td>
<td>75±10</td>
</tr>
<tr>
<td>i</td>
<td>29.44</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>29.44</td>
<td>29.44</td>
<td>[29.44]</td>
<td>[29.44]</td>
<td>[29.44]</td>
<td>75±10</td>
</tr>
<tr>
<td>j</td>
<td>29.86</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>29.86</td>
<td>29.86</td>
<td>[29.86]</td>
<td>[29.86]</td>
<td>[29.86]</td>
<td>75±10</td>
</tr>
<tr>
<td>k</td>
<td>30.33</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>30.33</td>
<td>30.33</td>
<td>[30.33]</td>
<td>[30.33]</td>
<td>[30.33]</td>
<td>75±10</td>
</tr>
<tr>
<td>l</td>
<td>31.30</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>31.30</td>
<td>31.30</td>
<td>[31.30]</td>
<td>[31.30]</td>
<td>[31.30]</td>
<td>75±10</td>
</tr>
<tr>
<td>m</td>
<td>31.71</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>31.71</td>
<td>31.71</td>
<td>[31.71]</td>
<td>[31.71]</td>
<td>[31.71]</td>
<td>75±10</td>
</tr>
<tr>
<td>n</td>
<td>32.12</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>32.12</td>
<td>32.12</td>
<td>[32.12]</td>
<td>[32.12]</td>
<td>[32.12]</td>
<td>75±10</td>
</tr>
<tr>
<td>o</td>
<td>32.40</td>
<td>[3s3p^6]1^2P^1s^2(5P)</td>
<td>32.40</td>
<td>32.40</td>
<td>[32.40]</td>
<td>[32.40]</td>
<td>[32.40]</td>
<td>75±10</td>
</tr>
</tbody>
</table>

Brackets placed around an energy indicate that a different designation was given by the authors.

(a) Because of the very close correspondence between this data and our own, we have included the energies of the features which most closely correspond to the equivalent features in our data. These authors list and discuss many other smaller features which are apparent on their spectra.

(b) Features not tabulated by authors but apparent on graphs.

(c) These widths were obtained by fitting a Pan's profile to the data.
### TABLE 3.4 Krypton Data

<table>
<thead>
<tr>
<th>Present Work</th>
<th>Prediction</th>
<th>Tentative Classification</th>
<th>Sanche &amp; Schultz</th>
<th>Roy et al.</th>
<th>Valin &amp; Marmet</th>
<th>Boulay &amp; Marchand</th>
<th>Width (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>23.27</td>
<td>23.36</td>
<td>(4s4p(^6))[2S]5s5p(^2)[2P]</td>
<td>23.30</td>
<td>23.14-23.26</td>
<td></td>
<td>23.17</td>
</tr>
<tr>
<td>c</td>
<td>24.08</td>
<td></td>
<td>(4s(^2))[2P]5s5p(^2)</td>
<td>24.13/24.25</td>
<td>b</td>
<td></td>
<td>24.03</td>
</tr>
<tr>
<td>d</td>
<td>24.51</td>
<td></td>
<td>(4s(^2))[2P]5s5p(^2)</td>
<td>24.46-24.54</td>
<td>[24.43-24.58]</td>
<td>[24.5]</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>25.04</td>
<td></td>
<td>(4s(^2))[2D]5s(^2)5p(^2)</td>
<td>25.13</td>
<td>b</td>
<td>[25.11-25.18]</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>25.59</td>
<td></td>
<td>(4s(^2))[2D]5s5p(^2)</td>
<td>25.70(^b)</td>
<td>25.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>25.92</td>
<td>25.80</td>
<td>(4s4p(^6))[2S]6s(^2)[2S]</td>
<td>[25.95-26.17]</td>
<td></td>
<td>25.88</td>
<td></td>
</tr>
<tr>
<td>j</td>
<td>26.55</td>
<td></td>
<td>(4s(^2))[2D]5s5p(^2)</td>
<td>26.56-26.68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>26.89</td>
<td></td>
<td>(4s(^2))[2D]5s5p(^2)</td>
<td>26.90</td>
<td>[26.90]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>l</td>
<td>27.19</td>
<td></td>
<td>(4s(^2))[2S]5s(^2)5p</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>28.80</td>
<td></td>
<td>(4s(^2))[2S]5s5p(^2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Only those features designated to be resonances by the authors have been listed.

(b) Features not tabulated by authors but apparent on their figure.

(c) Obtained by fitting a Fano profile to the data.

Brackets around an energy indicate that a different designation was given by the authors.
as (1) and (2), there seems to be a good correspondence between the relative strengths of features based on the same core in both sets of data.

These facts strongly suggest that the features in Ne are due to negative ion resonances, rather than to autoionization, for example. In some cases there is no possible ambiguity since there are no neutral excited states in the vicinity. Feature b and e (Fig. 3.6(a) and Table 3.2) fall into this category. Further support for the identification of the Ne features with resonances comes from the data of Sanche and Schulz and the data of Boy et al.7. In both cases, techniques were used which are known to be sensitive to the detection of resonances, and the close correspondence between the present data and that of these authors is very convincing evidence for our identifications. Thus, assuming that our features are due to Ne- resonances and that Spence's classifications as given in Table 3.2 are valid, it is reasonable to suppose that similar features will probably occur in the other rare gases. This would be consistent with the situation found at lower energies5. Using the graphical approach discussed in section 3.2.2 it was found possible to identify which features might correspond to which resonance configurations. This is illustrated in Figures 3.9(a) and (b), and 3.10(a) and (b), which show that very good straight lines can be drawn through equivalent resonances in the doubly excited state region, as was the case for lower energies. Figure 3.9(a) shows a plot of ionization potential vs reso-
FIG 3.9(a)
I. P. vs Energy: [nsnp\\(^6\)](s)mlml'

Ionization Potential (eV)

Resonance Energy (eV)

Ne'

Ar'

Kr'

Xe'
FIG 3.9(b): B.E. vs Energy.
[nsp^5](2S)mml States

Ne^+ (n+1)s^2 3.393x10^{-2}
(n+1)s(n-1)p 2.933x10^{-2}
(n+1)p^2 1.180x10^{-2}
(n+2)s^2 1.712x10^{-2}
(n+2)s(n-2)p 0.811x10^{-2}
nance energy for the singly ionized cores (inner shell excitation) and Fig. 3.9(b) shows the equivalent plot of binding energy vs. resonance energy for the same configurations. Also indicated on these figures are the slopes of the lines connecting equivalent resonances. The lines are best fits to the data points. These states have a $^2S_1$ configuration and no fine structure splitting. Five different states have been positively identified in Xe, and the three lowest energy features in Kr have also been unambiguously identified by many authors. Also, the two lowest energy features in Kr and Xe have been identified. Fig. 3.9(a) illustrates that the equivalent resonances [core]$^+(n+1)s^2$
and [core]$^+(n+1)s(n+1)p$ are connected by excellent straight lines. Now if a straight line joining the [core]$^+(n+1)p^2$
configurations is drawn and extrapolated to Kr, it is immediately seen that the Kr$^-$ feature at 24.74 eV may be identified with this configuration. It is interesting to note that a $p^2$ resonance gives rise to a broad feature in the spectra of Figs. 3.6(a) to 3.8. It is also noted that the feature 5.7 of Sanche and Schulz at 24.78-24.91 eV and that of Roy et al. near 24.65 eV might also be identified with this resonance. Furthermore, if the feature observed at 24.65 eV by Roy et al. (which they identify with a $p^2$ resonance) is plotted on Fig. 3.9(a), it would not fall on the straight line connecting the $p^2$ configuration. Of course, the $p^2$ configuration is split into a number of terms, and it is possible that one term may decay into the metastable channel while another decays into the channel.
observed by Boy et al. Now if the line is extrapolated back to Xe, the Xe—p² resonance should occur at an energy of about 20.8 eV. Delage et al. observe a feature at 20.89—21.10 eV, but they classify it as a neutral autoionizing state rather than as a resonance. Having established that these resonances lie on straight lines, the other features in Ar and Kr can be plotted and joined to the equivalent resonances in Ne. The slopes of these lines must lie between 1 (appropriate to the bare core, indicated by the dashed line on Fig. 3.9(a)) and the larger slope of the (n+1)p⁴ configuration. This restriction enables the features to be identified with little effort.

Now consider the plot of binding energy vs resonance energy in Fig. 3.9(b). Note that because of the more sensitive scale used, the straight line fit does not appear to be quite so good. This is due to either inaccuracies in assigning energies to the features or the effects of configuration interaction causing departures from the linear relationship. As discussed in section 3.2.2, the significant bit of information to note is the slope of the lines connecting equivalent configurations. It can be seen at once that the core perturbations are greatest for the (n+1)s² states and the least for the (n+2)s(n+2)p states. By comparing the slopes of each line, the relative strengths of the core perturbations can be deduced as \( V((n+1)s²) > V((n+1)s(n+1)p) > V((n+2)s²) = V((n+1)p²) > V((n+2)s(n+2)p) \).

It should also be noted that the straight line fit is the poorest for the (n+1)s² and (n+1)s(n+1)p configurations.
This probably reflects the influence of configuration interaction effects on these states. If this is indeed the case, then it might be concluded that configuration interaction is negligible for the other states.

The next bit of information to look at is the possibility of a systematic behaviour of the slopes of the lines connecting equivalent resonances. Figure 3.9(c) shows a plot of slope vs principal quantum number for the photoabsorption data of Codling and co-workers\cite{24-27} as indicated by the appropriate configurations. A clear trend is apparent for the \{\nu^2\}(^2S)\textup{np} series. Turning to the negative ion data it can be seen that similar trends exist, namely, a sharp decrease in slope as the principal quantum number of the excited electrons increases. It is not possible to use the photoabsorption data to give more than a rough estimate of the slopes for the negative ion data, since electron-electron interactions are not present for that data. Without more series terms for the negative ion data it is also not possible to determine the quantitative behaviour of the slopes.

One other problem associated with this or any approach is due to the considerable amount of overlap of features, as can be seen in Fig.s 3.6(a), 3.7 and 3.8. Thus, even allowing that all of the observed features are due to negative ions, the overlap between different channels can make it difficult to decide which feature belongs to which channel. Also, the interference effects make accurate assignment of a
particular feature difficult in some cases. Little help can be expected at the moment from theoretical considerations because of the complexity of the problem (a large number of available and overlapping channels).

It should be pointed out that no attempt has been made to position the \((2S)_{n^2}\) resonances. These should occur at energies close to the equivalent \((n+2)s^2\) resonances and may account for some of the observed strength of these features in the metastable spectra. In the lower energy region, however, the \(n^2\) resonances were found to be much weaker than the \((n+2)s^2\) ones\(^{20}\).

The main usefulness of the graphical approach is in the area of classification of features. It may not always be possible to provide an unambiguous classification, but is certainly able to limit the possibilities.

Now consider Figs. 3.10(a) and (b). These plots are based on the \([ns^2np^2]^{++}\) cores, and the situation is now more difficult to sort out. The core configuration is split into 5 terms: \(3p_{1/2}\), \(1d_3\), and \(1s_0\). In He the \(3p\) splitting is small, but this is not the case with the other gases: the splitting in Xe covers 1.21 eV. This is indicated in Fig. 3.10(a) and Fig. 3.10(b). Thus there are effectively five ionization potentials to deal with for each gas, and resonances could be associated with each of these. This inevitably leads to some overlap in the spectral features resulting from different configurations.
FIG 3.10(a): I.P. vs. Energy
\([ns^2np^6](^3P)mlml'ml''\) States

Ionization Potential (eV)

Resonance Energy (eV)

Ne**
Ar**
Kr**
Xe**
FIG 3.10(b): I.P vs Energy
\[ns^2np^4(1D,1S)mlml'ml'' \text{ States}\]
To establish the validity of the graphical approach for the doubly ionized cores it would be preferable to consider the first resonances in the family, namely the \( ^3P^{++}(n+1)s^2(n+1)p \) ones. Unfortunately, these resonances seem to decay rather weakly into the metastable channel, so only the \( Ne^- \) member could be positioned at 42.10 eV. Suggested positions for the other members of this family by other authors are scarce. For example, no other author has claimed to observe the \( ^3P^{++}4s^24p \) resonance in \( Kr \) at the present time; the \( ^3P^{++}5s^25p \) resonance in \( Kr \) has been positioned at 22.68 eV\(^3\) and near 23.4 eV\(^3\); in \( Xe \) the \( ^3P^{++}6s^26p \) resonance is possibly observed at 19.10 eV\(^3\).

Another complication which enters the problem when working with the doubly ionized core states is that of configuration interaction. This is highlighted by the work of Codling et al\(^{24\text{-}27} \), who pointed out the large amount of configuration interaction occurring in neutral states based on this core, so much so that they were unable to classify many of their observed features, especially in \( Kr \) and \( Xe \). These effects will almost certainly be present in the resonance states based on this core, so the present assignments must be considered tentative.

The \( ^3P^{++}(n+1)s(n+1)p^2 \) terms seem to be the best ones to consider using the graphical approach. Two features have been classified in \( Ne\(^1\) \) at 44.05 eV and 44.37 eV. These features occur strongly in the present data, particularly the one at higher energy, so it is very probable that simi-
lar features will occur in the other gases. In Ar two strong features are observed at 28.30 and 28.57 eV, and in Xe, two features are apparent at 24.08 and 24.51 eV, making them possible candidates for this classification. As can be seen from Fig. 3.10(a), rather good straight lines can be drawn to link these points. Fig. 3.10(c) shows the plot of binding energy vs resonance energy for these core configurations. The straight lines linking equivalent resonances are lines of best fit to the data. It should be noted that the slopes are much larger for the doubly ionized core states than they were for the singly ionized core states, and that the fit is not as good. This reflects the increased difficulties in assignments, the increased influence of core penetration effects, and probably also increased correlation effects.

At higher energies the [1D]++ and [1S]++ configurations will become involved and probable resonances based on these cores are included in the tables. These will be discussed in the following sections.

In order to carry out a more detailed comparison with the data of other authors, it is helpful to consider each gas separately, as has been done in previous literature.

3.4.2 Neon

This is the most widely studied of the heavy rare gases and classification of the major resonances is reasonably sure, as discussed previously. A few additional points,
however, might be made:

(1) The inaccuracies in the widths given in Table 3.2 are largely due to difficulties in properly fitting the data. Considerable increase in the statistical accuracy of the data would be needed to gain any significant improvement here. Also, a more sophisticated fitting routine, one that could handle overlapping features, might give more reliable results.

(2) The only previous data obtained using the metastable channel is that of Huard et al. Their data (curve a) is compared with a sample of the present data (curve b) in Fig. 3.6(b). The greatly increased resolution over their results is quite evident. Also shown in Fig. 3.6(b) is the broadband photon data of Veilletto and Marchand (curve c). Although the overall shape of the photon spectrum is quite different from our data, there is an almost one to one correspondence in the number and position of the features. This adds weight to Spence's suggestion that these authors may be seeing much more negative ion resonance structure than they thought.

(3) The designations in Table 3.2 are taken from Spence with one exception. The relative strength of the [3P]++3s3p^2 resonances seems to suggest that similar structures could be
associated with the \([^3D]^{++}\) core. It should be noted from Fig. 3.10(c) that the binding energies of this configuration in \(\text{Ne}\) appear to be independent of the core configuration. Thus, knowing the \(J^P-\Gamma\) splitting, it is possible to make a good prediction of the energy of the \([^1D]^{++}3s3p^2\) configuration. Feature 1 is therefore given this designation rather than the \([^2S]^+5s5p\) designation given by Spence.

3.4.3 Argon

The spectrum obtained for this gas is given in Fig. 3.7 and is essentially identical to the one obtained by Marchand and Cardinal\(^{17}\). Any small differences may be attributed to the rather better energy resolution of the present work and/or to the effect of background subtraction techniques used in the two experiments.

Marchand and Cardinal assumed that the majority of their features were due to the decay of doubly or singly excited neutral states, but, based on our experience with \(\text{Ne}\), a different approach, with resonances being responsible for the major features, is suggested.

To justify this first consider the results of the two techniques known to be very sensitive to resonance detection, namely electron transmission spectroscopy\(^8\) and differential inelastic electron scattering\(^13\). In the case of \(\text{Ne}\) very good agreement was obtained between the present data
and that obtained with these techniques. A comparison of the work of the two groups mentioned reveals an almost one to one correspondence between the two sets of data with the exception that Sanche and Schulz observe a sharp feature at 27.41 eV and also some unlisted features around 30 eV not seen by Roy and Carette. This slight difference is probably due to the fact that Roy and Carette were using a single observation channel (3p^54s(^1P)), whereas Sanche and Schulz's technique integrated over all channels.

The vertical lines plotted on Fig. 3.7 are taken from the data observed by Sanche and Schulz and Roy and Carette and the close correspondence observed between their data and many of our features is evident. Therefore these features are denoted as resonances in Table 3.2 and the techniques discussed previously were used to aid in their classification.

Features Based On [3s3p^6(^2S)]^+ Cores

The features below 29.23 eV are candidates for states based on this core. The first three features, a, b and c, have all been recognized as resonances by Roy and Carette and were also noted by Sanche and Schulz. The classifications in Table 3.2 follow that of Roy and Carette. It should be noted that in further support there is good agreement between the observed values and predictions based on the graphical approach (illustrated on Fig. 3.9(a) and (b)). Marchand and Cardinal identify their feature A at 24.55 eV as a resonance but prefer neutral states for the other two
features.

Features d and e also seem to be good candidates for resonances based on this core, with classifications $5s^2(^2S)$ and $5s5p(^3P)$, respectively. Roy and Carette assign the possible $5s^2(^2S)$ classification to features which they observe at 26.92 and 27.45 eV but, assuming that the equivalent $4s^2(^2S)$ designation is correct in Ne, the graphical approach would suggest that these assignments are incorrect, and that this state must lie considerably higher in energy than these. It is more probable that the features they observe are resonances based on the $[3s^23p^4]^{2S}$ core as discussed later. Feature f could have a contribution from $[3s^23p^6]^{2S}6s6p$ which is predicted to occur at 28.44 eV, but quite likely there is overlap with the $[3s^23p^4]^{2P}43p^2$ configuration which is expected in this region. Marchand and Cardinal suggest that their feature j at 27.95 eV could have a contribution from this configuration.

It should be noted that resonances where the two electrons have different principal quantum numbers or those involving d electrons have not been considered in this analysis, for reasons discussed in the literature.**

** Features Based On $[3s^23p^4]^{2S}$ Cores

Both Saatché and Schutz and Roy and Carette observe a couple of features close to 27 eV. A dip in that region is consistently observed in the present data. It is designated \( \lambda \) in Table 3. j because of its weak statistical significance. Assuming that these features are resonances, for the reasons
Given in the previous section, it is unlikely that they are associated with the \(^2S\) core, as suggested by Roj and Carrette. The only real alternative is the \([3s^23p^4](^3P)4s^24p\) configuration. Support for this identification comes from Fig. 3.10(a) and (b) where the slope of the line linking the equivalent resonance in Ne with the feature at 27 eV in Ar is consistent with the slopes of the lines linking the known \((^3P)4s^24p^2\) terms, with the slight change (in slope) reflecting the change in the core perturbation effects. A further bit of information in favour of this identification with the \(^3P\) core is the fact that the splitting (close to 0.2 eV) observed by both Sanche and Schulz and Roj and Carrette closely matches the known splitting (0.195 eV) of the \(Ar^{++}(^3P)\) term. Finally, if the modified Rydberg equation is used to predict the energy of this configuration, a value close to 27 eV is obtained.

As mentioned earlier in section 3.4.1, it seems very plausible to associate features \(i\) and \(j\) with the \((^3P)4s^24p^2\) configuration, although feature \(i\) may be a composite involving \((^3S)6s6p\) as discussed previously. The Rydberg analysis lends additional support to this designation. Marchand and Cardinal suggest that the \((^3P)4s^24p^2\) configuration may contribute to their feature at 27.95 eV, a suggestion also put forward by Leflaivre and Marlet for their feature some 10 meV higher in energy.

An examination of Fig. 3.10(c) shows that the binding energy of equivalent resonances is almost independent of the
configuration in Ne, and this suggests that the same would be true in the other rare gases as well. This approximation turns out to be less valid in the cases of Ar and Kr, but it does allow a rough estimate of the energies of resonances based on the $^1D$ and $^3S^o$ cores, knowing the core splittings of the parent ion. This suggests that the strong feature n, near 29 eV, and also the features observed by Sanchez and Schulz and by Roy and Carette near this same energy should have the $^1D4S^24P$ classification. The relative strengths of this configuration based on the $^1D$ and $^3P$ cores is consistent with what was observed in Ne. The observed 2 eV splitting between the $^1D$ and $^3P$ terms is close to the known (1.74 eV) splitting of the core. It should be stressed that configuration interaction effects are known to be very strong for doubly excited states based on these cores, so this classification must be viewed as tentative.

In a similar fashion, the feature p, at 31.30 eV and those of Sanchez and Schulz and Roy and Carette at about the same energy may be identified with the $^1S4S^24P$ configuration. Here the observed splitting is 4.22 eV, compared with the known $^3P-1S$ splitting of 4.12 eV. Feature l is also a candidate for this classification.

The final assignments given in Table 3:3 are made by assuming that the separation of the $4S^24P$ and $4S^24P$ configurations are approximately independent of the core. This is consistent with the approximate independence of the binding energies with the core configurations. Thus, based on the
previous identifications for the $^3P$ core, features $j$ and $k$ are linked with the $^1P$ core while $o$ and $p$ are linked with the $^1S$ core. Clearly, a lack of precise knowledge of the configuration interaction effects involved, along with the large number of possible states which could arise from a combination of three electrons, precludes more definitive statements about the classification. Leclaire and Marmet identify the $^3P_2^1D$ term with their feature at 29.58 eV, somewhat lower in energy than suggested here.

Note that when the states identified as in Table 3.3 are plotted on Fig. 3.10(a) along with the equivalent state of Kr, rather good straight lines are obtained. This adds some support to the identification, as does the Rydberg analysis done in section 3.4.c.

3.4.4 Krypton

The spectrum obtained for this gas is shown in Fig. 3.8 and the data for the most prominent features are tabulated in Table 3.4. Also given in the table are resonance data from other sources for comparison purposes. Table 3.4 reveals again the close correspondence between the electron transmission work of Sanche and Schulz and the inelastic electron scattering data of Koy et al. Thus, the same procedure as was used for Ar will be used for Kr, namely working under the assumption that the features observed by these authors were predominantly resonances rather than neutral autoionizing states. Where a feature in Fig. 3.8 corresponds to one observed by these workers it is assumed that
a resonance is responsible and the techniques discussed previously are used to aid in the identification. Two other techniques which employ electron impact, namely electronization measurements and broadband photon yield measurements, have revealed a wealth of structure most of which has been attributed to neutral autoionizing states. The resonances observed by these authors are also listed in Table 3.4.

Features Based On $[4s^4p^6]^+(2S)$ Cores

If it is assumed that the graphical approach works reasonably well with this core (as it did with Ar), then Fig. 3.9(a) and Fig. 3.9(b) can be used to predict where resonances based on this core will occur. These are listed in the second column of Table 3.4 and enable features a, b, e, h and i to be identified with the 5s$^2$, 5s5p, 5p$^2$, 6s$^2$ and 6s6p resonances respectively. Note that this classification agrees with Roy et al$^{14}$ for the first two features but not thereafter. They identify feature d, some 0.23 eV lower than e, with the p$^2$ resonance and suggest that the 6s$^2$ resonance occurs at 25.35 eV, 0.45 eV below the predicted value and inconsistent with the trends of Fig. 3.9(a). Valin and Harmet$^{31}$ only suggest one resonance, the 4d$^2$, based on this core. They identify a feature at 24.92 eV with this configuration. Boulay and Marchand$^{29}$ identify resonances 5s$^2$ and 5s5p in good agreement with our features a and b, but suggest that the 6s$^2$ resonance may occur at 25.40 eV in agreement with Roy et al$^{14}$.
In Kr there is clearly even more overlap of features based on different parent or grandparent cores than in the case of Ar, so precise identification becomes correspondingly more difficult. Feature b is probably a composite, and in fact both Sanche and Sculz and Joy et al. identify two resonances in this region, probably one with a two-electron configuration based on the $2\nu$ core, and the other with a three-electron configuration based on the $3\nu$ core.

Features Based On The [4s$^2$4p$^4$]$^{++}$ Cores

Because of the large core splitting involved here and also the large amount of configuration interaction which is to be expected, accurate identification of the features is very difficult. The overlap of different channels mentioned above introduces still further complications. For these reasons the proposed identifications given for the features in Table 3.4 should be regarded as fairly speculative. However, in spite of this, comparison of the Kr-spectrum with those of Ne and Ar suggests some approaches which may be helpful. For example, experience with the other two gases indicated that resonances of the type $^{1}D(n+1)s^2(n+1)p$ and $^{1}S(n+1)s^2(n+1)p$ should show up quite strongly. In addition, if the binding energies of these configurations are approximately independent of the core configuration (as in Ne and Ar - see Fig. 3.10(c)) then these resonances should be separated by the $1L-1S$ core splitting of the parent ion. The known position of the $^{3}P5s^25p$ resonance near 23.4 eV helps to position approximately the resonances based on the $1\nu$ and $1\sigma$ cores. These ideas suggest that the strong fea-
tureds \( f \) at 25.04 eV and \( l \) at 27.19 eV can be identified in this way. Their splitting of 2.15 eV can be compared with the 2.23 eV splitting of the parent core. The Rydberg analysis also suggests that feature \( k \) at 28.39 eV should also be considered with \( l \) for this classification.

Again analogously with Ne and Ar it is expected that a pair of \( (n^p)(n^{{*}}+1)^0(l^p) \) p\(^2\) resonances, with the higher energy one predominating, should be seen. By classifying features \( e \) and \( d \) in this way we have a basis for identifying the same outer configuration—but based on the \( 1\sigma \) and \( 1\delta \) cores. A \( 1\sigma \) configuration can almost certainly be identified with feature \( m \) since it is the only strong feature in the expected region above 28 eV. The \( 1\pi \) ones are much more difficult to identify because they will lie in a region where there is much overlap with the resonances based on the \( 2\delta \) core. All features between 25.5 and 26.5 eV, namely \( j \), \( k \), \( l \) and \( m \) should be considered for this identification, as indicated in Table 3.4. Clearly, much further experimental and theoretical work is required to help elucidate this situation.

It should be added that the restriction to resonances where the principal quantum numbers of all the excited electrons are the same, a situation which seemed to hold for Ne and Ar, may not be a valid assumption for Ar and Xe. In addition, the discrimination against possible significant contributions from neutral states may be an over-simplification.
The present assignments are rather different from those of Roy et al. for all of the resonances based on these cores with the exception of \( (3P)5s^25p \) and \( (1D)5s5p \). They suggest a \( (3S)4d^2 \) assignment for the strong feature, \( f \), near 25 eV (compared with \( (2S)6s^2 \) at 25.36 eV). They assign a \( (1D)5s4d^2 \) configuration at 26 eV, and their other assignments include a number of higher cusps associated with neutral states.

Valin and Marmet have suggested resonance assignments based on this core for some of their features observed in the total ionization yield and these are noted in Table 3.4. They assign \( (3P)5s^25p \) to the feature they observe at 22.68 eV. Roy et al. suggest that their feature at 23.33-23.50 eV, some 0.7 eV higher in energy, has a similar outer configuration, but is based on the \( (3P_{1/2}) \) cores. The separation is fairly consistent with the splitting (≈0.9 eV) between the \( 3P \) and \( 3F_{1/2} \) terms of the bare core. No feature near 22.7 eV was observed in the present work, but this is not surprising since the \( (3P)5s^25p \) resonances decay weakly into the metastable channel. Valin and Marmet agree with the present identification of the \( 5s5p^2 \) configuration based on the \( 3P \) and \( 1P \) cores as indicated in Table 3.4. Their other resonance feature at 24.5 eV is attributed to \( (1D)5s^25p \) based on their assignment of the \( (3P)5s^25p \) resonance at 22.68 eV and the expected splitting of the terms.

Boulay and Marchand also observe numerous features in this energy region in their integrated photon yield. How-
ever, they only attribute one of these (at 23.80 ev) to the resonance $^{3}P_{2}$, based on this core. This is in reasonable agreement with the present assignment of the feature near 24 ev in Fig. 3.3.

None of the other authors suggest that any of their features could be due to resonances based on the $1s$ core.

3.4-3 Extension to Xe

Although no measurements were made with Xe as a target gas, it is possible to make some predictions based on the graphical analysis. The work indicates that resonances based on the [nsnp]($^{2}S$) cores are more or less well behaved and that the graphical approach works fairly well with them. Thus Fig. 3.9(a) can be used to predict the energies of the $Xe$-resonances based on this core. The results of this are given in Table 3.5, along with the data of Sanche and Schulz and Delage et al. for comparison purposes.

It is obvious from Table 3.5 that there is good agreement between the prediction for the $6s^{2}$ resonance and the observations of both sets of authors. This adds weight to the other predictions since the identification of the $6s^{2}$ resonance is well established. The present prediction also confirms the assignment of Delage et al. of their feature at 19.36-19.55 ev as $6s6p(2P)$ and at the same time rules out their suggested designation of the same configuration to a feature at a significantly lower energy of 19.1 ev. This illustrates the usefulness of the technique.
Table 3.5
Predicted and Observed Resonances in Xenon

<table>
<thead>
<tr>
<th>Resonance Configuration</th>
<th>Predicted Energy (from Fig. 3.9)</th>
<th>Sanche and Schulz[3]</th>
<th>Delage et al. [15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5s5p^6 ^2S]os^2 ^2S</td>
<td>18.84</td>
<td>18.85-18.96</td>
<td>18.83-18.95</td>
</tr>
<tr>
<td>[5s5p^6 ^2S]6s6p ^2E</td>
<td>19.37</td>
<td>19.4(a)</td>
<td>19.38-19.55</td>
</tr>
<tr>
<td>[5s5p^6 ^2S]6p^2</td>
<td>20.61</td>
<td></td>
<td>[20.89-21.10]</td>
</tr>
<tr>
<td>[5s5p^6 ^2S]7s^2</td>
<td>21.73</td>
<td></td>
<td>[21.64-21.79]</td>
</tr>
<tr>
<td>[5s5p^6 ^2S]7s7p'</td>
<td>22.02</td>
<td></td>
<td>[22.04-22.26]</td>
</tr>
</tbody>
</table>

(a) Feature not listed by authors but apparent on figure.

Energies in brackets indicate that a different designation was given by the authors.
It can also be suggested that their designation of (2S)6p² to their feature 6-6' at 20.48-20.62 eV would be more appropriate to their feature 7-7' at 20.89-21.10 eV. They should probably also consider the 7s² and 7s7p configurations for their features 9-9' and 10-10' in addition to the other possibilities which they list.

Making predictions for resonances based on the (5s²5p⁴)⁺⁺ cores will be far less reliable than they were for the 2S core since configuration interaction effects will almost certainly cause significant deviations from the simple relationships used. However, for the sake of completeness, these predictions are listed in Table 3.6, along with observations of other authors where they see features at or near the predicted energy. It should be stressed that these predictions are only speculative and indicate the approximate positions of these resonances that one might expect.

Future experiments are being planned to study the metastable excitation spectrum of Xe to examine the validity of some of these suggestions. However, it does seem clear from the work of Roy et al.¹⁴ and Delage et al.¹⁵ that as one progresses to the heavier rare gases, decay of neutral states becomes more significant in the inelastic scattering channel as compared to the decay of resonances. Clearly there remains a great deal of work to be done on this problem.
Table 3.6
Predicted and Observed Resonances in Xe:[5s5p*]++ Cores

<table>
<thead>
<tr>
<th>Resonance Configuration</th>
<th>Predicted Energy (eV)</th>
<th>Sanche and Schulz[8]</th>
<th>Delage et al (ref 15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3p)6s26p</td>
<td>19.22</td>
<td>19.78-19.88</td>
<td>[19.73-19.87]</td>
</tr>
<tr>
<td>(3p)6s5p2</td>
<td>19.79</td>
<td>[20.05-20.19]</td>
<td></td>
</tr>
<tr>
<td>(3p)6s6p2</td>
<td>20.10-20.17</td>
<td>21.15</td>
<td></td>
</tr>
<tr>
<td>(1D)6s26p</td>
<td>21.41</td>
<td>[21.25-21.40]</td>
<td></td>
</tr>
<tr>
<td>(1D)6s5p2</td>
<td>21.05</td>
<td>[22.04-22.26]</td>
<td></td>
</tr>
<tr>
<td>(1S)6s26p</td>
<td>23.17</td>
<td>[23.22]</td>
<td></td>
</tr>
</tbody>
</table>

Energies in brackets indicate that a different designation was given by the authors.
3.4.6 Application of the Modified Rydberg Equation

The framework of this equation was discussed in section 3.2.2, and now its application to the present data will be examined.

Application to \([n^SN^6](2S)\text{m}m\text{l}'\) States

As discussed in section 3.2.2, one first requires a knowledge of the quantum defects for the \(m\text{l}\) and \(m\text{l}'\) electrons. These can be deduced from the corresponding singly excited neutral states, such as \([\text{core}]^\text{+}m\text{l}\), for example, by using the normal Rydberg equation. In the neutral state is split into several components by magnetic interactions and exchange effects, the center of gravity of the multiplet structure must be used, as discussed by Read.

One of the significant things observed by Read was that the value of \(\sigma\), the screening constant, remained almost constant for a given configuration in various gases. His values of \(\sigma\) are listed in Table 3.7 for Ne, Ar, and Kr based on the \(n^5\) cores. Notice that the value of \(\sigma\) is fairly constant for equivalent configurations in each gas. This suggests that one could evaluate the screening constants for the \((n+1)s^2, (n+1)s(n+1)p, (n+1)p^2, (n+2)s^2\) and \((n+2)s(n+2)p\) configurations in Ne, and then use these values to predict the energies of the equivalent resonances in the other rare gases. These predictions are given in column 5 of Table 3.7. Also shown in Table 3.7 are the energies predicted using the graphical approach (last column). As can be seen
<table>
<thead>
<tr>
<th>Gas</th>
<th>Configuration</th>
<th>Observed Energy (eV)</th>
<th>Screening Constants</th>
<th>Rydberg Analysis</th>
<th>Graphical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Present Data</td>
<td>Read (23)</td>
<td></td>
</tr>
<tr>
<td>Neon</td>
<td>( ^2S ) 3s^2</td>
<td>43.10</td>
<td>0.267</td>
<td>0.254</td>
<td>43.11</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 3s3p</td>
<td>43.67</td>
<td>0.225</td>
<td>0.216</td>
<td>43.68</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 3p^2</td>
<td>45.45</td>
<td>0.290</td>
<td>0.295</td>
<td>45.45</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 4s^2</td>
<td>46.53</td>
<td>0.291</td>
<td></td>
<td>46.53</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 4s4p</td>
<td>46.97</td>
<td>0.326</td>
<td></td>
<td>46.97</td>
</tr>
<tr>
<td>Argon</td>
<td>( ^2S ) 4s^2</td>
<td>24.54</td>
<td>0.252</td>
<td>24.77</td>
<td>24.50</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 4s4p</td>
<td>25.05</td>
<td>0.225</td>
<td>25.07</td>
<td>24.99</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 4p^2</td>
<td>26.45</td>
<td>0.286</td>
<td>26.43</td>
<td>26.45</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 5p^2</td>
<td>27.57-27.72</td>
<td></td>
<td>27.50</td>
<td>27.63</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 5s5p</td>
<td>27.88</td>
<td></td>
<td>27.87</td>
<td>27.89</td>
</tr>
<tr>
<td>Krypton</td>
<td>( ^2S ) 5s^2</td>
<td>22.79</td>
<td>0.252</td>
<td>23.46</td>
<td>22.83</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 5s5p</td>
<td>23.27</td>
<td>0.220</td>
<td>23.65</td>
<td>23.32</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 5p^2</td>
<td>24.74</td>
<td>0.276</td>
<td>24.83</td>
<td>24.74</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 6s^2</td>
<td>25.92</td>
<td>0.26</td>
<td>25.89</td>
<td>25.93</td>
</tr>
<tr>
<td></td>
<td>( ^2S ) 6s6p</td>
<td>26.20</td>
<td></td>
<td>26.23</td>
<td>26.18</td>
</tr>
<tr>
<td>Gas</td>
<td>Configuration</td>
<td>Observed</td>
<td>Screening</td>
<td>Rydberg</td>
<td>Graphical</td>
</tr>
<tr>
<td>-----</td>
<td>---------------</td>
<td>----------</td>
<td>-----------</td>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Energy</td>
<td>Constants</td>
<td>Analysis</td>
<td>Analysis</td>
</tr>
<tr>
<td>Neon</td>
<td>((3p)^3s^23p^2)</td>
<td>42.11</td>
<td>0.262</td>
<td></td>
<td>42.09</td>
</tr>
<tr>
<td></td>
<td>((3p)^3s^3p^2)</td>
<td>44.05</td>
<td>0.261</td>
<td></td>
<td>44.06</td>
</tr>
<tr>
<td></td>
<td>((3p)^3s^23p^2)</td>
<td>44.36</td>
<td>0.268</td>
<td></td>
<td>44.35</td>
</tr>
<tr>
<td></td>
<td>((1d)^3s^23p^2)</td>
<td>45.25</td>
<td>0.262</td>
<td></td>
<td>45.25</td>
</tr>
<tr>
<td></td>
<td>((1d)^3s^3p^2)</td>
<td>47.38</td>
<td>0.265</td>
<td></td>
<td>47.39</td>
</tr>
<tr>
<td></td>
<td>((1d)^3s^23p^2)</td>
<td>47.64</td>
<td>0.270</td>
<td></td>
<td>47.64</td>
</tr>
<tr>
<td></td>
<td>((1s)^3s^23p^2)</td>
<td>49.62</td>
<td>0.263</td>
<td></td>
<td>48.98</td>
</tr>
<tr>
<td>Argon</td>
<td>((3p)^4s^24p^2)</td>
<td>27.88</td>
<td></td>
<td>27.45</td>
<td>27.20</td>
</tr>
<tr>
<td></td>
<td>((3p)^4s^4p^2)</td>
<td>28.30</td>
<td></td>
<td>28.88</td>
<td>28.26</td>
</tr>
<tr>
<td></td>
<td>((3p)^4s^24p^2)</td>
<td>28.67</td>
<td></td>
<td>28.88</td>
<td>28.61</td>
</tr>
<tr>
<td></td>
<td>((1d)^4s^24p^2)</td>
<td>28.92</td>
<td></td>
<td>28.92</td>
<td>28.96</td>
</tr>
<tr>
<td></td>
<td>((1d)^4s^4p^2)</td>
<td>29.66</td>
<td></td>
<td>30.46</td>
<td>29.83</td>
</tr>
<tr>
<td></td>
<td>((1d)^4s^24p^2)</td>
<td>30.33</td>
<td></td>
<td>30.46</td>
<td>30.34</td>
</tr>
<tr>
<td></td>
<td>((1s)^4s^24p^2)</td>
<td>31.50</td>
<td></td>
<td>31.50</td>
<td>31.12</td>
</tr>
<tr>
<td></td>
<td>((1s)^4s^4p^2)</td>
<td>32.12</td>
<td></td>
<td>32.94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>((1s)^4s^24p^2)</td>
<td>32.40</td>
<td></td>
<td>32.94</td>
<td></td>
</tr>
<tr>
<td>Krypton</td>
<td>((3p)^5s^5p^2)</td>
<td>23.39</td>
<td></td>
<td>23.27</td>
<td>23.29</td>
</tr>
<tr>
<td></td>
<td>((3p)^5s^3p^2)</td>
<td>24.08</td>
<td></td>
<td>24.74</td>
<td>24.11</td>
</tr>
<tr>
<td></td>
<td>((3p)^5s^5p^2)</td>
<td>24.51</td>
<td></td>
<td>24.74</td>
<td>24.48</td>
</tr>
<tr>
<td></td>
<td>((1d)^5s^5p^2)</td>
<td>25.04</td>
<td></td>
<td>24.56</td>
<td>25.05</td>
</tr>
<tr>
<td></td>
<td>((1d)^5s^3p^2)</td>
<td>25.59</td>
<td></td>
<td>26.10</td>
<td>25.61</td>
</tr>
<tr>
<td></td>
<td>((1d)^5s^3p^2)</td>
<td>26.20</td>
<td></td>
<td>26.10</td>
<td>26.19</td>
</tr>
<tr>
<td></td>
<td>((1s)^5s^5p^2)</td>
<td>27.19</td>
<td></td>
<td>26.77</td>
<td>27.01</td>
</tr>
<tr>
<td></td>
<td>((1s)^5s^3p^2)</td>
<td>28.60</td>
<td></td>
<td>28.31</td>
<td></td>
</tr>
</tbody>
</table>
there is rough agreement between the observed energies and those predicted by the modified Rydberg equation, and that the graphical approach appears to work much better in most cases.

The reason that the modified Rydberg formula approximates the resonance energies is, of course, that the screening is deduced from the data, and that the core interaction is built into the quantum defects. What this formula will not handle well at all is the fact that configuration interaction will probably have an effect on the screening constants as one goes from Ne to Kr, and also, the interaction of the core with two electrons will not be quite the same as a core-one electron case.

Application to Doubly Ionized Cores

The present work also provides an opportunity to test an extension of the modified Rydberg equation to a system of three electrons attached to a positive ion core. It should be pointed out, however, that correlation effects will probably make this approach somewhat unreliable.

Proceeding as in the case of the 2s core, the quantum defects for the [core]**el electrons are deduced from known data and then the screening constants for Ne are calculated. These constants are then used to predict the resonance energies in the other gases, and the results are given in Table 3.8. As can be seen from the table, surprisingly good agreement between predicted and observed values is obtained, considering the possible problems mentioned above.
1.5 CONCLUSIONS AND SUGGESTIONS

1.5.1 Conclusions

Metastable excitation spectra in the doubly excited state region have been obtained for the rare gases Ne, Ar and Kr. The most prominent features in these spectra have been identified with negative ion resonances based on the \([nsap^+](2S)\) and \([ns^2ap^+](3P, 4D, 1S)\) cores, and similarities between equivalent resonances in the different gases have been demonstrated.

The graphical approach used by Spence to analyze negative ion resonances below the first ionization threshold in these gases has been extended to the higher energy region and has been shown to work very well in the present case. The method works particularly well for features based on the \(^2S\) cores and hence the identification of these resonances is reasonably sure. This approach has been shown to work for features based on the \(^3P\), \(^1D\) and \(^1S\) cores, but because of the effects of configuration interaction and the large number of possible terms involved, the classifications of these features must be regarded as tentative.

In addition to demonstrating the power of the graphical approach as a tool for identifying resonances, the deviations from the linear behaviour of binding energy vs resonance energy have been considered and were suggested to be related to perturbations of the outer electrons by the positive ion core. The significance of the slope of the line
joining equivalent resonances in such a plot has also been considered, and has been shown to be related to the amount of interaction between the core and the outer electrons.

The modified Rydberg equation proposed by Read has been applied to the present data. Effective screening constants were deduced from the Ne data, and following Read, these were used to predict the energies of equivalent resonances in Ar and Kr. It was found that the predicted energies were not as good as energies given by the graphical approach, differing from the experimentally determined energies by several hundred MeV in some cases. It was also found that the effective screening constants deduced from the data were close to the values expected for completely correlated electrons, particularly when two outer electrons were considered. From this result it can be concluded that a high degree of correlation between the outer electrons is to be expected for these resonances.

Based on the relative success of the graphical approach in Ne, Ar, and Kr, the energies of the equivalent resonances in Xe were predicted. A comparison of these predicted energies with the results of other authors indicated that there were indeed features present at or near the predicted energy, although in many instances the observed features were not classified as negative ion resonances by these authors.

Comparisons of the present data were made with the data of other authors. In many cases there was disagreement be-
between the present classification scheme and the classifications given to similar features by these authors. Agreement was found between our data and the data of authors who used techniques which were sensitive to the detection of negative ion resonances, thus adding weight to the present conclusions.

Finally, widths were determined for some of the more isolated features in the spectra. Because of the statistical uncertainty in the data, it was not possible to determine the widths with any great precision. Also, uncertainties were introduced because of the overlapping of features in some instances.

3.5.2 Suggestions for Future Research

It can be seen that there is still a great deal of work to be done with the rare gases in connection with negative ion resonances. Several avenues of approach can be envisioned for future experimental work:

1. A study of the metastable excitation functions for Xe in the doubly excited state region. This can be used to test the predictions of the graphical approach for this gas, as well as to look for a continuation of the similarities between equivalent resonances as was found for Ne, Ar, and Kr. Because the metastable excitation energies are lower in Xe than the other rare gases, a special low-workfunction detector is currently being developed for
use with this target gas.

(2) A continuation of the present work with the aim of obtaining a significant improvement in the statistical accuracy of the data, allowing an examination of the finer details superimposed on the major features to be carried out.

(3) An extension of the present work to even higher impact energies. It would be useful to look for higher lying members of the Rydberg series based on the 2S core in particular, so that a true multichannel quantum defect theory could be used to analyze the data.

(4) To further aid in the identification and classification of resonances, differential inelastic scattering studies will be performed. This type of experiment will also allow the contributions of different partial waves to the scattering process to be evaluated, as well as the branching ratios into different decay channels.

(5) To aid in the assignment of energies to features observed in the metastable channel, more sophisticated data analysis techniques should be developed. In particular, a technique which would be able to handle overlapping spectral features would be extremely useful.
### 2-6 APPENDICES

## 2-6.1 Ionization Potentials for the Rare Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Configuration</th>
<th>Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>([2s2p^6]^{2S}) +</td>
<td>46.463</td>
</tr>
<tr>
<td></td>
<td>([2s^22p^4]^{3P}_2) ++</td>
<td>62.512</td>
</tr>
<tr>
<td></td>
<td>([2s^22p^4]^{3P}_1) ++</td>
<td>62.593</td>
</tr>
<tr>
<td></td>
<td>([2s^22p^4]^{3P}_0) ++</td>
<td>62.627</td>
</tr>
<tr>
<td></td>
<td>([2s^22p^4]^{1D}_2) ++</td>
<td>65.712</td>
</tr>
<tr>
<td></td>
<td>([2s^22p^4]^{1S}_0) ++</td>
<td>69.422</td>
</tr>
<tr>
<td>Argon</td>
<td>([3s3p^6]^{2S}) +</td>
<td>39.231</td>
</tr>
<tr>
<td></td>
<td>([3s^23p^4]^{3P}_2) ++</td>
<td>43.375</td>
</tr>
<tr>
<td></td>
<td>([3s^23p^4]^{3P}_1) ++</td>
<td>43.513</td>
</tr>
<tr>
<td></td>
<td>([3s^23p^4]^{3P}_0) ++</td>
<td>43.570</td>
</tr>
<tr>
<td></td>
<td>([3s^23p^4]^{1D}_2) ++</td>
<td>45.112</td>
</tr>
<tr>
<td></td>
<td>([3s^23p^4]^{1S}_0) ++</td>
<td>47.458</td>
</tr>
<tr>
<td>Krypton</td>
<td>([4s4p^6]^{2S}) +</td>
<td>27.507</td>
</tr>
<tr>
<td></td>
<td>([4s^24p^4]^{3P}_2) ++</td>
<td>38.1350</td>
</tr>
<tr>
<td></td>
<td>([4s^24p^4]^{3P}_1) ++</td>
<td>38.914</td>
</tr>
<tr>
<td></td>
<td>([4s^24p^4]^{3P}_0) ++</td>
<td>39.009</td>
</tr>
<tr>
<td></td>
<td>([4s^24p^4]^{1D}_2) ++</td>
<td>40.165</td>
</tr>
<tr>
<td></td>
<td>([4s^24p^4]^{1S}_0) ++</td>
<td>42.450</td>
</tr>
<tr>
<td>Xenon</td>
<td>([5s5p^6]^{2S}) +</td>
<td>23.395</td>
</tr>
<tr>
<td></td>
<td>([5s^25p^4]^{3P}_2) ++</td>
<td>33.110</td>
</tr>
<tr>
<td></td>
<td>([5s^25p^4]^{3P}_1) ++</td>
<td>34.324</td>
</tr>
<tr>
<td></td>
<td>([5s^25p^4]^{3P}_0) ++</td>
<td>34.106</td>
</tr>
<tr>
<td></td>
<td>([5s^25p^4]^{1D}_2) ++</td>
<td>35.230</td>
</tr>
<tr>
<td></td>
<td>([5s^25p^4]^{1S}_0) ++</td>
<td>37.746</td>
</tr>
</tbody>
</table>
3.5.2 **Calculation of $\sigma$**

This appendix briefly describes the relationship between the screening constant used in the modified Rydberg formula and electron correlations. To illustrate this we will confine ourselves to the situation where the outer electrons are completely correlated.

\[ \text{Consider first the case for two outer electrons, as shown above. The electrons are on opposite sides of the core, and at the same distance from the core. The potential energy of this system is given by:} \]

\[ V(r) = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_1 + r_2} \]  \hspace{1cm} (3.5.1)\]

where $z$ is the charge of the core. Using the fact that the radii are equal yields:
\[ V(r) = \frac{2(z-0.25)e^2}{r} \quad (3.6.2) \]

Thus the effective charge seen by each electron is \( z-0.25 \), and so the screening constant has the value of 0.25.

\[ r_1 = r_2 = r_3 = r \]

Now consider the case of three correlated electrons, as shown above. These should sit on the "vertices of an equilateral triangle", and the potential energy of the system is:

\[ V(r) = \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{Ze^2}{r_3} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} \quad (3.6.3) \]

and the separation between each electron is:

\[ r_{ij} = \sqrt{3} r \]

Thus the effective potential seen by one electron (due to the core field and the other two electrons) is

\[ V(r) = -(z-2(0.289))e^2/r \quad (3.6.4) \]
which gives the screening constant a value of 0.289.

3.5.3 Background Subtraction

Recall from section 3.3.2 that the features of interest in the metastable excitation spectra were highlighted by removal of the large background present in the data. In many cases, this background was highly "non-linear", so a subtraction routine was written that would remove the low frequency oscillations (see ref. 36). This was done by an averaging routine which replaced the point \( y(i) \) by:

\[
y(i) \leftarrow \frac{y(i-1) + 2y(i) + y(i+1)}{4}
\]

except for the endpoints of the spectrum, which were obtained by:

\[
y(1) \leftarrow \frac{y(1) + y(2)}{2}
\]

\[
y(n) \leftarrow \frac{y(n-1) + y(n)}{2}
\]

This was repeated a large number of times, usually 100-1000 passes through the data, and then this smoothed data was subtracted from the original data, leaving behind the small features to be studied.
CHAPTER 4

POLARIZATION CORRELATION EXPERIMENTS WITH SIMPLE MOLECULES
4.1 INTRODUCTION

The subject of electron-photon coincidence experiments has received a great deal of attention over the past 12 years since the initial theoretical work of Nácek and Jaecks. A massive effort has been put into angular and polarization correlation studies and related topics, both experimentally and theoretically. Electron-photon coincidence studies yield basic information about the magnitudes and relative phases of the scattering amplitudes which describe the scattering process, and also information about the elements of the density matrix which describes the excited state. Such studies provide the most sensitive tests of existing theoretical approximations.

Most of the experimental work has been concentrated on $^4\text{He}$, because the situation is relatively simple. $^4\text{He}$ can be described by LS coupling, and there are no fine or hyperfine structure effects to contend with. Some work has also been done with $\text{Ne}^+$, $\text{Ar}^{3+}$, and $\text{Kr}^{8+}$, as well as with atomic hydrogen. Some work has also been performed with $^4\text{He}$ as a target gas, as well as with $\text{Kr}$ and the heavy rare gases. Spin polarization effects have also been under investigation in electron-photon coincidence experiments. Very little work has been done with molecules. The only previous study has been a preliminary investigation of polarization correlation in $^4\text{He}$, by McCoukey and Malcolm. On the theoretical side, the only treatment which exists is the density matrix formalism of Plum and Jakubowicz for
molecules obeying Hund's Case (b) coupling.

The present work examines the excitation of the \( \text{Cl}^+ \) state of \( \text{H}_2 \) and the \( \text{Cl}^+ \) state of \( \text{He} \) using the electron-polarized photon coincidence technique. Two Stokes' parameters of the emitted radiation were measured as a function of incident electron energy and electron scattering angle. Because the radiation lies in the VUV spectral range, no measurements of circular polarization were possible.

This work begins with a theoretical framework necessary to understand the coincidence experiments. This is done in section 4.2. Section 4.3 describes the details of the experiment and the reduction of coincidence spectra to obtain the Stokes' parameters. Section 4.4 contains the experimental results and a discussion of the data obtained. Lastly, section 4.5 puts forward some conclusions and suggestions for future research.
4.2 THE THEORETICAL FRAMEWORK

4.2.1 Introduction

In this section, a discussion of the theory upon which an electron-photon coincidence experiment is based is presented. The first topic of discussion is polarized light and the Stokes' parameters and how they can be determined by a series of polarization measurements. Next, a review of coincidence experiments with He is given, using the density matrix formalism, followed by the density matrix approach applied to molecules. Lastly, a discussion of threshold polarization of molecular radiation and pseudo-threshold polarization measurements is presented.

4.2.2 Polarized Light and the Stokes' Parameters

Consider the diagram illustrated in Fig. 4.1. This shows schematically a source of polarized light being observed from the y-direction. In this case, the light source consists of two dipole oscillators, one oscillating along the z-direction, and one oscillating along the x-direction. In general, the two dipoles can be described by both a magnitude and a phase angle. Now this light source can be characterized by 4 quantities known as the Stokes' parameters. These parameters are:

1. The total unpolarized intensity, \( I \), of light observed in the y-direction.

2. The degree of linear polarization, \( s_\perp \), measured with respect to the two orthogonal axes.
(3) The degree of linear polarization, \( s_1 \), measured with respect to two orthogonal axes oriented at 45 degrees to \( z \) and \( x \).

(4) The degree of circular polarization, \( s_2 \).

The first three parameters can be determined by placing a linear polarizer between the source and the detector. If the 'polarization vector' of the polarizer, \( \epsilon \), is rotated through an angle \( \beta \) with respect to the \( z \) axis, then:

\[
\epsilon(\beta) = \cos \beta \hat{z} + \sin \beta \hat{x}
\]  

(4.2.2.1)

If \( E(y) \) is the observed electric field along the \( y \) axis, then the observed intensity transmitted by the polarizer is given by:

\[
I(\beta) = |E(y) \epsilon(\beta)|^2
\]

(4.2.2.2)

and the Stokes' parameters are given by:

\[
I = I(0) + I(90)
\]

\[
I_{s_1} = I(0) - I(90)
\]

\[
I_{s_2} = I(45) - I(135)
\]

The degree of circular polarization can be measured by inserting a quarter-wave plate in front of the linear polarizer and measuring the intensities at 45 and 135 degrees, and it is given by:

\[
I_{s_2} = I(RHC) - I(LHC)
\]

where \( I(RHC) \) is the intensity of Right Hand Circularly polarized light, and \( I(LHC) \) is the intensity of Left Hand Circularly polarized light.
The electric field along the \( y \) direction produced by the two dipole oscillators is given by:

\[
\vec{E}(y,t) = e^{i\omega t}(a_x e^{i\phi x} \hat{x} + a_x e^{i\phi x} \hat{z})
\]  

(4.2.2.3)

If the \( x \) component of the electric field is subject to a retardation \( \eta \) (by a quarter-wave plate, for example), the field is then given by:

\[
\vec{E}(y,t) = e^{i\omega t}(a_x e^{i\phi x} \hat{z} + a_x e^{i(\phi x + \eta)} \hat{x})
\]  

(4.2.2.4)

Using this in equations 4.2.2.2 along with eq 4.2.2.1 gives the intensity of light transmitted by the polarizer:

\[
I(\beta; \eta) = a_x^2 \cos^2 \beta + a_x a_z \cos(\delta - \eta) \sin 2\beta + a_z^2 \sin^2 \beta
\]  

(4.2.2.5)

where \( \delta \) is the relative phase (apart from the retardation \( \eta \)) between the \( z \) component and the \( x \) component of the field.

Equation 4.2.2.5 can now be used to express the Stokes' parameters in terms of the oscillator amplitudes and the relative phase. With \( \eta = 0 \), the first three parameters are given by:

\[
I = a_x^2 + a_z^2
\]  

(4.2.2.6a)

\[
I s_3 = a_x^2 - a_z^2
\]  

(4.2.2.6b)

\[
I s_1 = 2a_x a_z \cos \delta
\]  

(4.2.2.6c)

The insertion of a quarter-wave plate is equivalent to putting the retardation \( \eta \) to \( \pi/2 \), and the circular polarization is then given by:
\[ I_{s_z} = 2a_x a_z \sin \delta \]  

(4.2.2.6d)

By measuring the Stokes' parameters, the oscillator amplitudes and their relative phase can be determined. Once this is done, the complete angular distribution of the emitted radiation can be found. From electrodynamics, the electric field of a dipole observed in the direction \( \hat{n} \) is given by (in the radiation zone):

\[ \vec{E}(\hat{n}) = \vec{E} - \hat{n} (\hat{n} \cdot \vec{E}) \]

Now the dipole moment is given by:

\[ \vec{p} = a_z \hat{z} + a_x e^{i\phi} \hat{\phi} \]

and the unit vector \( \hat{n} \) (in spherical polar coordinates) is:

\[ \hat{n} = \sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y} + \cos \theta \hat{z} \]

The intensity is proportional to \(|E|^2\), and is given by:

\[ I(\theta, \phi) = a_x^2 \sin^2 \theta + a_x^2 (1 - \sin^2 \theta \cos^2 \phi) - a_z a_x \cos \delta \sin 2\theta \cos 2\phi \]  

(4.2.2.7)

The intensity pattern in the \( x-z \) plane is of particular interest in coincidence experiments, and this is given when \( \phi = 0 \):

\[ I(\theta) = c (a_x^2 \sin^2 \theta - a_z a_x \cos \delta \sin 2\theta + a_x^2 \cos^2 \theta) \]

where \( c \) is an appropriate constant. For 'historical' reasons, the angle \( \theta \) in the \( x-z \) plane is measured in the clockwise direction instead of the counterclockwise direction, and this means that \( \theta \) is negative in the above equation. Thus the intensity is given by:
This sign convention is now firmly entrenched in the literature, so to avoid any confusion it will be maintained throughout all subsequent discussions.

Another quantity of interest in coincidence experiments is the orientation of the radiation pattern in the x-z plane. This is specified by the angle at which the minimum intensity is observed. Differentiating eq 4.2.2.8 with respect to \( \theta \) and setting the derivative equal to zero gives:

\[
\tan 2\theta = -\frac{2a_z a_x \cos \delta}{a_z^2 - a_x^2} \quad (4.2.2.9a)
\]

Comparing eq. 4.2.2.9a with equations 4.2.2.6b and c, the orientation angle is given by:

\[
\tan 2\theta_{\text{min}} = -s_1/s_3 \quad (4.2.2.9b)
\]

It is apparent from equation 4.2.2.8 that the oscillator amplitudes and the magnitude of their relative phase can be determined by measuring the angular distribution of the radiation in the x-z plane. This is equivalent to measuring the Stokes' parameters \( l, s_1 \) and \( s_3 \). In an electron-photon coincidence experiment, measuring the angular distribution of the radiation is known as angular correlation and measuring the Stokess' parameters is known as polarization correla-
Note that only the magnitude of the circular polarization can be determined from angular correlations, and not its sign.

It should be emphasized that the above discussion assumed that the radiation was completely monochromatic. If the radiation is quasi-monochromatic or made up of a large number of different frequencies then a time averaging must be performed on the observed intensity. In such a situation the time-averaged amplitudes and relative phase must be used in the expressions for the Stokes' parameters.

One further point which should be noted is that the above example is completely coherent, in the sense that the total polarization, given by:

\[ \mathcal{P} = (s_1^2 + s_2^2 + s_3^2)^{1/2} \]  

(4.2.2.10)

is equal to 1. In general this is not the case, since there may be a large unpolarized contribution to the intensity. In this case the total polarization will be less than 1. This is equivalent to saying that the radiation is composed of an incoherent superposition of polarization states.

4.2.3 Coincidence Experiments with Atoms

To illustrate the usefulness of electron-photon coincidence experiments, we now turn our attention to the atomic case. Since angular correlation experiments are equivalent to polarization correlation experiments, the discussion will be restricted to the latter type of experiment. We
shall further restrict the discussion to the density matrix formalism and outline the steps necessary to arrive at expressions for the Stokes' parameters. A complete discussion can be found in Karl Blum's book *Density Matrix Theory and Applications* which gives an excellent presentation of the subject. An excellent review article by Blum and Kleinpoppen also discusses this material.

Consider first the experimental geometry shown schematically in Fig. 4.2. The z axis is defined by the incident electron beam and is used as the quantization axis. The scattering plane is defined by the momenta of the incident and scattered electrons, p and p'. Note that the scattering plane is taken to be the x-z plane. Photons emitted by atoms excited by collisions are observed in the y-direction after passing through a linear polarizer which is rotated about the y axis. The scattered electrons are analyzed for both energy and scattering angle, determining the magnitude and direction of p'. The measured coincidence rate between the photons and scattered electrons thus comes from a subensemble of atoms that have been excited to the same state by electrons scattered into the direction p'.

Having defined the experimental geometry we can now discuss the excitation process in terms of the density matrix formalism. A number of assumptions are made in this discussion, and these are:

(1) The excitation and decay processes can be treated independently. This means that the
EXPERIMENTAL GEOMETRY

FIG 4.2
excitation is 'instantaneous'; i.e., it takes place in a time which is much shorter than the lifetime of the excited state and any spin-orbit precession times.

(2) The Hamiltonian describing the scattering process contains no explicit spin dependent terms. Thus a change in spin can only occur by electron exchange, which we shall not consider.

(3) LS coupling is adequate to describe the atomic states.

(4) No observation of initial and final spins of any particle is made.

(5) Both the incident electron beam and the initial atomic ensemble are unpolarized.

(6) The initial atomic ensemble has \( L_0 = 0 \) and all atoms are in the ground state.

The states of the system are described by:

**INITIAL STATE:**

Atoms: \( |n_0 L_0 S_0 \rangle \langle n_0 S_0 |_{L_0} \) \( n_0 S_0 \rangle \); \( L_0 = L^* = 0 \)

Electrons: \( |p_{n_0 m_0} \rangle \)

**EXCITED STATE:**

Atoms: \( |n_1 L_1 S_1 \rangle \langle n_1 S_1 |_{L_1} \) \( n_1 S_1 \rangle \)

Electrons: \( |p_{1 m_1} \rangle \)

where \( m_0 \) and \( m_1 \) refer to the \( z \) component of the orbital angular momentum of the incident and scattered electrons, respectively.

The density matrix of the combined system of atoms+electrons...
for the initial state is:

\[ \rho_0 = \frac{1}{2(2S_0+1)(2I_0+1)} \sum_{m_0 M_{S_0}} |a_0 s \cdot p_0 M_{S_0} m_0 > < a_0 s \cdot p_0 M_{S_0} m_0 | \]

With the restriction that \( L_0 = 0 \), \( \rho_0 \) can be written as:

\[ \rho_0 = \frac{1}{2(2S_0+1)} \sum_{m_0 M_{S_0}} |a_0 s \cdot p_0 M_{S_0} m_0 > < a_0 s \cdot p_0 M_{S_0} m_0 | \]  \hspace{1cm} (4.2.3.1)

and its matrix elements are given by:

\[ <a_0 s \cdot p_0 M_{S_0} m_0 | \rho_0 | a_0 s \cdot p_0 M_{S_0} m_0 > = \frac{\delta_{m_0^* m_0} \delta_{M_{S_0}^* M_{S_0}}} {2(2S_0+1)} \]  \hspace{1cm} (4.2.3.2)

The scattering process is characterized by the scattering amplitudes \( f(n, l_1, s_1, M_{l_1}, s_{l_1}, m_{l_1}; P_1, n_0 s_0 M_{S_0} m_0; P_0) \), which are the matrix elements of the corresponding transition operator \( T \).

The density matrix describing the excited state is given by:

\[ \rho_1 = T \rho_0 T^+ \]  \hspace{1cm} (4.2.3.3a)

and its matrix elements are given by:

\[ <a_1 l_1, s_1, M_{l_1}, s_{l_1}, m_{l_1}; P_1 | \rho_1 | a_1 l_1, s_1, M_{l_1}, s_{l_1}, m_{l_1}; P_1 > = \]

\[ \frac{1}{2(2S_0+1)} \sum_{m_0 M_{S_0}} f(n, l_1, s_1, M_{l_1}, s_{l_1}, m_{l_1}; P_1 + n_0 s_0 M_{S_0} m_0; P_0) \times f^*(n, l_1, s_1, M_{l_1}, s_{l_1}, m_{l_1}; P_1 + n_0 s_0 M_{S_0} m_0; P_0) \]  \hspace{1cm} (4.2.3.3b)

Since the spins of the scattered electrons and the excited atoms are not observed, the density matrix \( \rho_1 \) must be summed over the diagonal elements of the unobserved spin components \( M_{S_1} \) and \( s_1 \). The result is known as the reduced density matrix which describes the orbital states of the excited
atoaa. This is given by:

\[<n_{1}L_{1}S_{1}S_{1} \{P_{1} \mid n_{1}L_{1}S_{1}S_{1} \{P_{1}> =

(4.2.3.3c)

\[<f(n_{1}L_{1}S_{1}S_{1} \{P_{1} \mid n_{0}S_{0}S_{0} \{P_{0}> f^{*}(n_{1}L_{1}S_{1}S_{1} \{P_{1} \mid n_{0}S_{0}S_{0} \{P_{0})>

where \(<...>\) denotes the averaging over unobserved spins.

For convenience of notation the dependence on \(n_{1}, L_{1}, S_{1}, \rho_{1}, n_{0}, S_{0}\) and \(P_{o}\) will be suppressed since these are fixed. The reduced density matrix of the system is then given by:

\[<L_{1}^{*} \mid \rho(L_{1}) L_{1}^{*}> = <f^{*}(L_{1}^{*}) f(L_{1})>

(4.2.3.4)

Note that the normalization of this density matrix is such that the trace is equal to the differential cross-section for exciting the state \(|n_{1}L_{1}S_{1}>\). For the case where \(L_{1}=1\) the density matrix can be written out explicitly and is:

\[\rho_{1}(1) = \\
\begin{pmatrix}
    <f^{*}(1) f(1)> & <f^{*}(1) f(-1)> \\
    <f^{*}(0) f(1)> & <f^{*}(0) f(-1)> \\
    <f^{*}(-1) f(1)> & <f^{*}(-1) f(0)> & <f^{*}(-1) f(-1)> & <f^{*}(-1) f^{*}(0)> & <f^{*}(-1) f^{*}(-1)> \\
\end{pmatrix}
\]

It can be seen that the density matrix is Hermitian, and since the scattering amplitudes are complex, there are 6 independent parameters which are necessary to describe the density matrix, namely the magnitudes and relative phases of the scattering amplitudes. Symmetry considerations can be used to reduce the number of parameters needed. Because the scattered electrons are detected the symmetry of the system is reduced from axial to planar, and the system is invariant under reflections in the scattering plane. This gives the
condition that:

\[ \langle M' | \rho | M \rangle = (-1)^{M' + M} \langle -M' | \mathcal{P}_1 | -M \rangle \]

for the density matrix and:

\[ f(M, S_1, S_0, M' = -M, S_1, -S_0) \]

for the scattering amplitudes. If spin conservation is also taken explicitly into account, the number of independent parameters needed to specify the density matrix is reduced to 4, and in the special case where \( S_0 = S_1 = 0 \), the number is reduced to 3. In this case \( f(M) = (-1)^M f(-M) \), and there is no need to perform a spin averaging. The density matrix is given by:

\[ \langle M' | \rho | M \rangle = f(M') f^*(M) \]  

(4.2.3.5)

The parametrization used in the literature for this case is given by:

\[
\sigma = \bar{r}^2(0) + 2\bar{r}^2(1) \\
\lambda = \bar{r}^2(0)/\sigma \\
\cos \chi = \text{Re} \bar{r}(0) \bar{r}(1)/\sigma
\]

In general it is possible to excite states of different total angular momentum, and the density matrix must be written (in a \( |J\rangle \) basis) as:

\[ \rho (J'J) = \sum_{J'M'} \langle J'M' | \mathcal{P}_1 | J'J \rangle |J'M'\rangle \]

where the \( (J'M'J) \) are the density matrix elements. The density matrix can be expressed in terms of its irreducible components, or state multipoles, by defining a new set of tensor operators \( T(J'J)_{\mathcal{P}_1} \).
\[ T(J'J)_{KQ} = \sum_{M'M} (-1)^{J' - M'}(2K+1)^{1/2} \left[ \frac{J' - J}{M' - M} \frac{K}{Q} \right] |J'M'\rangle <JM| (4.2.3.6) \]

The density matrix is expressed in terms of these operators as:

\[ \rho = \sum_{J'JKQ} <T(J'J)_{KQ}^\dagger T(J'J)_{KQ} \]

where \(<T(J'J)_{KQ}>\) are the state multipoles, given by:

\[ <T(J'J)_{KQ}^\dagger> = \sum_{M'M} (-1)^{J' - M'}(2K+1)^{1/2} <J'M'|\rho|JM> (4.2.3.7) \]

The state multipoles have the property:

\[ <T(J'J)_{KQ}^\dagger> = (-1)^{K+Q} <T(J'J)_{K-Q}^\dagger> \]

For the case where the excited state has a well-defined angular momentum \(J^* = J = L_1\), the state multipoles can be written as:

\[ <T(L_1^L_{1'})_{KQ}^\dagger> = \sum_{M'M'_L_{1'}} (-1)^{L_1 - M'_L_{1'}}(2K+1)^{1/2} \left[ \frac{L_1 - L_{1'}}{M'_L_{1'} - M_L_{1'}} \frac{K}{Q} \right] |L_1'L_1'\rangle |^* (M_L_{1'})> (4.2.3.8) \]

Thus, it can be seen that for \(L_1 = 1\), the state multipoles \(<T(1)_{00}^\dagger>, <T(1)_{11}^\dagger>, <T(1)_{20}^\dagger>, <T(1)_{12}^\dagger>\) and \(<T(1)_{22}^\dagger>\) must be determined. Note that because of the symmetry properties of the state multipoles, \(<T(J'J)_{K0}^\dagger>\) is 0 for odd \(K\). Thus \(<T(1)_{10}^\dagger> = 0\).

The state multipoles have a much deeper physical signifi-
cance than the density matrix elements. For \( K=0 \), \( \langle T(L)^0_0 \rangle \) is proportional to the differential cross-section and is:

\[ \langle T(L)^0_0 \rangle = \sigma/(2L+1)^2 \]

It can be shown for \( K=1 \) that:

\[ \langle T(L)^1_1 \rangle \sim (3/(2L(L+1)(2L+1)))^{1/2} \sigma L_Q \]

where \( L_Q \) are the spherical components of the orbital angular momentum. Thus the tensor with \( K=1 \) is related to the net amount of orbital angular momentum transferred to the atom during the collision. \( \langle T(L)^1_1 \rangle \) are known as the components of the orientation vector. It turns out that only \( \langle L_y \rangle \) is non-zero, and this is related to \( \langle T(L)^1_1 \rangle \) by:

\[ \langle T(L)^1_1 \rangle \sim -i\alpha/\sqrt{2} (3/(2L(L+1)(2L+1)))^{1/2} \sigma L_y \]

Fig. 4.3 illustrates a semiclassical model of grazing collisions, used to illustrate the production of orientation in atomic collisions. Electrons can be scattered into the direction of \( \hat{T}_i \) by the long-range attractive force due to the atomic polarizability as in Fig. 4.3(a), or by the short-range repulsive force of the atomic electrons, as in Fig. 4.3(b). In the attractive case the atom acquires a net negative angular momentum and \( \langle L_y \rangle < 0 \). This will be the case for scattering into small angles. In the repulsive case, the atom acquires a net positive angular momentum and \( \langle L_y \rangle > 0 \). Scattering into large angles will be dominated by this effect.

Lastly, the tensors with \( K=2 \) can be shown to be:
\[ \langle T(L)_{20} \rangle \propto <L_z^2 - L_z \rangle \sigma / \sqrt{6} \]
\[ \langle T(L)_{2+1} \rangle \propto <L_x^2 + L_y^2 \rangle \sigma / 2 \]
\[ \langle T(L)_{2+2} \rangle \propto <L_x^2 - L_y^2 \rangle \sigma / 2 \]

and these are known as the components of the alignment tensor. It will be shown later that the orientation vector is responsible for the production of circular polarization and that the alignment tensor is responsible for linear polarization.

Time Dependence of the State Multipoles

Because of the influence of fine and hyperfine structure and the finite lifetime of the excited state, the state multipoles (and of course, the density matrix) are not constant but are time dependent. It can be shown that the state multipoles evolve according to an equation of the form:

\[ \langle T(j';j;t)_{k_q} \rangle = \sum_{J'J} \langle T(J'J)_{k_q} \rangle G(J'J,j';j;t)_{kK} \]

where the \( G(J'J,j';j;t)_{kK} \) are known as perturbation coefficients which include the effects of fine and hyperfine structure and the finite lifetime of the excited state. For the case of fine structure only the perturbation coefficients can be shown to be:

\[ G(L_1,t)_{kK} = \frac{\delta_{kK}}{2S_{\overline{1}+1}} \sum_{J'J} \left\{ \begin{array}{c} L_1 \ J \ K \\ J' \ L_\overline{1} \ S \end{array} \right\}^2 \]

\[ \times \exp\left(i(E_J - E_{J'})t/\hbar - (\gamma_J + \gamma_{J'})t/2\right) \]

These are independent of \( Q \) and can be written simply as
Note that the complex terms in this expression imply the existence of quantum beats in the observed radiation. Now if the time resolution of the coincidence electronics is very large compared to the periods of the quantum beats, the beats cannot be observed, and this is equivalent to a time integration of equation 4.2.3.9a. If this is done it turns out that only states with \( J' = J \) can contribute to the state multipolesthe contributions from states with \( J' \) different from \( J \) are negligible.

Finally, if states with zero spin are considered, the perturbation coefficients reduce to:

\[
G(L_1; t) = \exp(-\bar{\gamma}_1 t) \tag{4.2.3.9b}
\]

The Radiative Decay Process

To consider the radiative decay process it is convenient to work in the helicity basis of the emitted photons. In this basis, the quantization axis is taken to be the direction of propagation, \( \mathbf{n} \). Since photons are massless, they have only two components of spin angular momentum along \( \mathbf{n} \), namely \(+1\) and \(-1\). A density matrix of the emitted photons can be constructed in this representation, and is given by:

\[
\langle \lambda' | \rho | \lambda \rangle = \begin{pmatrix}
\rho_{11} & \rho_{1-1} \\
\rho_{-11} & \rho_{-1-1}
\end{pmatrix}
\]

The density matrix is of course Hermitian, so \( \rho_{-11} = \rho_{11}^* \).

The Stokes' parameters can be expressed in terms of the density matrix elements, and are given by:

\[
I = \text{tr} \rho = \rho_{11} + \rho_{-1-1}
\]
\[ I_{3} = -\rho_{1-1} - \rho_{11} \]

\[ I_{1} = -i(\rho_{1-1} - \rho_{1-1}) \]

\[ I_{2} = \rho_{11} - \rho_{1-1} \]

By transforming the state multiplets from the collision \((x, y, z)\) system into the helicity system (using a rotation matrix), the photon density matrix can be shown to be:

\[
\rho(x, y, z) = C(\omega) \sum_{J'J_JJ_f} \left| J' \right| \left| J \right> \left< J' \right| \left| J \right>^* (-1)^{J+J_f+\lambda} (2K+1)^{1/2} \times \exp\left(i(E_J-E_J')/\hbar - (\gamma_J+\gamma_{J_f})/2\right) <T(J'J_J)_KQ> (4.2.3.10)
\]

\[
\times D(n)_KQ \left( \begin{array}{c} 1 \ 1 \ K \\ \lambda \ \lambda \ q \end{array} \right) \left( \begin{array}{c} 1 \ 1 \ K \\ J' \ J_f \ J \end{array} \right)
\]

For the case of 0 spin, the Stokes' parameters are finally given by:

\[
I = \frac{C(\omega)}{\gamma} \left| L_1 \right| \left| L_1 \right> \left< L_1 \right| \left| L_1 \right|^2 (-1)^{L_1+L_f} \frac{2(-1)^{L_1+L_f}}{3(2L_1+1)^{1/2}} \left< T(L_1)_00 \right>
\]

\[
\times \left\{ \begin{array}{c} 1 \ 1 \ 2 \\ L_1 \ L_1 \ L_f \end{array} \right\} \left< T(L_1)_22 \right> \sin^2 \theta \cos 2\phi - \left< T(L_1)_21 \right> \sin 2\theta \cos \phi + \left< T(L_1)_20 \right> (3\cos^2 \theta - 1)/\sqrt{6}
\]

\[
I_{3} = \frac{C(\omega)}{\gamma} \left| L_1 \right| \left| L_1 \right> \left< L_1 \right| \left| L_1 \right|^2 (-1)^{L_1+L_f} \left\{ \begin{array}{c} 1 \ 1 \ 2 \\ L_1 \ L_1 \ L_f \end{array} \right\}
\]

\[
\times \left< T(L_1)_22 \right> (1+\cos^2 \theta) \cos 2\phi + \left< T(L_1)_21 \right> \sin 2\theta \cos \phi
\]

\[
\times (3/2)^{1/2} \left< T(L_1)_20 \right> \sin^2 \theta
\]

\[
(4.2.3.11a)
\]

\[
(4.2.3.11b)
\]
\[ I_{S_1} = - \frac{C(\omega)}{\gamma} \left| \langle L_f | \vec{T} | L_1 \rangle \right|^2 (-1)^{L_1+1} \]
\[ \times \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ L_1 & L_1 & L_f \end{array} \right\} 2(\langle T(L_1)_{2,2}^+ \rangle \cos\theta \sin2\phi + \langle T(L_1)_{2,1}^+ \rangle \sin\theta \sin\phi) \]

\[ I_{S_2} = -2\frac{C(\omega)}{\gamma} \left| \langle L_f | \vec{T} | L_1 \rangle \right|^2 (-1)^{L_1+1} \]
\[ \times \left\{ \begin{array}{ccc} 1 & 1 & 1 \\ L_1 & L_1 & L_f \end{array} \right\} \langle T(L_1)_{1,1}^+ \rangle \sin\theta \sin\phi \]

where \( C(\omega) \) is given by:

\[ C(\omega) = \frac{e^2 \lambda \phi}{2\pi \hbar} \]

and \( \langle L_f | \vec{T} | L_1 \rangle \) is the reduced matrix element (Edmonds' normalization) of the dipole transition operator from the excited state to the final state \( L_f \). As stated earlier, equations 4.2.3.11 show that the orientation vector is related to the circular polarization and the alignment tensor is related to the linear polarization.

**Excitation of the \( n^1P \) States of \( \text{He} \)**

As a specific example, the excitation of the \( n^1P \) state of \( \text{He} \) and the subsequent radiative decay to \( 1^1S \) will be considered. In this case \( L_1 = 1 \) and \( L_f = 0 \). The state multipoles can be evaluated and are:

\[ \langle T(1)_{00} \rangle = (a_0^2 + 2a_1^2)/(3) \]
\[ \langle \Gamma(1) | T_1 \rangle = \sqrt{2} \text{Im} (a_0 a_1^*) \]
\[ \langle \Gamma(1) | T_0 \rangle = \sqrt{3} (a_0^2 - a_0^*) \]
\[ \langle \Gamma(1) | T_2 \rangle = -\sqrt{2} \text{Re} (a_0 a_1^*) \]
\[ \langle \Gamma(1) | T_3 \rangle = -a_0^3 \]

where \( f(0) \) has been denoted by \( a_0 \) and \( f(1) \) by \( a_1 \). Using the expressions for the state multipoles in equations 4.2.3.11, evaluating the 6-j symbols, and using the fact that the observation direction is \( \theta = \phi = 90 \) degrees, the Stokes' parameters are given by:

\[ I = C(\omega) |\langle 0 | j \hat{r} | 1 \rangle|^2 (a_0^2 + 2a_0a_1^*) / 3 \]  
\[ S_3 = (a_0^2 - 2a_0a_1^*) / (a_0^2 + 2a_0a_1^*) \]  
\[ S_1 = -2/2 \text{Re} (a_0a_1^*) / (a_0^2 + 2a_0a_1^*) \]  
\[ S_2 = 2/2 \text{Im} (a_0a_1^*) / (a_0^2 + 2a_0a_1^*) \]

It can be shown that equations 4.2.3.12 are equivalent to the Stokes' parameters of the complex dipole oscillator given in section 4.2.2. This is done as follows. The excited state is composed of a coherent superposition of the magnetic substates, and can be written as:

\[ \psi = a_{-1/1} -1 > + a_{0/1} 0 > + a_{1/1} 1 > \]

The excited state wavefunction can also be written in the form (by changing to a Cartesian basis set):

\[ \psi = a_x |x> + a_y |y> + a_z |z> \]

The Cartesian basis vectors can be transformed to the angular momentum basis by noting that \( \langle \ell | m \rangle = c_{\ell m}(\hat{r}) \) = normalized spherical harmonic. It turns out that \( a_z = a_0, a_y = 0 \), and \( a_x = -a_0 \). Thus there is a one-to-one correspondence between the scattering amplitudes and the dipole oscillator amplitudes.
He \textsuperscript{1}P Excitation and the Born Approximation

As a final example we shall consider the predictions of the Born approximation for the excitation of \textsuperscript{1}P states of He. This can be done by making the following assumptions:

1. The He target states are properly antisymmetrized linear combinations of products of hydrogenic wavefunctions.
2. Spin and exchange effects are neglected.
3. The incident electron interacts with the Coulomb field of a positive ion core + the other target electron. Now the interaction with the core does not contribute to excitation, so this simplifies the calculation.

The results of the Born calculation show that the scattering amplitudes are given by:

\begin{align*}
a_0 &= I(ka)Y_0^0(k) \\
a_1 &= I(ka)Y_1^1(k)
\end{align*}

where $I(ka)$ is a radial integral and $k$ is the momentum transfer vector $\vec{p}_1 - \vec{p}_0$. In the scattering plane $\phi_k = 0$ and so the scattering amplitudes are:

\begin{align*}
a_0 &\propto \cos \theta_k \\
a_1 &\propto \sin \theta_k / 2
\end{align*}

Thus the Stokes' parameters are given by:

\begin{align*}
s_3 &= \cos 2\theta_k \\
s_1 &= -\sin 2\theta_k \\
s_2 &= 0
\end{align*}

Recall that the orientation angle of the radiation pattern in the scattering plane is given by:
\[ \tan 2\theta_{\text{min}} = -s_1/s_3 = \tan 2\theta_k \]

Thus the momentum transfer direction also specifies the orientation of the radiation pattern. The momentum transfer direction can be found from the electron scattering angle, the incident electron energy, and the scattered electron energy (see Appendix 4.6.2). For a fixed incident energy and scattered energy, the Stokes' parameters can be calculated as a function of electron scattering angle and compared with experiment. In the Born approximation the scattering amplitudes are real, and thus the relative phase between them is 0. Also, the circular polarization is predicted to be 0, and the emitted photons are completely polarized; i.e., the magnitude of the polarization vector is 1. A comparison with actual experimental data shows that the Born approximation predicts the value of \( s_3 \) reasonably well for small electron scattering angles, but not \( s_1 \) or \( s_2 \). Also there is a noticeable difference between the momentum transfer direction and the orientation of the radiation pattern.

4.2.4 Coincidence Experiments with Molecules

Having seen how the density matrix formalism works for atomic excitation, we can now turn our attention to molecules. The basic approach is the same, but in molecules the situation is complicated by the fact that electronic, vibrational and rotational excitation must be considered. In addition to this, there is a Maxwellian distribution in the population of different rotational states in the molecular ground state, which is also affected by nuclear spin statis-
tics. Thus the excitation is more complicated than in the atomic case, since several rotational states can contribute to the same excited state. For the sake of brevity we shall simply list the assumptions involved in the calculation and give the expressions for the Stokes' parameters. The reader is referred to the work of Flus and Jakubowicz\textsuperscript{7} for complete details of the calculation. Having done this we shall proceed to work out some simple examples and discuss some of the difficulties associated with the experimental aspects of working with molecules.

Assumptions Involved

Several assumptions are made in this calculation, most of which are similar to the ones made for atomic excitation. These are:

1. The excitation process is much quicker than the radiative decay process and the characteristic vibrational and rotational periods of the molecule. This means that the molecule is essentially frozen during the collision (the Franck-Condon principle).

2. The electronic motion and the nuclear motion can be considered separately, and electronic, vibrational and rotational motion can be separated (Born-Oppenheimer approximation).

3. The molecule obeys Hund's case (b) coupling (see Appendix 4.6.1).

4. The initial state of the molecular ensemble is such that $\lambda_0$, $\nu_0$, and $S_0$ are fixed.
(5) The incident electron beam has fixed momentum $p_0$ and is unpolarized.

(6) The molecular ensemble is also unpolarized.

(7) The Hamiltonian describing the scattering process contains no explicit spin-dependent terms. Thus, as in the atomic case, spin changes can only occur by electron exchange, which is neglected.

(8) No observations of initial and final spins of any particles are made.

(9) Conservation of spin angular momentum is taken explicitly into account in the scattering amplitudes. This means that there are two channels with spin $S=S_0+1/2$ and $S_0-1/2$.

Results.

We now list the results obtained by Blum and Jakubowicz for the state multipoles, perturbation coefficients and the Stokes' parameters. The state multipoles $\langle T(N_1)_{KQ} \rangle$ are given by:

$$
\langle T(N_1)_{KQ} \rangle = \frac{1}{2(2S_0+1)} \sum_{N_0'N_0 N_1'N_1} (2S+1)(2K+1)^{1/2} \Lambda(N_0)/\Lambda(2N_0+1)
$$

$$
\times (-1)^{N_1+K+Q-N_1'} \left( \begin{array}{ccc}
N_1 & N_1' & K \\
N_0 & N_0' & -Q
\end{array} \right) f_{N_1'N_1'0N_0}^{S} f_{N_1'N_1'0N_0}^{S*}
$$

where $\Lambda(N_0)$ is the rotational population distribution in the ground state, and is:

$$
\Lambda(N_0) = (2N_0+1) \exp(-\bar{B}cN_0(N_0+1)/kT)
$$
k is Boltzmann's constant.

\( s \) is the rotational constant of the molecular ground state.

\( T \) is the temperature of the ensemble.

Note that \( \omega(N_0) \) also must include the effect of nuclear spin statistics. The \( S_{1 N_1 M_1 N_0 M_0} \)'s in equation 4.2.4.1 are the scattering amplitudes in the channel with total spin \( S \) (formed by coupling the molecular spin with the spin of the incident electron) for the process:

\[
|\alpha N_0 N_0 \rangle \rightarrow |\alpha_{1 N_1 M_1} \rangle
\]

Note also that it is possible to excite a number of rotational levels coherently, hence the appearance of \( N_1 \) and \( M_1 \) in the state multipoles.

The perturbation coefficients \( G(t)^{Q_1}_{K_k} \) due to the fine structure interaction and the lifetime of the excited state are given by:

\[
G(t)^{Q_1}_{K_k} = \frac{\delta_{K_k} \delta_{Q_1}}{2S_{1} + 1} \prod_{j} (2J_{j} + 1)(2J_{j} + 1) \exp(i(E_{j} - E_{f, j})t/\hbar - (\gamma_{j} + \gamma_{f,j})t/2) \times \left\{ J_{j} N_{1} S_{1} \right\}^{2}
\]

(4.2.4.3)

Once again, notice the appearance of quantum beat terms in this expression. As in the atomic case, if the time resolution of the electronics is large compared to the quantum beat periods, the beating cannot be observed, and a time integration must be carried out. This means that only states with \( N_1 = N_1 \) contribute in equation 4.2.4.3. Furthermore, if only singlet states are considered, the perturba-
tion coefficients reduce to:

\[ G(t)_K = \frac{1}{Y} \delta_{N_1^I N_1} \]

Finally, the Stokes' parameters are given by:

\[
I = C(\omega) \left| \langle \alpha'_f | \tau^\dagger | \alpha_1 \rangle \right|^2 \sum_{N_1 N_1}^\dagger \frac{W(N_1 N_1) \sqrt{2(-1)^{N_1} N_1}}{3(2N_1+1)^{1/2}} \times G(t)_0 \langle T(N_1 N_1^\dagger)_{00} \rangle \left[ \sum_{N_1 N_1}^\dagger W(N_1 N_1 N_f) G(t)_2 \right] \left\{ \begin{array}{c} 1 \\ 1 \\ N_1 \end{array} \right\}^2 \\
\times \left( \langle T(N_1 N_1^\dagger)_{22} \rangle \sin^2 \theta \cos 2 \phi - \langle T(N_1 N_1^\dagger)_{21} \rangle \sin \theta \cos \phi \\
+ \langle T(N_1 N_1^\dagger)_{20} \rangle (3 \cos^2 \theta - 1) / \sqrt{6} \right) 
\]

\[
I_{s_1} = -2C(\omega) \langle \alpha'_f | \tau^\dagger | \alpha_1 \rangle \left| \sum_{N_1 N_1}^\dagger W(N_1 N_1 N_f) G(t)_2 \right| \left\{ \begin{array}{c} 1 \\ 1 \\ N_1 \end{array} \right\}^2 \\
\times \left( \langle T(N_1 N_1^\dagger)_{22} \rangle \cos \theta \sin 2 \phi \\
+ \langle T(N_1 N_1^\dagger)_{21} \rangle \sin \theta \sin \phi \right) 
\]

\[ (4.2.4.5a) \]

\[ (4.2.4.5b) \]
\[ I_{s_2} = -2iC(\omega) |<\alpha_F^+|\Lambda_1^- - \Lambda_f^-|\alpha_1^->|^2 \sum_{N_1^N_1^N_f} \hat{W}(N_f N_1 N_1') G(t)_1 \]

\[ x \left\{ \begin{array}{ccc} 1 & 1 & 1 \\ N_1 & N'_1 & N_f \end{array} \right\} \times \langle T(N'_1 N_1)^{+} \rangle \sin^2 \sin \phi \]

\[ I_{s_3} = C(\omega) |<\alpha_F^+|\Lambda_1^- - \Lambda_f^-|\alpha_1^->|^2 \sum_{N_1^N_1^N_f} \hat{W}(N_f N_1 N_1') G(t)_2 \]

\[ x \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ N_1 & N'_1 & N_f \end{array} \right\} \times \langle T(N'_1 N_1)^{+} \rangle (1 + \cos^2 \phi) \cos 2\phi \]

\[ + \langle T(N'_1 N_1)^{+} \rangle \sin 2\phi \cos \phi \]

\[ + \sqrt{3/2} \langle T(N'_1 N_1)^{+} \rangle \sin^2 \phi \]

where \( \hat{W}(N_f N_1 N_1') \) is given by:

\[ \hat{W}(N_f N_1 N_1') = \frac{N_f + N_1'}{\sqrt{4(N_f + 1)(N_1' + 1)(N_1 + 1)}} \]

\[ \times \left( \begin{array}{ccc} N_1 & N_f & 1 \\ \Lambda_1^- - \Lambda_f^- & \Lambda_f^- - \Lambda_1^- \end{array} \right) \]

and \( C(\omega) \) is the same as for the atomic case, except that \( \omega \) is now the mean frequency of the emitted radiation, and \( |<\alpha_F^+|\Lambda_1^- - \Lambda_f^-|\alpha_1^->| \) is the matrix element describing a vibrational transition. The refer to all other quantum numbers necessary to describe the molecular states. If the rotational structure of a given vibrational band is not resolved in the experiment, a new set of state multipoles.
\[ \langle T(t^\dagger)_{KQ} \rangle \text{ can be defined by the formal summation:} \]

\[ \langle T(t^\dagger)_{KQ} \rangle = \sum_{N_1 N_1^* N_2} W(N_1, N_1^*, N_2) G(t) \left\{ \begin{array}{ccc} 1 & 1 & K \\ 1 & 1 & 0 \end{array} \right\} \langle T(N_1 N_1^*, N_2^*)_{KQ} \rangle \]  

(4.2.4.6)

The Stokes' parameters are then given by (for the observation direction \( y \)):

\[ I = A[\langle -2\langle T_{J2} \rangle^\dagger \rangle \langle J_{J0} \rangle + \langle T_{J2} \rangle^\dagger \langle J_{J0} \rangle \rangle \]  

(4.2.4.7a)

\[ I_{S_1} = -2A\langle T_{J2} \rangle^\dagger \]  

(4.2.4.7b)

\[ I_{S_2} = -2A\langle T_{J2} \rangle^\dagger \]  

(4.2.4.7c)

\[ I_{S_3} = A[\langle T_{J2} \rangle^\dagger \rangle \langle J_{J0} \rangle + \sqrt{3/2} \langle T_{J2} \rangle^\dagger \]  

(4.2.4.7d)

where \( A = C(\omega) |\langle a_{J2}^\dagger |F_{J2}^\dagger \rangle |^2 \) \( |\alpha_1 \rangle \).

In the case \( s_0 = s_1 = \sigma_{e} \), the formal summation 4.2.4.6 can be carried out over \( N_2 \) and the result for the state multipole is:

\[ \langle T(t^\dagger)_{KQ} \rangle = \frac{(2K+1)^{1/2}}{\sqrt{\gamma}} \sum_{N_1 N_1^*} \left( \begin{array}{ccc} 1 & 1 & K \\ 1 & 1 & 0 \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & K \\ 1 & 1 & 0 \end{array} \right) \]

\[ \times \sum_{N_0 N_1 N_1^* N_2 N_2^*} (2N_1 + 1) \left( \begin{array}{ccc} N_1 & N_1 & K \\ N_1^* & N_1^* & K \end{array} \right) \left( \begin{array}{ccc} N_0 & N_0 & 0 \\ N_0^* & N_0^* & 0 \end{array} \right) \]

(4.2.4.8)

Note that the finite resolution time of the electronics has been taken into account and the assumption that the lifetimes are independent of \( N_1 \) has been made. Equation 4.2.4.8 shows that information about individual scattering amplitudes is lost when the rotational structure is unresolved.
Also, by not resolving the quantum beats, information about the coherence between states of different \( N \) is lost.

Some Examples

Let us consider the situation where a single rotational line is resolved, say the strongest one in the band. In practice this will only be possible for the lightest molecules, so the case of \( \text{H}_2, \chi \Sigma^+ \rightarrow \chi \Pi \) excitation will be considered. For this system the Q(1) line is expected to be the strongest, and this comes from \( \lambda_0 \rightarrow \lambda_1 = \lambda_2 = 1 \) only. The assumption that excitation and decay proceeds via a dipole route only has been made. Using equation 4.2.4.2 for the state multipoles, with \( V_1 = V_2 = 1, \ N_0 = N_2 = 1, \ A_0 = \ A_2 = 0 \) and \( A_1 = 1 \), \( \langle T(1) | a \rangle \) is given by:

\[
\langle T(1) | \beta \rangle = \frac{N(1)}{3\sqrt{3}} \sum_{M_{N_0}M_{N_2}} |f(1M_{N_1}1M_{N_0})|^2 .
\]

The scattering amplitudes \( f(1M_{N_1}1M_{N_0}) \) are denoted by \( a(M_{N_1}M_{N_0}) \), and reflection invariance in the scattering plane implies that \( a(-M_{N_1}1-M_{N_0}) = (-1)^{N_1+M_{N_0}} a(M_{N_1}M_{N_0}) \). The summation over \( M_{N_0} \) can be performed first, giving a new set of amplitudes \( \langle a(M_{N_0}) \rangle \). Then \( \langle T(1) | \beta \rangle \) is:

\[
\langle T(1) | \beta \rangle = \frac{1}{3\sqrt{3}} (\langle a^2(0) \rangle + 2\langle a^2(1) \rangle).
\]

The other state multipoles are given by:

\[
\langle T(1) | \gamma \rangle = (2i \langle W(1) / 3 \rangle \text{Im} \langle a(0) a(1) \rangle)
\]

\[
\langle T(1) | \delta \rangle = \langle 2(1) / 3 \rangle \text{Re} \langle a(0) a(1) \rangle
\]

\[
\langle T(1) | \theta \rangle = \left( -\frac{1}{3} \langle W(1) / 3 \rangle \right) \text{Re} \langle a(0) a(1) \rangle
\]

\[
\langle T(1) | \phi \rangle = \left( -\frac{1}{3} \langle W(1) / 3 \rangle \right) \text{Im} \langle a(0) a(1) \rangle
\]

The Stokes' parameters are then given by:
\[ I = A \frac{W(1)}{12} \left( \langle a^2(0) \rangle + 2\langle a^2(1) \rangle \right) \]
\[ I_{s_1} = -A \frac{W(1)}{6} \sqrt{2} \Re(\langle a(0) a^*(1) \rangle) \]
\[ I_{s_2} = A \frac{W(1)}{6} \Im(\langle a(0) a^*(1) \rangle) \]
\[ I_{s_3} = A \frac{W(1)}{12} \left( \langle a^2(0) \rangle - 2\langle a^2(1) \rangle \right) \]

where \( A = \frac{\mathcal{C}(w)}{\gamma} \frac{|\langle A_f | R_{1f} | \hat{A}_1 \rangle|^2}{\langle a(0) a^*(1) \rangle} \).

and:

\[ s_1 = -2 \sqrt{2} \Re(\langle a(0) a^*(1) \rangle) \sqrt{\langle a^2(0) \rangle + 2\langle a^2(1) \rangle} \]
\[ s_2 = 2 \sqrt{2} \Im(\langle a(0) a^*(1) \rangle) \sqrt{\langle a^2(0) \rangle + 2\langle a^2(1) \rangle} \]
\[ s_3 = \langle a^2(0) \rangle - 2\langle a^2(1) \rangle \sqrt{\langle a^2(0) \rangle + 2\langle a^2(1) \rangle} \]

Thus the Stokes' parameters for the resolved J(1) line are somewhat similar to the np case in He, except that the scattering amplitudes have been summed over the ground state magnetic sublevels.

In practice it is very difficult to resolve the rotational structure in a coincidence experiment because of the corresponding loss of intensity in the photon channel. Another approach would be to prepare the initial molecular ensemble in such a way that only one rotational level is populated. This can be done by using a supersonic nozzle arrangement. During the expansion the vibrational and rotational states are frozen out, and only the \( N_0 = 0 \) state is populated. In this case the only allowed dipole excitation route is to \( N_f = 1 \), and the only allowed decay routes are to \( N_f = 0 \) and 2, corresponding to the \( R(0) \) and \( P(2) \) branches. The state multiplets can be evaluated easily, and are given by:
\[ \langle T(1)_{00} \rangle = \left( \frac{2}{\sqrt{3}} \right) (a_0^2 + 2a_1^2) \]

\[ \langle T(1)_{11} \rangle = (i \frac{\sqrt{2}}{2} \langle 0 |(a_0 a_1) | 0 \rangle) \]

\[ \langle T(1)_{00} \rangle = \frac{2}{\sqrt{3}} \langle 0 |(a_0^2 - a_1^2) \rangle \]

\[ \langle T(1)_{11} \rangle = -\frac{\sqrt{2}}{2} \langle 0 |(a_0 a_1) \rangle \]

\[ \langle T(1)_{02} \rangle = -\langle 0 |a_1 \rangle \]

where the scattering amplitudes \( f(1100) \) and \( f(1000) \) have been denoted by \( a_1 \) and \( a_n \), respectively. The Stokes' parameters can be evaluated by summing equations 4.2.4.2 over \( N_f = 0 \) and 2, and are:

\[ I = A \frac{16\sqrt{5} + 3}{36\sqrt{5}} (a_0^2 + 2a_1^2) \]

\[ I_{s_1} = -A \frac{2(12\sqrt{5} + 9)}{18\sqrt{5}} \text{Re}(a_0 a_1^*) \]

\[ I_{s_2} = A \frac{5}{6} \text{Im}(a_0 a_1^*) \]

\[ I_{s_3} = A \frac{12\sqrt{5} + 9}{36\sqrt{5}} (a_0^2 - 2a_1^2) \]

where \( A = C(0) \frac{\langle 0 | (a_0 a_1^*) | 1 \rangle^2}{\gamma} \).

Thus \( s_1, s_2, \) and \( s_3 \) are given by:

\[ s_1 = \frac{12\sqrt{5} + 9}{16\sqrt{5} + 3} \frac{-2\sqrt{2} \text{ Re}(a_0 a_1^*)}{a_0^2 + 2a_1^2} \]

\[ s_2 = \frac{15\sqrt{5}}{16\sqrt{5} + 3} \frac{-2\sqrt{2} \text{ Im}(a_0 a_1^*)}{a_0^2 + 2a_1^2} \]

\[ s_3 = \frac{12\sqrt{5} + 9}{16\sqrt{5} + 3} \frac{a_0^2 - 2a_1^2}{a_0^2 + 2a_1^2} \]

It can be seen that these parameters are the same as the ones obtained for the He n=4 case, apart from the numerical
factors.

It should be pointed out that the scattering amplitudes \( r(N_1^N_0; p_1 \leftarrow N_0^N_0; p_0) \) depend on the orientation of the molecular axis with respect to \( p_0 \). The initial molecular ensemble contains all possible orientations, so the scattering amplitudes used in the above expressions must be integrated over all orientations of the molecules. It is expected that this will cause an overall reduction of the polarization, and it may also result in a change in the relative phases of the scattering amplitudes. It is difficult to ascertain the exact nature of the effect without knowing the explicit angular dependence of the scattering amplitudes.

4.2.5 Threshold and Pseudo-Threshold Polarization

Consider the situation where the scattered electron is not detected. This requires that the state multipoles must be integrated over all electron scattering angles. When this is done, only multipoles with \( Q=0 \) can contribute, and the new state multipoles are given by:

\[
\langle T_e(N_1^k_0) \rangle = \Sigma W(N_0) (-1)^{N_1} \frac{N_1-M_1}{(2k+1)} \{ \begin{array}{c} N_1 & N_1 & M \\ N_0 & M_1 & 0 \end{array} \} Q(N_0^N_1^N_1) N_1^N_1^N_1^N_1 \text{ (4.2.5.1)}
\]

where \( Q(N_0^N_1^N_1) \) is the total cross-section for exciting the state \( | q^N_1^N_1^N_1^N_1^N_1^N_1 \rangle \), and is given by:
\[ Q_{N_0 N_1 M_1}^{N_0 N_1 M_0} = \frac{1}{2(2S_0+1)(2N_0+1)} \sum_{N_0} \left| \langle f_{N_1 M_1 N_0 M_0}^{N_1 M_1 N_0 M_0} | \right|^2 d\Omega \] (4.2.5.2)

In addition to integration over the scattered electron directions, not observing the scattered electrons means that the time at which photons are observed is not uniquely defined with respect to the time at which excitation took place, and an integration over all observation times must be performed. Blum and Jakubowicz give expressions for the total unpolarized intensity \( I \) and the intensity of light with polarization vector parallel to the z-axis, \( I_z \), as:

\[ I \sim \sum_{N_1 N_1^f} \left( \begin{array}{c} N_1 + N_1^f \\ 2N_1 + 1 \end{array} \right) W(N_1 N_1 N_1) \] (4.2.5.3a)

\[ I_z \sim \sum_{N_1 N_1^f} \left( \begin{array}{c} 1 + N_1^f \\ 2N_1 + 1 \end{array} \right) W(N_1 N_1 N_1) \left( \begin{array}{c} 1 \\ 0 \\ 0 \end{array} \right) \left( \begin{array}{c} 1 \\ 0 \\ N_1 N_1^f \end{array} \right) \] (4.2.5.3b)

For singlet transitions \( I_z \) reduces to:
\[
I_\mu \sim \sum_{N_0} (2K+1) W(N_0 N_1) \left[ \begin{array}{c} 1 \ 1 \ K \\ 1 \ 1 \ K \\ 0 \ 0 \ N_1 N_1 N_1 \end{array} \right] \times \sum_{N_1} W(N_0) (-1)^{N_1-M_1} \left[ \begin{array}{c} N_1 \ N_1 \ K \\ N_1 \ N_1 \ 0 \\ M_1 \ M_1 \ 0 \end{array} \right] Q(N_0 N_1) M_{N_1}^{N_1} \quad (4.2.5.3c)
\]

and the sum over \( K \) can be performed explicitly, giving:

\[
I_\mu \sim \sum_{N_0 N_1 N_f} \left( \begin{array}{c} N_1 + N_f \\ N_0, N_1, N_f \end{array} \right) W(N_0) W(N_f N_1) \sum_{M_1 = -N_1}^{N_1} \left( \begin{array}{c} N_1 \ 1 \ N_f \\ 0 \ M_1 \ 0 \end{array} \right)^2 Q(N_0 N_1) M_{N_1}^{N_1} \quad (4.2.5.4)
\]

The polarization \( P \) is defined by:

\[
P = \frac{3I_\mu - I}{I_\mu + I} \quad (4.2.5.5)
\]

Using the expressions for \( I \) and \( I_\mu \), the polarization is:

\[
P = \sum_{N_0 N_1 N_f} \left( \begin{array}{c} N_1 + N_f \\ N_0, N_1, N_f \end{array} \right) W(N_0) W(N_f N_1) \sum_{M_1 = -N_1}^{N_1} \left( \begin{array}{c} N_1 \ 1 \ N_f \\ 0 \ M_1 \ 0 \end{array} \right)^2 \frac{A^2 + 1/(2N_1+1)}{A^2 - 1/(2N_1+1)} Q(N_0 N_1) M_{N_1}^{N_1} \quad (4.2.5.6)
\]

If the scattering amplitudes \( f(N_1 M_1 N_0 M_0) \) are written as:

\[
f(N_1 M_1 N_0 M_0) = \sum_{k_0 k_1} \left< \alpha_1 N_1 M_1 | J \right| k_0 k_1 \left| \alpha_0 N_0 M_0 \right> \]

where \( k_0 k_1 \) represents an angular momentum change of \( \{J_{k_0} k_0 \} \).

then the total cross section can be written as:
\[ Q(N_0, N_1)_{M_0, M_1} = (2N_1+1)^2 (2N_0+1) \sum_{k,k'} q^k q^{* k'} \int <\alpha_1 | R_k | \alpha_0 > <\alpha_1 | R_{k'} | \alpha_0 >^* d\Omega_e \]

\[
\times \left( \begin{array}{cc}
N_1 & N_0 \\
N_0 & N_1 \\
N_1 - q - M_1 & N_0 - q - M_1
\end{array} \right) \left( \begin{array}{cc}
N_0 - M_0 & \Lambda_1 \\
\Lambda_1 & N_0 - \Lambda_1 - \Lambda_0
\end{array} \right) \left( \begin{array}{cc}
N_1 & 1 \\
1 & N_0
\end{array} \right)^2
\] (4.2.5.7)

In particular if the excitation is restricted to dipole routes alone, then \( k = k' = 1 \) and the result is:

\[ Q(N_0, N_1)_{M_0, M_1} = (2N_1+1)^2 (2N_0+1) \int |<\alpha_1 | R_1 | \alpha_0 >|^2 d\Omega_e \]

\[
\times \sum_q |c_q|^2 \left( \begin{array}{cc}
N_0 & N_1 \\
N_1 & N_0
\end{array} \right)^2 \left( \begin{array}{cc}
N_0 - M_0 & \Lambda_1 \\
\Lambda_1 & N_0 - \Lambda_1 - \Lambda_0
\end{array} \right) \left( \begin{array}{cc}
M_1 - q & M_1 - M_0 \\
M_0 - q & M_0
\end{array} \right)
\] (4.2.5.3)

Now conservation of total angular momentum and its \( z \) component requires that:

\[ N_0 + \Lambda_0 = N_1 + \Lambda_1 \] (4.2.5.9a)

and

\[ M_0 + m_0 = M_1 + m_1 \] (4.2.5.9b)

where \( k = 1, -1, \) and \( q = m_1 - m_0 \). The incident electron beam defines the \( z \)-axis, so \( \alpha_0 \) is always \( 0 \). Consider what happens at the excitation threshold. The scattered electrons leave the collision with \( p_1 \neq 0 \) and carry away no angular momentum. Thus \( m_1 = 0 \) and we have the threshold selection rule:

\[ m_1 = m_0 \] (4.2.5.10)

The threshold polarization is then given by:

\[
\begin{align*}
P_{th} &= \frac{\sum (-1)^{N_f^1 + N_f^2} \mathcal{W}(N_0^1) \mathcal{W}(N_0^2, N_1^1, N_1^2) \Sigma(3 \mathcal{A}^2 - 1/(2N_1^1 + 1)) Q(N_0^1, M_{N_0}^1)}{\sum (-1)^{N_f^1 + N_f^2} \mathcal{W}(N_0^1) \mathcal{W}(N_f^1, N_1^1, N_1^2) \Sigma(\mathcal{A}^2 + 1/(2N_1^1 + 1)) Q(N_0^1, M_{N_0}^1)} \quad (4.2.5.11)
\end{align*}
\]

where \( A = \begin{pmatrix} N_1^1 & N_f^1 \\ N_0^1 & 0 & -M_{N_0}^1 \end{pmatrix} \).

Notice that the threshold polarization is not independent of the dynamics of the scattering process as would be the case for atoms. However, using equation 4.2.5.8 with \( N_1^1 = N_0^1 \), the th is given by:

\[
\begin{align*}
P_{th} &= \frac{\sum (-1)^{N_f^1 + N_f^2} \mathcal{W}(N_0^1) \mathcal{W}(N_f^1, N_1^1, N_1^2) \Sigma(3 \mathcal{A}^2 - 1/(2N_1^1 + 1)) B^2}{\sum (-1)^{N_f^1 + N_f^2} \mathcal{W}(N_0^1) \mathcal{W}(N_f^1, N_1^1, N_1^2) \Sigma(\mathcal{A}^2 + 1/(2N_1^1 + 1)) B^2} \quad (4.2.5.12)
\end{align*}
\]

\[
\mathcal{V}(N_0, N_1) = (2N_1 + 1)^2(2N_0 + 1) \begin{pmatrix} 0 & N_1 & 1 \\ N_0 & -\Lambda_1 & -\Lambda_0 \end{pmatrix} B = \begin{pmatrix} N_0 & 1 & N_1 \\ N_0 & 0 & -M_{N_0} \end{pmatrix} A \text{ given in 4.2.5.11}
\]

If \( N_0^1, N_1^1, \) and \( N_f^1 \) are fixed, equation 4.2.5.11 is:

\[
P_{th} = \frac{\sum \left[ \begin{pmatrix} N_1 & 1 & N_f^1 \\ M_{N_0} & 0 & -M_{N_0} \end{pmatrix} \right]^2 - \frac{1}{2N_1 + 1} Q(N_0^1, M_{N_0}^1)}{\sum \left[ \begin{pmatrix} N_1 & 1 & N_f^1 \\ M_{N_0} & 0 & -M_{N_0} \end{pmatrix} \right]^2 + \frac{1}{2N_1 + 1} Q(N_0^1, M_{N_0}^1)} \quad (4.2.5.13a)
\]

and equation 4.2.5.12 is:
\[ P_{th} = \frac{\sum_{M_{N_0}} \left[ \left( \begin{array}{c} N_1 \\ M_{N_0} \\ 0 \\ -M_{N_0} \end{array} \right) \right]^2 - \frac{1}{2N_1+1} \left( \begin{array}{c} N_0 \\ 1 \\ N_1 \\ 0 \end{array} \right)^2}{\sum_{M_{N_0}} \left[ \left( \begin{array}{c} N_1 \\ M_{N_0} \\ 0 \\ -M_{N_0} \end{array} \right) \right]^2 + \frac{1}{2N_1+1} \left( \begin{array}{c} N_0 \\ 1 \\ N_1 \\ 0 \end{array} \right)^2} \]  

Equation 4.2.5.13b is identical to the results obtained if excitation with linearly polarized light is considered.

Consider for the moment the general expression for the threshold polarization for fixed rotational quantum numbers given by equation 4.2.5.13a. The predicted polarization cannot be evaluated unless the cross-sections are known or some additional selection rules can be invoked to eliminate the dependence on the cross-sections. This problem has been discussed extensively in the literature, so only a brief summary will be given here.

The Approach of Jette and Cahill

These authors made the assumption that electronic orbital angular momentum was conserved during the collision. Thus, in particular for the z component:

\[ \langle v_{0,0,0} M_0 | L_z | v_{1,1,1} M_1 \rangle = \langle v_{1,1,1} N_1 | L_z | v_{1,1,1} N_1 \rangle \]

The matrix element can be evaluated and is:

\[ \frac{M_{N_0}}{N_0(N_0+1)} \frac{\lambda_0^2}{N_0(N_0+1)} = \frac{M_{N_1}}{N_1(N_1+1)} \frac{\lambda_1^2}{N_1(N_1+1)} \]

For a \( \Sigma \) to \( \Pi \) transition, \( M_0 = 0 \) and \( \lambda_1 = 1 \), implying that only the \( M_{N_1} = 0 \) substate will be populated. Then only the \( M_{N_0} = 0 \)
term contributes in equation 4.2.5.13a and the dependence on the cross-section vanishes. It should be pointed out that conservation of $l_z$ does not agree with the threshold selection condition. The predicted threshold polarizations obtained in this way do not agree with the experimentally determined values\textsuperscript{73}, and this approach has been discredited.

The Approach of Baltayan and Medelec.

These authors\textsuperscript{77,78} used the united atom approximation and a partial wave analysis to determine the cross-sections $\sigma (N_1, N_0)_{M_N}$. In this approximation the electronic orbital angular momentum, $l$, is a good quantum number, and results in the additional coupling rule:

$$l_0 + l_n = l,$$

where $l_n$ refers to the $l_n$-th partial wave. With $l_0=0$, only the partial wave $l_n=1$ contributes to the excitation. The resulting expression for the threshold polarization is identical to equation 4.2.5.13b, and this was found to give reasonably good agreement with experiment.

The Approach of Malcolm, Dassen and McConkey

These authors\textsuperscript{75} applied the symmetry rules of Dunn\textsuperscript{79} to the excitation process to determine the threshold polarization. Basically, Dunn's symmetry rules relate the transition probability to the orientation of the molecule with respect to the incident electron beam. For a $\Sigma^+_g$ to $\Sigma^+_u$ transition, the transition probability is a maximum when the molecular axis is parallel to the incident beam, and zero when the axis is perpendicular to it. For a $\Sigma^+_g$ to $\Pi^+_u$ tran-
sition, the reverse is true. The transition probability is zero when the axis is parallel to the incident beam and a maximum when the axis is perpendicular to it. Thus, for \( \Sigma^g \) to \( \Sigma^u \) transitions, states with \( N_1 = 0 \) should then be preferentially populated, and for \( \Sigma^g \) to \( \Pi^u \) transitions, states with \( N_1 = \pm 1 \) should be preferentially populated. These predictions gave results which agreed with experiment much better than the predictions of Jette and Cahill, but it must be emphasized that the selection rules are not, strictly obeyed because of the distribution of orientations of the molecular axes. For the \( \Sigma^g \) to \( \Pi^u \) case, the cross-sections would have a \( \sin^2 \theta \) dependence, and thus only \( N_0 \) would be excluded from the expression 4.2.5.12a. Blum has developed these ideas in a rigorous fashion and has obtained an expression for the scattering amplitudes which depend on the orientation of the molecular axis. This is given by:

\[
A(\hat{n}) = (4\pi)^{-3/2} \frac{1}{(2N_0 + 1)(2N_1 + 1)^{1/2}} D^{N_1}(\hat{n})_{L_0}^{L_1} \times (\Sigma(-1))_{L_1}^{L_0} \rho (L_0) \rho (L_0) \langle \psi_{N_1} | T | \psi_{N_0} \rangle \langle \psi_{N_1} | T | \psi_{N_0} \rangle x D(\hat{n})_{L_0}^{L_1} \rho (L_0)
\]

where \( D(\hat{n})_{L_1}^{L_0} \) is a rotation matrix, \( \hat{n} \) is the orientation of the molecular axis with respect to \( z \), and \( L_0 \) refers to the \( L_0 \)-th partial wave. Blum shows that for \( \Sigma^g \) to \( \Sigma^u \) transitions, states with values of \( N_1 = 0 \) are preferentially populated. For \( \Sigma^g \) to \( \Pi^u \) transitions, it can be shown that the amplitudes vanish if the axis is parallel to \( z \), and that they will vanish if the axis is perpendicular to \( z \) unless
\( \gamma_n = t_n \). It can also be shown that the amplitudes vanish if
\( \gamma_n = 0 \).

The cross-sections \( Q(N_1, N_0) \) can be determined by integrating the scattering amplitude over all orientations of the axis, squaring the result, and integrating over all electron scattering angles. If this is done, the cross-sections are given by:

\[
Q(N_0, N_1) = \frac{2}{2\pi} \left( \frac{N_1}{N_0} \right)^2 \left( \frac{L_0}{L_0} \right)^2 \left( \frac{N_0}{N_0} \right)^2 \left( \frac{L_0}{L_0} \right)^2
\]

(4.2.5.15)

where \( a = \langle N_1 \Lambda_1 | T | N_0 \Lambda_0 \rangle \) and we have assumed that only one partial wave contributes to the excitation. This result applies only at the excitation threshold. The threshold polarization can be determined, and is given by:

\[
\Sigma(-1) \frac{\Sigma(1) \gamma(N_0) \gamma(N_1, N_1, N_0) \gamma^2 \Sigma \left( 3B^2 - 1/(2N_0 + 1) \right) C^2}{\gamma(1) \gamma(N_0) \gamma(N_1, N_1, N_0) \gamma^2 \Sigma \left( B^2 + 1/(2N_0 + 1) \right) C^2}
\]

(4.2.5.16)

Note that equation 4.2.5.16 is very similar to equation 4.2.5.12 when \( L_0 = 1 \). Table 4.1 lists the predicted threshold polarizations for the \( p' \) and \( s \) branches of the \( N_0, 1 \Sigma_g^+ \) to \( Cu_{1s} \) Werner bands, and the \( p' \) and \( s \) branches of the \( N_0, 1 \Sigma_g^+ \) to \( Cu_{1s} \) bands. The first column gives the predicted values of equation 4.2.5.12, and the second column gives the pred-
Table 4.1
Predicted Threshold Polarizations in H₂ and N₂

| Hydrogen C⁺⁺⁺⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻··|   |   |   |
|--------------------------------------------------|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|
predicted values of equation 4.2.5.16.

The Approach of Macpherson et al

Macpherson et al used a semiclassical approach to predict the polarization of molecular radiation. Their predicted polarizations should be approached for high values of the rotational quantum number. The predicted polarization is given by:

\[
p = \frac{3\cos^2 \gamma - 1}{\cos^2 \gamma + 3}
\]

where \(\gamma\) is the average angle between the dipole moment for absorption, \(\vec{u}_{\text{abs}}\), and the dipole moment for emission, \(\vec{u}_{\text{em}}\) for Σ to Π transitions (\(\Pi\) and \(\Delta\) branches). Both \(\vec{u}_{\text{abs}}\) and \(\vec{u}_{\text{em}}\) lie in a plane perpendicular to the internuclear axis with no correlation between them. The average angle \(\gamma\) is then 45 degrees, and the predicted polarization is 0.743. For the \(\Sigma\) branch, \(\vec{u}_{\text{abs}}\) and \(\vec{u}_{\text{em}}\) both lie along the rotation vector, and hence the value of \(\gamma\) is 0, and the predicted polarization is 0.5. For \(\Sigma\) to \(\Sigma\) transitions, there are only the \(\Pi\) and \(\Delta\) branches to consider, and \(\vec{u}_{\text{abs}}\) and \(\vec{u}_{\text{em}}\) lie in the plane of the internuclear axis with no correlation between them. Thus the average value of \(\gamma\) is 45 degrees and the predicted polarization is 0.743.

Pseudo-Threshold Polarization

Estimating the threshold polarization from straightforward polarization measurements is often difficult because of intensity limitations near the threshold and cascade contributions from higher lying states. In addition to these, the assumption of impulse excitation is questionable close to
threshold, the possibilities of electron correlations and near threshold resonances exist. These effects would cause the measured polarization to vary rapidly with energy, making extrapolation to threshold somewhat dubious. If these effects are known to be occurring, it is possible to estimate the threshold polarization from energies well above threshold, but the accuracy of the estimate may be questionable. It is possible to simulate the threshold selection rule (eq. 4.2.5.10) by use of the pseudo-threshold measurement suggested by King et al. In this type of measurement the photons are detected in coincidence with the forward scattered electrons, forcing $m_1=0$. The work by Wykes on the angular dependence of the scattering amplitudes shows that setting the scattering angle equal to 0 forces the selection rule $\Delta m=0$, since they contain an associated Legendre polynomial. At $e_0=0$, only $p_0(\cos e_0)$ is non-zero. This measurement can be performed at energies well away from threshold, where intensity is no problem and impulse excitation is a valid assumption. Also, the measurement is rendered cascade-free because of the coincidence nature of the experiment. King et al. used this technique to measure the "threshold" polarization of the He $2^1P$ radiation and obtained a value of 1, the expected theoretical value. They did however find that it was important to accept only those electrons scattered very close to $e_0=0$. The finite angular resolution of any spectrometer results in the usefulness of this technique being limited to incident energies less than approximately three times the threshold excitation energy.
Above this 'critical energy' the measured value of $\theta$th decreased rapidly with increasing energy. More will be said about this later.
4.3 Description of the Experiment

4.3.1 Interaction Region and Detectors

The interaction region is identical to the one used to detect metastable atoms, with the following exceptions:

1) The gas beam was moved from the y-axis to the x-axis so that gas would not be effusing straight into the photon detector sitting above the interaction region. This modification reduced the chances of radiation trapping of the photons by the gas.

2) The metastable detector was replaced by a polarized photon detector, consisting of a reflection polarizer and a channeltron (see Fig. 4.4(a) and Fig. 4.4(b)). This detector could be rotated automatically through 90 degrees by a synchronous motor attached to it.

3) The analyzer half of the spectrometer was used to perform energy loss measurements on the scattered electrons as discussed in Chapter 2. The analyzer could be rotated about the y-axis to detect electrons scattered into non-zero angles.

A schematic diagram of the experimental geometry has already been discussed in section 4.2.3 (see Fig. 4.2), so we need not discuss this further.

Polarized Photon Detectors
Fig's. 4.4(a) and 4.4(b) show diagrams of the two polarized photon detectors used in this work. Fig. 4.4(a) illustrates a double-reflection device identical to the one used by Malcolm and McConkey, except that aluminum mirrors coated with MgF<sub>2</sub> were used instead of gold mirrors. The reason for this is that any mercury vapour (from the diffusion pumps) reaching the gold surface would attack it and severely reduce the reflectivity of the surface. The double-reflection polarizer was used to perform the polarization correlation experiments in H<sub>2</sub>. The polarization sensitivity of the device was measured, and found to be 0.40 for the H<sub>2</sub> emissions.

Fig. 4.4(b) shows a single-reflection polarized photon detector, used for the measurements with H<sub>2</sub>. It was found that the double-reflection polarizer had a polarization sensitivity of 0 for the H<sub>2</sub> emissions, so a new device had to be used. The mirror in the single-reflection polarizer was made out of glass, which was found to have significant polarization sensitivity over a large wavelength range. For the H<sub>2</sub> emissions, the polarization sensitivity of this device was measured and found to be 0.55.

No wavelength selection was performed in the photon channel other than that which occurred due to the decrease in the channeltron sensitivity toward longer wavelengths. For this reason, a number of vibrational bands contributed to the observed signal in the photon channel. However, this is not expected to be a problem, since vibrational transitions do
not contribute any angular momentum to the excitation or decay processes, and will not affect the polarization. In fact, straightforward polarization measurements using different vibrational bands in H2 confirmed this aspect.

Coincidence Counting Electronics

The coincidence counting electronics are shown in Fig. 4.5 and Table 4.2 lists the components used. Note that the photon channel is used to start the time-to-amplitude converter (TAC) and the electron channel is used to stop it. The timing single channel analyzers have adjustable delays which were used to vary the overall relative delay between the photon and electron channels. The position of the coincidence peak in the time spectrum could be adjusted in this way. Normally, the integral discriminators are not necessary, since the TSCA's(*) have constant fraction discriminators built in, but it was found that the timing resolution of the electronics could be improved significantly by including them. Output pulses from the TAC were fed into a TA-1710 pulse height analyzer which was used to obtain the coincidence spectrum (more will be said about this later).

Fig. 4.6 shows a logic diagram of the electronics used to rotate the polarized photon detector. The TA-1710 issued a TTL pulse to the device, telling it to rotate the polarizer through 90 degrees. Microswitches on the motor mounting were used to signal the controller that rotation was com-

(*) Timing Single Channel Analyzers
**Table 4.2**

Coincidence Counting Electronics

<table>
<thead>
<tr>
<th>Module</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenelec ABC-5000</td>
<td>Channeltron High Voltage Supply</td>
</tr>
<tr>
<td>Kepco H32AM</td>
<td>Photon Channeltron Bias Supply</td>
</tr>
<tr>
<td>Ortec 461</td>
<td>Delay Line Amplifier</td>
</tr>
<tr>
<td>Ortec 421</td>
<td>Integral Discriminator</td>
</tr>
<tr>
<td>Ortec 551</td>
<td>Timing Single Channel Analyzer</td>
</tr>
<tr>
<td>Ortec 467</td>
<td>Time to Pulse Height Converter</td>
</tr>
<tr>
<td>Ortec 441</td>
<td>Rate meter</td>
</tr>
<tr>
<td>Ortec 484</td>
<td>Scaler</td>
</tr>
<tr>
<td>Tracer Northern TN-1710</td>
<td>PNA Mainframe</td>
</tr>
<tr>
<td>TK-1710-4</td>
<td>200MHz ADC</td>
</tr>
</tbody>
</table>
4.1.2 Data Collection and Analysis

The steps necessary to produce polarization correlation data are relatively straightforward and are as follows:

(1) An energy loss spectrum was acquired (as outlined in Chapter 2) over an energy range which covers the transition to be studied. This was normally done at a scattering angle of 0 degrees to obtain the maximum amount of signal, and at an energy well above the excitation threshold. Acquisition times were on the order of 1-2 hours, since the electron counts were on the order of 20 kHz or more for the largest energy loss peaks. From the energy loss spectrum, an estimate of the overall resolution of the spectrometer could be obtained. The signal-to-noise ratio in the electron channel could also be maximized this way. Once the energy loss spectrum was obtained, the peak corresponding to the desired transition was identified, and the analyzer was tuned to that energy.

(2) The coincidence electronics was then set up to provide optimum timing resolution and the relative delay between the photon and electron channels was adjusted so that the coincidence peak appeared approximately in the middle of a
512 channel spectrum. This was to ensure that a reliable value for the background would be obtained on both sides of the peak. The timing range of the TAC was chosen to be 400ns in the present work.

(3) The TN-1710 PHA was then programmed to acquire data in both halves of its memory, the first half corresponding to the polarizer at the angle $\theta$ and the second half corresponding to the polarizer rotated to the angle $\theta + 90$. Coincidence counts were accumulated in each half of memory for a preset amount of live time, after which it sent a pulse to the polarizer controller, telling it to rotate the polarizer. After a suitable delay (allowing the rotation to complete), the TN-1710 switched memory halves and resume counting. This sequence was repeated until sufficient statistics were accumulated. Systematic variations in beam current and target gas pressure were averaged out in this way, and the two coincidence spectra were automatically normalized to the total live time. Because of the low coincidence rates, typical data collection times were 30 to 80 hrs, and the statistics were then only about 3 percent at best.

Before using $N_2$ or $H_2$ as target gases, the operation of the system was checked out using He. This was done to
ensure that reliable results could be obtained and to determine the orientation of the polarization ellipse. Also, any asymmetry in the polarization ellipse could be estimated from this. This was necessary since the measurements were made at only 2 angles instead of all four. Thus any asymmetry would affect the measured value of the polarization and would have to be corrected for. It was found that the asymmetry in the polarization ellipse was negligible in the present work. Of course, it would have been better to measure the coincidence data at all four angles $\beta$, $\beta + 90$, $\beta + 180$ and $\beta + 270$, since this would average out any asymmetry. This modification is being planned for future experiments of this type.

Another experimental parameter which had to be determined was the acceptance angle (angular resolution) of the analyzer. This was done by observing the electron signal with no target gas present as a function of the angular position of the analyzer. It has been shown by Hertel and Ross that the angular resolution of the analyzer is given by the angle at which the electron signal disappears. In the present work, this occurred at about 2 degrees.

Analysis of the Coincidence Data

Fig. 4.6 shows a typical set of coincidence spectra obtained in the present work. The peak in the spectrum comes from electron-photon pairs which are correlated. Uncorrelated electron-photon pairs produce chance coincidences which appear as a uniform background in the spectrum.
FIG 4.7 Typical Coincidence Spectra
The number of true coincidences is then the area under the peak minus the number of chance coincidences which contribute to the peak. The polarization is then defined as:

$$P_C(\beta) = \frac{1}{2} \frac{N_C(\beta) - N_C(\beta+90)}{\alpha N_C(\beta) + N_C(\beta+90)}$$  \hspace{1cm} (4.3.2.1)

where $N_C(\beta)$ is the number of true coincidences obtained with the polarizer set to the angle $\beta$ and $\alpha$ is the polarization sensitivity of the polarizer. With this definition, the Stokes' parameters that were measured are:

$$s_3 = P_C(0)$$
$$s_1 = P_C(45)$$

Assuming Poisson statistics, the error in $P_C(\beta)$ can be determined, and is given by:

$$\sigma(P_C(\beta)) = \frac{2((\alpha^2 N_C(\beta+90)(N_C(\beta) + 2N_B(\beta))) + 2N_B(\beta)(N_C(\beta+90) + 2N_B(\beta+90)))^{1/2}}{\alpha(N_C(\beta) + N_C(\beta+90))^2}$$  \hspace{1cm} (4.3.2.2)

where $N_C(\beta)$ is the number of true coincidences and $N_B(\beta)$ is the number of chance coincidences obtained at the polarizer angle $\beta$.

The pseudo-threshold polarization was obtained by measuring $P_C(0)$ at a scattering angle of 0 degrees.

For lack of a better model, the polarization correlation data was analyzed in terms of two dipole oscillators as discussed in section 4.2.2. This is bound to have its shortcomings, of course, since this model necessarily implies complete coherence. There is no reason to suppose that this will be the case for molecules when the rotational structure is not resolved, as discussed in section 4.2.4. The follow-
ing equations list the various parameters deduced from the
polarization correlation data and the associated errors.

\[ R = \frac{a_x}{a_z} = \frac{1 - P_C(0)}{1 + P_C(0)}^{1/2} \]  \hspace{1cm} (4.3.2.3a)

\[ \sigma(R) = \frac{P_C(0)}{1 + P_C(0)} \frac{\sigma(P_C(0))}{(1 - P_C(0))^2}^{1/2} \]  \hspace{1cm} (4.3.2.3b)

\[ \delta = \cos^{-1}(P_C(45)/(1 - P_C(0))^2)^{1/2} \]  \hspace{1cm} (4.3.2.4a)

\[ \sigma(\delta) = \frac{180}{\pi} \frac{(\sigma^2(P_C(45)) + (P_C(0)P_C(45)/(1 - P_C(0))^2)^2)^{1/2}}{(1 - P_C(0)P_C(45)))^{1/2}} \]  \hspace{1cm} (4.3.2.4b)

\[ \phi_{\min} = \frac{1}{2} \tan^{-1}\frac{P_C(45)}{P_C(0)} \]  \hspace{1cm} (4.3.2.5a)

\[ \sigma(\theta)_{\text{min}} = \frac{180}{\pi} \frac{(P_C(0)\sigma^2(P_C(45)) + P_C(45)\sigma^2(P_C(0)))^{1/2}}{2(P_C(0) + P_C(45))} \]  \hspace{1cm} (4.3.2.5b)

The shape of the radiation pattern in the scattering plane
was determined by making the arbitrary normalization:

\[ a_z^2 + a_x^2 = 1 \]

and solving for \( a_z \) and \( a_x \) from equation 4.3.2.3a. These
values were then used in the following equation:

\[ I(\theta) = a_z^2 \sin^2 \theta + a_x a_z \cos \sin 2\theta + a_x^2 \cos^2 \theta \]  \hspace{1cm} (4.3.2.6)

The direction of momentum transfer is given by:

\[ \theta_k = \tan^{-1} \left( (\sin \theta_e (1 - \Delta E/E))^{1/2} - \cot \theta_e \right)^{-1} \]  \hspace{1cm} (4.3.2.7)

The derivation of this is given in Appendix 4.6.2.
4.4 RESULTS AND DISCUSSIONS

4.4.1 Nitrogen Data

Figures 4.8-4.16 present the results obtained for the excitation of the Cl $^1\Sigma^+ (v'=0)$ state of $N_2$. Fig. 4.6 shows the energy loss spectrum obtained at an incident energy of 80 eV and a scattering angle of 0 degrees. The Cl state is indicated on the diagram and occurs at 12.93 eV. The estimated energy resolution of the spectrometer is 100 meV. Typical electron count rates at the peak varied from 60kHz at $\theta_e = 0$ to about 10kHz at $\theta_e = 15$ degrees, and the photon count rates were about 10-30 Hz, reflecting the low transmission of the polarizer (about 10 percent). Not resolved in this spectrum are the peaks on the low energy flank of the Cl peak due to excitation of other states. This is not a problem, however, as the recent measurements performed by Read and co-workers(*) show that the main contribution to the coincidence rate comes from the Cl feature. They performed coincidence gated energy loss measurements in this energy region and found that the Cl state is the dominant contribution to the photon signal; contributions from the $b^1\Pi_u$ state are negligible.

Figure 4.9 shows the variation of $C_1$ with gas pressure at an energy of 35 eV and $\theta_e = 0$ degrees. Table 4.3 lists the data. Note that at pressures above 2 torr there is a significant decrease in the polarization due to resonance trap-

(*) G.C. King, private communication
FIG 4.8
\[ \text{e}^- + \text{N}_2 \lor \text{ENERGY LOSS SPECTRUM} \]
\[ E_{\text{inc}} = 80 \, \text{eV}; \theta_\text{e} = 0^\circ \]

\[ \Sigma^+_g(v' = 0) \rightarrow \Sigma^+_u(v' = 0) \]
<table>
<thead>
<tr>
<th>Head Pressure (torr)</th>
<th>Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0±0.1</td>
<td>0.14±0.02</td>
</tr>
<tr>
<td>1.5±0.1</td>
<td>0.16±0.02</td>
</tr>
<tr>
<td>1.9±0.1</td>
<td>0.18±0.02</td>
</tr>
<tr>
<td>2.4±0.1</td>
<td>0.18±0.03</td>
</tr>
<tr>
<td>2.9±0.1</td>
<td>0.10±0.02</td>
</tr>
<tr>
<td>3.6±0.1</td>
<td>0.10±0.02</td>
</tr>
<tr>
<td>4.4±0.1</td>
<td>0.07±0.02</td>
</tr>
</tbody>
</table>

Table 4.3
$E_C(0)$ vs Pressure: $N_2$

Incident Energy = 35.6 eV, Electron Scattering Angle = 0
ping or collisional effects. To ensure that subsequent measurements were free from such effects, a pressure of 1.5 torr was chosen as the working pressure throughout the rest of the experiment.

**Pseudo-threshold Polarization Measurements**

Fig. 4.10 shows the variation of $P_C(0)$ with incident energy at a scattering angle of 0 degrees, and Table 4.4 lists the results. This is the first such pseudo-threshold polarization measurement made in $N_2$. The data indicates a pseudo-threshold polarization value of $0.18 \pm 0.04$. Arrow a indicates the predicted threshold polarization using results of section 4.2.5 (equation 4.2.5.12), with a value of 0.19. Arrow b indicates the predicted polarization when hyperfine structure effects were taken into account (see details in Ref 85). This has a value of 0.17. The experimental value is in good agreement with these, but the statistical uncertainty in the data precludes a further distinction between the two approaches. The experimental value of $P_{th}$ is certainly above the predicted value of 0.143 using the semiclassical approach (arrow c), and more than a factor of 2 above the extrapolated threshold polarization obtained by Huscill et al. with a value of 0.07 (arrow d). The lack of agreement between the pseudo-threshold value and the predicted polarizations with the direct polarization measurements of Hüschill et al is rather puzzling, particularly since resonances or electron correlation effects do not appear to be dominating the excitation process in the near
FIG 4.10

$e^- + N_2$

$P_c(0)$ vs Energy

$\theta_e = 0^\circ$
threshold region in \( \text{N}_2 \). The influence of non-dipole terms in the excitation process was suggested by Huschilt et al., and the recent work of Hernández et al. lends support to this. These authors used a supersonically cooled \( \text{N}_2 \) beam and observed rotational transitions in the excitation process with changes in rotational quantum number of as much as 15. Since the entire ensemble was initially in the rotational ground state, this implies that non-dipole transitions were occurring in the excitation process. They found that these non-dipole effects were particularly significant at energies below 100 eV. The agreement of the pseudothreshold polarization with theoretical predictions (where dipole excitation was assumed) is then probably due to the fact that dipole excitation dominates the scattering process in the forward direction. Strong configuration interaction effects associated with the excitation of the \( \text{C}_1 \) state may also be involved.

It is interesting to note that the measurements of Huschilt et al. on the polarization of radiation emitted from the \( b^\Pi \) state of \( \text{N}_2 \) also showed a discrepancy between the theoretical predictions and the value they obtained. This result, along with the present results, suggests that non-dipole excitation is occurring for the \( b^\Pi \) state also.

Note the decrease in \( P \) at about 3 times the threshold energy in Fig. 4.10. This is due to the finite acceptance angle of the analyzer. This can be understood as follows. Assuming for the moment that the Born approximation is valid
Table 4.4
$P_e(0)$ vs Incident Energy: N₂

<table>
<thead>
<tr>
<th>Incident Energy (eV)</th>
<th>Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>0.19±0.03</td>
</tr>
<tr>
<td>35.0</td>
<td>0.18±0.03</td>
</tr>
<tr>
<td>40.0</td>
<td>0.19±0.02</td>
</tr>
<tr>
<td>45.0</td>
<td>0.14±0.02</td>
</tr>
<tr>
<td>50.0</td>
<td>0.13±0.02</td>
</tr>
<tr>
<td>60.0</td>
<td>0.09±0.02</td>
</tr>
<tr>
<td>75.0</td>
<td>0.08±0.02</td>
</tr>
<tr>
<td>100.0</td>
<td>0.10±0.02</td>
</tr>
</tbody>
</table>

Head Pressure = 1.5 torr, Electron Scattering Angle = 0
at all energies, the momentum transfer vector is the quantization axis. The finite angular resolution of the analyzer means that there will be a distribution in the direction of momentum transfer, and hence, a depolarization in the measured value of $P_C(0)$. At low energies, the momentum transfer vector is practically in the forward direction, and the quantization axis lies very close to the z axis; no significant depolarization would be observed. At higher energies, however, the momentum transfer vector rotates away from the z axis, and results in a larger angular distribution of this vector, even though the scattered electrons are detected close to $\theta_e=0$. This causes the observed depolarization in the data at higher energies.

Polarization Correlation Data

Figure 4.11 shows the variation of $P_C(0)$ and $P_C(45)$ with incident energy at a scattering angle of 5 degrees, and Table 4.5 lists the data. Several points should be noted about Fig. 4.11:

1. The small value of $P_C(0)$. It has essentially constant value of about 0.06 over the whole energy range studied, whereas the pseudo-threshold polarization measurement had a value of 0.18.

2. The dip in $P_C(0)$ towards 0 at an energy of about 67.5 eV is probably significant (see later). It appears that a minimum in $P_C(0)$ occurs whenever $P_C(45)$ goes through 0.
<table>
<thead>
<tr>
<th>E (eV)</th>
<th>E_C(0)</th>
<th>E_C(45)</th>
<th>a_x/a_z</th>
<th>Phase (deg)</th>
<th>θ^1_{min} (deg)</th>
<th>θ^1_{K} (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.0</td>
<td>0.06±0.02</td>
<td>0.08±0.01</td>
<td>0.94±0.02</td>
<td>85.7±0.7</td>
<td>-25.9±4.4</td>
<td>21.7</td>
</tr>
<tr>
<td>50.0</td>
<td>0.06±0.03</td>
<td>0.04±0.02</td>
<td>0.94±0.03</td>
<td>88.0±1.0</td>
<td>-15.1±8.4</td>
<td>27.8</td>
</tr>
<tr>
<td>60.0</td>
<td>0.05±0.03</td>
<td>-0.02±0.02</td>
<td>0.95±0.03</td>
<td>90.9±1.4</td>
<td>9.0±13.5</td>
<td>33.3</td>
</tr>
<tr>
<td>67.5</td>
<td>0.02±0.02</td>
<td>-0.02±0.02</td>
<td>0.98±0.02</td>
<td>91.1±1.3</td>
<td>19.8±4.5</td>
<td>36.9</td>
</tr>
<tr>
<td>75.0</td>
<td>0.06±0.03</td>
<td>-0.14±0.02</td>
<td>0.94±0.02</td>
<td>97.8±1.2</td>
<td>32.5±4.7</td>
<td>40.2</td>
</tr>
<tr>
<td>90.0</td>
<td>0.06±0.02</td>
<td>-0.07±0.03</td>
<td>0.95±0.02</td>
<td>94.2±1.7</td>
<td>26.5±8.1</td>
<td>45.9</td>
</tr>
</tbody>
</table>

Table 4.5
Polarization Correlation Data vs Energy: N₂

Electron Scattering Angle = 5 degrees, Pressure = 1.5 torr
(3) $P_C(\theta_0)$ is small and positive below $60$ eV and then decreases rapidly to about $-0.10$ at $75$ eV, after which it increases slowly again. The rapid variation of $P_C(65)$ near $67.5$ eV, along with the decrease in $Z_C(0)$ at this energy, suggests that something interesting is happening in the scattering process around $67.5$ eV.

Fig. 4.12 shows a typical radiation pattern deduced from the Stokes' parameters, as discussed in section 4.2.2. Indicated on the diagram is the electron scattering angle $\theta_e$, the direction of momentum transfer $\theta_k$, and the orientation of the pattern $\theta_\gamma^\min$.

Fig. 4.13(a) shows the variation of $\theta_k$ and $\theta_\gamma^\min$ with incident energy at a scattering angle of $5^\circ$ degrees. The horizontal error bars reflect the angular resolution of the spectrometer. Note that $\theta_k$ and $\theta_\gamma^\min$ do not seem to be related in any way to each other. This is distinctly different from the atomic case, where these angles should agree with each other for high energies and small scattering angles. Below $55$ eV, $\theta_\gamma^\min$ and $\theta_k$ are on opposite sides of the $z$ axis.

Fig. 4.13(b) shows the variation of the phase angle, $\delta$, with incident energy. Note that between $60$ and $67.5$ eV the phase angle is close to $90$ degrees, suggesting that a significant component of circular polarization is present in the
$N_2 \quad E = 40 \text{ eV}; \quad \theta_e = 10^\circ$
\theta_e = 5^\circ

FIG 4.13
\theta_k, \theta_{\min}^Y \text{ and Phase vs Energy: } N_2.
### Table 4.6
Polarization Correlation Data vs Scattering Angle: \( \text{N}_2 \)

#### Incident Energy = 40.0 eV, Pressure = 1.5 torr

<table>
<thead>
<tr>
<th>( \theta_e ) (deg)</th>
<th>( E_C(0) )</th>
<th>( E_C(45) )</th>
<th>( a_x/a_\perp )</th>
<th>Phase (deg)</th>
<th>( \theta_{\min} ) (deg)</th>
<th>( \theta_k ) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.18±0.02</td>
<td>0.01±0.04</td>
<td>0.83±0.02</td>
<td>89.6±2.0</td>
<td>-0.9±5.4</td>
<td>0.0</td>
</tr>
<tr>
<td>5.0</td>
<td>0.06±0.02</td>
<td>0.06±0.01</td>
<td>0.64±0.02</td>
<td>85.7±0.7</td>
<td>-25.9±4.4</td>
<td>21.7</td>
</tr>
<tr>
<td>7.5</td>
<td>0.05±0.02</td>
<td>0.03±0.02</td>
<td>0.95±0.02</td>
<td>88.1±1.4</td>
<td>-15.7±4.5</td>
<td>30.2</td>
</tr>
<tr>
<td>10.0</td>
<td>0.16±0.03</td>
<td>-0.11±0.02</td>
<td>0.85±0.02</td>
<td>96.4±1.3</td>
<td>16.9±3.5</td>
<td>36.6</td>
</tr>
<tr>
<td>15.0</td>
<td>0.14±0.02</td>
<td>-0.16±0.03</td>
<td>0.87±0.02</td>
<td>99.2±1.5</td>
<td>24.1±3.4</td>
<td>46.0</td>
</tr>
</tbody>
</table>

#### Incident Energy = 75 eV, Pressure = 1.5 torr

<table>
<thead>
<tr>
<th>( \theta_e ) (deg)</th>
<th>( E_C(0) )</th>
<th>( E_C(45) )</th>
<th>( a_x/a_\perp )</th>
<th>Phase (deg)</th>
<th>( \theta_{\min} ) (deg)</th>
<th>( \theta_k ) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.06±0.02</td>
<td>0.06±0.02</td>
<td>0.92±0.02</td>
<td>89.7±1.3</td>
<td>-1.8±4.5</td>
<td>0.0</td>
</tr>
<tr>
<td>5.0</td>
<td>0.06±0.02</td>
<td>-0.14±0.02</td>
<td>0.94±0.02</td>
<td>97.8±1.2</td>
<td>32.5±4.7</td>
<td>40.2</td>
</tr>
<tr>
<td>7.5</td>
<td>-0.03±0.02</td>
<td>-0.01±0.03</td>
<td>1.03±0.02</td>
<td>90.5±1.5</td>
<td>-8.1±4.5</td>
<td>50.4</td>
</tr>
<tr>
<td>10.0</td>
<td>0.07±0.03</td>
<td>0.26±0.05</td>
<td>0.94±0.03</td>
<td>73.8±2.8</td>
<td>-38.3±3.3</td>
<td>56.6</td>
</tr>
<tr>
<td>12.5</td>
<td>0.06±0.04</td>
<td>0.30±0.04</td>
<td>0.94±0.04</td>
<td>72.3±2.4</td>
<td>-39.6±3.5</td>
<td>60.4</td>
</tr>
</tbody>
</table>
emitted radiation.

Figs. 4.14(a) and (b) show the variation of the Stokes' parameters with electron scattering angle at 40 and 75 eV, respectively. Table 4.6 lists the data. The following points should be noted from these figures:

(1) The rapid decrease in $P_C(0)$ to the minimum which occurs at about 7.5 degrees. Note also that $P_C(45)$ goes through 0 at about this angle. At larger scattering angles, $P_C(0)$ remains essentially constant, but $P_C(45)$ shows large variations.

(2) The behaviour of $P_C(45)$ at 40 eV is almost exactly opposite to the behaviour at 75 eV. $P_C(45)$ goes through 0 at about 7.5 degrees, independent of energy, and the extremum (maximum or minimum) in $P_C(45)$ occurs at about 5 degrees, again independent of energy.

(3) $P_C(0)$ appears to be close to 0 at 7.5 degrees at the incident energy of 75 eV.

(4) Attention should be drawn to the large variations in $P_C(45)$. These are much larger than what was observed in $H_2$ (see section 4.4.2).

It would appear from this data that $P_C(0)$ goes through a minimum each time $P_C(45)$ goes through 0. This suggests that there is some sort of correlation between these Stokes' parameters, an effect which would not be expected from the simple model discussed in section 4.2.2.
FIG 4.15
$\theta_k, \theta_{\min}^Y$ vs Scattering Angle: N$_2$
Figures 4.15(a) and (b) show the variation of $\theta_k$ and $\theta_{\text{min}}$ with electron scattering angle at 40 and 75 ev, respectively. It can be seen at once that $\theta_{\text{min}}$ bears no relationship to $\theta_k$ whatsoever, suggesting that the Born approximation is clearly inadequate to describe the scattering process for $\theta_k$. The significant difference in the behaviour of $\theta_{\text{min}}$ at 40 and 75 ev should be noted also.

Figure 4.16 shows the variation of the phase angle, $\delta$, with electron scattering angle at 40 and 75 ev. Note once again the opposite behaviour of $\delta$ at the two energies. The phase angle is about 90 degrees at a scattering angle of 7.5 degrees, suggesting that a significant component of circular polarization may be present.

Because of the large number of rotational states contributing to the observed radiation, it is not possible to extract information about the scattering amplitudes from the present data. Also, it is not possible to extract information about the state multipoles $\langle \tau^k_{KQ} \rangle$ from the Stokes' parameters, except to say the following. Recall from the discussion of section 4.2.4, that the Stokes' parameters are given by:

$$P_C(0) = \frac{-\langle T^+_1 \rangle + \sqrt{3}/2 \langle T^+_2 \rangle}{I}$$

$$P_C(45) = -2 \langle T^+_2 \rangle / I$$

where

$$I = (-2 \langle T^+_0 \rangle \sqrt{3} + \langle T^+_1 \rangle + \langle T^+_2 \rangle \sqrt{3}/2 \langle T^+_0 \rangle / \sqrt{3}).$$

At a scattering angle of 7.5 degrees, where both $P_C(0)$ and $P_C(45)$ are essentially zero, $\langle T^+_1 \rangle = 0$ and $\langle T^+_2 \rangle = \sqrt{3}/2 \langle T^+_0 \rangle$. 
One may however, point out the following. Since the excitation and decay processes are independent the value of \( p_c(0) \) is determined solely by the relative populations of the different magnetic sublevels, and hence by the selection rules governing the excitation of these. If dipole selection rules are dominant it is difficult to see how \( p_c(0) \) could vary much, given the selection rules for homonuclear diatomic molecules. However, if non-dipole excitation is favoured at certain scattering angles and incident energies, then significant depolarization may occur, forcing \( p_c(0) \) to 0 or even negative. As pointed out previously, non-dipole excitation is certainly occurring in \( N_2 \), particularly at the low energies used in the present work. Next, even though a large number of rotational levels contribute to the observed coincidence signal and the coherence between states of different \( N_2 \) is not observed, it may still be possible that a reduction in \( p_c(0) \) may occur due to the effects of coherent excitation of the rotational levels. The amount of coherence is of course limited by the rigorous selection rule \( \text{sym} \rightarrow \text{antisym} \) in the total wavefunction. Thus only states with even \( N_1 \) can interfere with each other, and similarly, only states with odd \( N_1 \) interfere with each other. There is no coherence between states of even and odd \( N_1 \). Just as the influence of fine and/or hyperfine structure causes a reduction in the measured polarization even though the coherence between fine(or hyperfine) structure levels is not observed, the coherence between rotational levels could also reduce the measured polarization in the present case.
4.4.2 Hydrogen Data

The results of the polarization correlation experiments with $\text{H}_\text{g}$ are shown in Figures 4.17 to 4.22. Fig. 4.17 shows the energy loss spectrum obtained in $\text{H}_\text{g}$ at an incident energy of 30 eV and electron scattering angle of 0 degrees. Indicated on the diagram are the Lyman ($\chi_{\Sigma}^+(v''=0) \rightarrow \Sigma_u^+(v')$) bands and the Werner ($\chi_{\Sigma}^+(v''=0) \rightarrow \Pi_u^+(v')$) bands. The estimated energy resolution of the spectrometer was about 100 meV, as it was in $\text{N}_\text{g}$. Note that this is insufficient to resolve the overlap of the higher lying Lyman bands with the Werner bands, so the observed coincidence signal contained contributions from the Lyman (7,0) and (8,0) bands. However, these are so much weaker than the Werner (0,0) band, which was studied, that their contribution was considered negligible. Also, it is very probable that the Lyman (7,0) and (8,0) bands do not decay back to the $v''=0$ state, but to higher vibrational states, and hence the wavelengths of photons emitted in these transitions are beyond the cutoff limit of the channeltron sensitivity.

Electrons which lost 12.29 eV (corresponding to the Werner (0,0) band) were detected in coincidence with the emitted photons. Typical count rates in the electron channel varied from about 50 kHz at $\theta_e=0$ to about 6 kHz at $\theta_e=25$ degrees, and in the photon channel, typical count rates were about 10-40 Hz. In order to obtain reasonable statistics, data acquisition times were about 30 to 80 hours.
e\(^{-}\) + H\(_2\) ENERGY LOSS SPECTRUM

E\(_{\text{inc}}\) = 80 eV, \(\theta_e = 0^\circ\)

FIG 4.17

\(X^1\Sigma_g^+ (v''=0) \rightarrow \chi^1\Pi_u (v')\)

Werner Bands

\(X^1\Sigma_g^+ (v''=0) \rightarrow \chi^3\Sigma_g^+ (v')\)

Lyman Bands
FIG 4.18

$P_c(0)$ vs PRESSURE: $e^- + H_2$

$E_{inc} = 50$ eV, $\theta_c = 0^\circ$
Table 4.7
$P_c(0)$ vs Pressure and Energy: $H_2$.

<table>
<thead>
<tr>
<th>Incident Energy = 50.0 eV, Scattering Angle = 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head Pressure (torr)</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>1.2±0.1</td>
</tr>
<tr>
<td>2.0±0.1</td>
</tr>
<tr>
<td>3.2±0.1</td>
</tr>
<tr>
<td>5.0±0.1</td>
</tr>
</tbody>
</table>

Pseudo-Threshold Polarization Measurements:
Electron Scattering Angle = 0, Pressure = 1.5 torr

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.0</td>
<td>0.19±0.05</td>
</tr>
<tr>
<td>50.0</td>
<td>0.22±0.02</td>
</tr>
<tr>
<td>80.0</td>
<td>0.20±0.05</td>
</tr>
</tbody>
</table>
Figure 4.18 shows the variation of $P_c(0)$ with gas pressure for a scattering angle of 0 degrees and an incident energy of 50 eV, and Table 4.7 lists the data. To ensure that radiation trapping was not causing a depolarizing effect, a pressure of 1.5 torr was used throughout the experiment. It can be seen from Fig. 4.18 that the polarization is essentially constant near this pressure. A comparison of Fig. 4.18 with the polarization vs pressure data obtained in $N_2$ shows that the pressure dependence of $P_c(0)$ is not as strong in $N_2$.

**Pseudo-threshold Polarization Measurements**

The only other pseudo-threshold polarization measurements available in $N_2$ are those of Malcolm and McConkey\(^{60, 61}\). The present results are listed in Table 4.7. For the $N_2$ Werner bands, they measured a pseudo-threshold polarization of $0.17 \pm 0.03$, and the present measurements indicate a value of about $0.20 \pm 0.03$, both of which are in disagreement with the direct polarization measurements on the integrated Werner $(J,1)$ band\(^{75}\), which indicate an extrapolated threshold polarization of about 0.3 (assuming the rapid decrease near the threshold is due to resonance effects and electron correlations). The theoretical predictions of section 4.2.5 give a value of 0.35 for the threshold polarization, which is about 100 percent higher than the pseudo-threshold values. Note that the situation in $N_2$ is reversed from that of $N_2$. In the latter gas, there was agreement between the theory and pseudo-threshold value. More will be said about
this in section 4.4.3.

Polarization Correlation Results:

Fig. 4.19 shows the variation of $P_C(0)$ and $P_C(45)$ with electron scattering angle for incident electron energies of 50 and 80 eV. The smooth curves drawn through the data points are suggestive of the trends in the data only. Table 4.8 lists the data obtained at these energies. The following points should be noted from Fig. 4.19.

1. The slight increase in $P_C(0)$ between 0 and 5 degrees at 50 eV. This behavior was also observed by Malcolm and McConkey, but was not observed in $N_2$.

2. $P_C(0)$ reaches a minimum value at about 12.5 degrees for both 50 and 80 eV. The rather deep minimum which occurs at 50 eV as compared to the shallow one at 80 eV should be noted. $P_C(0)$ is probably 0 at 15 degrees for 80 eV.

3. $P_C(45)$ is less than zero for all scattering angles observed, except at 0 and 15 degrees, where it is close to $C(\epsilon=50 \text{ eV})$. A minimum in $P_C(45)$ occurs at a scattering angle of 10 degrees at both energies. Also, $P_C(45)$ increases faster from the minimum with increasing scattering angle at 50 eV than at 80 eV.

Fig. 4.20 shows a typical radiation pattern deduced from $P_C(0)$ and $P_C(45)$. Fig. 4.21 shows the variation of $\theta_k$ and
FIG 4.21

$\theta_k, \theta_{\text{min}}^\gamma$ vs Scattering Angle: $H_2$
FIG 4.22 Phase vs Scattering Angle: H₂
### Table 4.8
Polarization Correlation Data vs Scattering Angle: H₂

<table>
<thead>
<tr>
<th>x (deg)</th>
<th>θₑ (deg)</th>
<th>F₉(0)</th>
<th>F₉(45)</th>
<th>aₓ/aₜ</th>
<th>Phase (deg)</th>
<th>θₑ_min (deg)</th>
<th>θₖ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.22±0.02</td>
<td>-</td>
<td>0.80±0.02</td>
<td>90.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5.0</td>
<td>0.24±0.05</td>
<td>-0.23±0.05</td>
<td>0.78±0.04</td>
<td>103.9±2.9</td>
<td>21.6±4.1</td>
<td>29.3</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>0.14±0.05</td>
<td>-0.36±0.05</td>
<td>0.87±0.04</td>
<td>111.3±2.9</td>
<td>34.2±3.4</td>
<td>39.2</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>0.06±0.06</td>
<td>-0.46±0.01</td>
<td>0.94±0.06</td>
<td>113.7±2.6</td>
<td>40.7±4.4</td>
<td>46.2</td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>0.02±0.05</td>
<td>-0.31±0.06</td>
<td>0.98±0.05</td>
<td>108.0±3.4</td>
<td>43.5±4.5</td>
<td>51.0</td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>0.20±0.05</td>
<td>0.02±0.05</td>
<td>0.82±0.04</td>
<td>89.1±2.9</td>
<td>-2.3±7.2</td>
<td>54.4</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>0.18±0.05</td>
<td>-0.04±0.05</td>
<td>0.84±0.05</td>
<td>92.2±3.1</td>
<td>6.0±8.5</td>
<td>56.7</td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>0.23±0.05</td>
<td>-0.12±0.05</td>
<td>0.79±0.04</td>
<td>97.2±3.1</td>
<td>13.8±5.7</td>
<td>58.2</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>0.16±0.06</td>
<td>-0.22±0.05</td>
<td>0.85±0.05</td>
<td>102.8±3.0</td>
<td>26.9±5.8</td>
<td>59.9</td>
<td></td>
</tr>
</tbody>
</table>

**Incident Energy = 50.0 eV, Pressure = 1.5 torr**

<table>
<thead>
<tr>
<th>x (deg)</th>
<th>θₑ (deg)</th>
<th>F₉(0)</th>
<th>F₉(45)</th>
<th>aₓ/aₜ</th>
<th>Phase (deg)</th>
<th>θₑ_min (deg)</th>
<th>θₖ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.26±0.05</td>
<td>-</td>
<td>0.82±0.04</td>
<td>90.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5.0</td>
<td>0.12±0.06</td>
<td>-0.18±0.04</td>
<td>0.88±0.05</td>
<td>100.7±2.6</td>
<td>28.1±6.9</td>
<td>43.8</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>0.06±0.05</td>
<td>-0.29±0.05</td>
<td>0.92±0.04</td>
<td>106.8±3.1</td>
<td>37.1±4.5</td>
<td>53.8</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>0.04±0.06</td>
<td>-0.36±0.06</td>
<td>0.96±0.06</td>
<td>111.4±3.6</td>
<td>41.7±4.6</td>
<td>59.5</td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>-0.03±0.06</td>
<td>-0.34±0.08</td>
<td>1.04±0.06</td>
<td>109.9±4.6</td>
<td>-42.2±4.6</td>
<td>62.9</td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>-0.01±0.06</td>
<td>-0.15±0.07</td>
<td>1.01±0.06</td>
<td>98.4±4.0</td>
<td>-43.8±5.0</td>
<td>64.9</td>
<td></td>
</tr>
</tbody>
</table>
with electron scattering angle for 50 and 80 eV. As can be seen, $\theta_{\text{min}}$ appears to follow $\theta_k$ up to about 12.5 degrees at 50 eV (Fig. 4.21(a)), and then drops sharply to a slightly negative value at 15 degrees. (Recall that this small angle agreement between $\theta_k$ and $\theta_{\text{min}}$ was not at all observed in $\text{H}_2$). It increases after this, but is not related to $\theta_k$. At 80 eV (Fig. 4.21(b)) $\theta_{\text{min}}$ follows $\theta_k$ up to about 10 degrees and then drops quickly down to a large negative value at 12.5 degrees, after which it appears to remain constant.

Fig. 4.22 shows the variation of the phase angle, $\delta$, with electron scattering angle. The phase is about the same at both energies up to 12.5 degrees. The 50 eV data then drops quickly to about 90 degrees at a scattering angle of 15 degrees before increasing slowly, whereas the 80 eV data decreases more slowly and not as far.

### 4.4.3 Discussion of the results

#### Pseudo-threshold Polarization

The pseudo-threshold polarization measurements in $\text{H}_2$ and $\text{H}_2$ provide the following information:

1. The measured pseudo-threshold polarization agrees rather well with theoretical predictions for $\text{H}_2$, but not for $\text{H}_2$.

2. A comparison of the pseudo-threshold polarization data with the results of direct polarization measurements indicates that there is disagreement between them for both $\text{H}_2$ and $\text{H}_2$. 
In addition to the above two facts, the results of direct polarization measurements on the resolved rotational structure in H$_3^+$ indicate that the extrapolated threshold polarizations agree with the predicted values using the results of section 4.2.5.

The disagreement between the pseudo-threshold measurement and the direct polarization measurements in H$_3^+$ has already been discussed, and the possibility of non-dipole excitation is most probably the cause of this, especially in the light of the results of Hernandez et al. Dipole excitation dominates the forward scattering, so this effect would not be observed in a pseudo-threshold measurement, giving agreement with theory. In addition, the agreement between theory and the pseudo-threshold measurements in H$_3^+$ indicates that the relative intensities of the P and S branches of the (0,0) band are predicted correctly by theory, even at energies well above the excitation threshold. This also suggests that the configuration interaction effects associated with the C$_2$ state are not altering the relative intensities of the P and S branches significantly at the energies used in the present experiment.

The disagreement between the pseudo-threshold measurement and theory for H$_3^+$ is rather puzzling. With the present data all that can be done is to suggest possible reasons for the discrepancy. It will not be possible to decide which reason is actually responsible without further detailed measurements.
Suppose that the theoretical predictions of the threshold polarization are indeed correct. Then the discrepancy is due to some experimental effect. Suppose further that $P_c(0)$ varies rapidly near 0 degrees; that is to say, it decreases sharply from a value of about 0.35 to a very small value before rising again to about 0.20 at 5 degrees. If this variation occurs over 2 degrees or less, chances are that it would not be observable because of the finite angular resolution of the spectrometer. Instead some average value (integrated over the angular resolution of the spectrometer) which was lower than the 'true' value at 0 degrees would be observed. This may also account for the apparent increase in $P_c(0)$ between 0 and 5 degrees. Such variations can be expected in the atomic case (see the paper by Wykes), but they occur over a much larger range of scattering angles. However, a comparison with He and with H indicates that everything seems to happen at much smaller scattering angles for molecules than for atoms (the minimum in $P_c(0)$ is an example of this). Not much can be said for or against this hypothesis from a theoretical point of view; the large number of interference terms between states of the same $N_1$ and different $\mathbf{N}$ appearing in the state multipoles (cf. equation 4.2.4.8) could either cause such a rapid variation or wash it out, depending on the relative phases of each scattering amplitude. The agreement between theory and experiment for the pseudo-threshold measurements in He suggests that the above-mentioned interference effects are a
real possibility. If the above discussion is correct, then it implies that $P_C(0)$ does not behave in this fashion for $\frac{N}{P}$, at least not at the energies used in the present work. It could be that any interference effects conveniently cancel out in $\frac{N}{P}$, leaving a smooth behaviour, and agreement with theory. The only way to test this suggestion is to repeat the polarization correlation measurements with a significant improvement in the angular resolution of the spectrometer.

The other possibility which could account for the discrepancy is that the theory incorrectly predicts the relative intensities of the P, Q and R branches of the Werner bands in $\frac{N}{P}$. Thus the experimental value could be correct. Note that this does not contradict the statements made earlier about the agreement between theory and experiment for the resolved rotational lines. These measurements were made at energies approaching the excitation threshold, whereas the pseudo-threshold measurement was carried out at energies well away from the threshold. The relative intensities are crucial when an estimate of the polarization is to be made. It may be that the deviation in the relative intensities from the theoretical values (at threshold) becomes significant only at energies well above the threshold. One possible reason for incorrect relative intensities is the known perturbations on the P and R branches of the Werner system by mixing with the $B^1\Sigma^+_u$ state. These effects would complicate the calculation of the threshold polarization and are not taken into account in the discussions of section
4.2.5. Another possibility has to do with the fact that the
pseudo-threshold polarization measurements do not reproduce
the threshold conditions exactly. First of all, the scattered
electron does not leave the collision with a angular
momentum as in the threshold case. Thus the calculation of
Blum\textsuperscript{70} as discussed in section 4.2.5 in connection with
Dunn's symmetry rules would have to be modified to take this
into account. Secondly, in a pseudo-threshold measurement,
it is the differential cross-sections which are involved,
and not the total cross-sections. In the case of the n-p
excitation, this does not matter since all dependence on the
dynamics of the scattering process cancels out anyway. This
is certainly not the case for molecules. It could be that a
combination of the above two facts could cause the relative
intensities of the F, Q and R branches to differ signifi-
cantly from the expected values. If the R branch contrib-
utes more to the emitted radiation than the Q or R
branches, then, since the predicted polarization of the R
branch is much less than the R or the Q branches, an overall
reduction of the observed polarization would occur.

Another possibility might be the effects of non-dipole
excitation, as discussed for N\textsubscript{2}. However, the agreement
between the extrapolated threshold polarizations and theor-
etical predictions\textsuperscript{73} for H\textsubscript{2}, would seem to preclude this.
Further work is necessary to determine which, if any, of the
above suggestions are correct.
Polarization Correlation Data

It is interesting to compare the $N_2$ data with the $H_2$ data. Of course, a strict comparison between $H_2$ and $N_2$ is unjustified because of the different electronic transitions involved ($\Sigma$ to $\Sigma$ in $H_2$ and $\Sigma$ to $\Pi$ in $N_2$). Similar features are observed in both gases, but there are some rather striking differences.

1. In both cases $P_C(0)$ is approximately constant except where it dips toward 0. The scattering angle at which this occurs seems to be independent of energy within a particular gas, but occurs at smaller scattering angles in $N_2$.

2. In both gases, variations in $P_C(45)$ were much more significant than those in $P_C(0)$. This probably reflects the fact that $P_C(45)$ carries phase information which is significant. Note also that $P_C(45)$ changed sign in $N_2$, but not in $H_2$.

3. The Born approximation was inadequate to describe the scattering process in $N_2$, but appeared to work fairly well for small scattering angles in $H_2$ (this can be seen from the graphs of $\theta_k$ and $\theta_{\gamma_{\text{min}}}$ for these gases).

4. In $N_2$, the 'effective' phase deduced from the data was always close to 90 degrees, whereas in $H_2$, much larger deviations from 90 were observed.
It is surprising that the phase is non-zero, given the large number of interference terms in the state multipoles. One would expect a net phase of 0 from this. Clearly there must be some simplifying factors involved which produce a net phase as large as was observed in the present results. Is it possible, for example, that there could be a relatively constant phase relationship between terms in the state multipoles with $\Delta M = 0$ and $\Delta M = \pm 1$? Further experimental work is clearly necessary to shed light on this problem, and some suggestions are put forward in Section 4.5.2.
4.5 CONCLUSIONS AND SUGGESTIONS

4.5.1 Conclusions

Pseudo-threshold polarizations in \( N_2 \) and \( H_2 \) have been measured and compared with the results of direct polarization measurements and theoretical predictions. This is the first such measurement performed in \( N_2 \). It was found that the pseudo-threshold measurements in \( N_2 \) for the \( \chi^1 \Sigma^+ \rightarrow \chi^1 \Pi_u \) system was consistent with theoretical predictions, with a value of 0.18±0.04, but not with the direct polarization measurement, which suggested a value of 0.07. The discrepancy between the two measurements has been attributed to the possibility of non-dipole excitation channels. In the \( H_2 \chi^1 \Pi_g \rightarrow \chi^1 \Pi_u \) system, it was found that the pseudo-threshold measurement was also inconsistent with the direct polarization measurement, with a value of 0.20±0.03, thus verifying the earlier work of Malcolm and McConkey. Theoretical predictions indicated that a value of about 0.35 should have been measured. Reasons for these discrepancies have been discussed.

Polarization correlation data were also obtained for \( N_2 \) and \( H_2 \). It was found that there were dramatic differences in the behaviour of the two Stokes' parameters \( P_\perp (0) \) and \( P_\perp (45) \) between the two gases. The Stokes' parameters have been analyzed in terms of two perpendicular dipole oscillators with a relative phase between them. Based on this oversimplified treatment, the parameters describing the radiation outside the scattering plane were deduced from
the data. The orientation of the radiation pattern, specified by the angle $\theta_y$, was compared to the predictions of the Born approximation (momentum transfer direction). It was found that the Born approximation was inadequate to describe the results in $N_2$, but seemed to work for very small scattering angles in $N_2$. The relative phase between the dipole oscillators was found to be large and close to 90 degrees in both cases, suggesting that a significant component of circular polarization is present in molecular radiation. It was suggested that the presence of an overall phase could be due to the possibility that the relative phase between each scattering amplitude is related only to the change in the magnetic quantum number $m$ in going from the initial state to the excited state. Of course, the presence of a large unpolarized component in the emitted radiation may also account for this, so such a conclusion must be taken as very tentative. Clearly, an actual measurement of the circular polarization is needed to sort this out.

The model used to analyze the polarization data is clearly not adequate to describe the situation in the molecular case, so further work will require the use of a more general description of polarized light.

On the theoretical side, the results of the density matrix formalism have been applied to some simple cases in $N_2$ excitation. It was found that information about the scattering amplitudes could only be extracted from the Stokes' parameters if single rotational lines could be
resolved or if the initial molecular ensemble is prepared so that all molecules are in the $N_0=0$ state.

4.5.2 Suggestions for Future Research

Based on the discussion of the pseudo-threshold polarization measurements and the difficulties encountered there, it is possible to suggest ways in which one should proceed in dealing with electron-molecule excitation.

1. Experiments in which single rotational lines can be resolved should be carried out. This involves working in the visible region and using narrow band filters. In this way single decay channels can be isolated. Such experiments are currently being developed, and have the distinct advantage that the circular polarization can be measured.

2. To reduce the number of excitation channels, new developments in supersonic beam technology can be used to cool the molecular ensemble so that only the lowest rotational level is populated. This would enable actual scattering amplitudes to be extracted from the Stokes' parameters. This type of experiment is being planned here at the present time.

3. A further possibility arises using the supersonic expansion technique. By obtaining a hydrogen target with all molecules in the $N_0=0$ level and using very high resolution electron
spectroscopy it should be possible to do
differential inelastic scattering involving
selected rotational transitions. This would
allow some of the ideas regarding non-dipole
excitation channels to be checked directly.
Collaboration between the Windsor and Manches-
ter groups is already underway on this prob-
lem.

(4) It might be possible to use the time inverse
approach in which electrons are superelasti-
cally scattered from molecules prepared in
selected magnetic substates. This awaits the
development of suitable ultraviolet lasers.

(5) Prior to these developments it would be inter-
esting to look for isotope effects. In this
regard the $X^1Σ^+ → \Sigma^1Π_u^g$ excitation in \textit{D}_2 will
be investigated in the very near future, and
the results will be compared with the present
\textit{H}_2 data.
4.6 AFFENDICES

4.6.1 Hund's Case (b) Coupling

Hund's case (b) coupling is as follows:

\[ \vec{J} \]

\( \vec{N} \)

\( \vec{R} \)

\( \vec{A} \)

\( \vec{A} \) is the component of the total electronic orbital angular momentum along the internuclear axis; \( \vec{N} \) (with z component \( M_N \)) is formed by coupling the rotation with \( \vec{A} \). \( \vec{N} \) then couples with the total electronic spin \( \vec{S} \) (with z component \( M_S \)) to give a total angular momentum \( \vec{J} \) (with z component \( M_J \)). Note that in this coupling scheme the spin is coupled weakly to the internuclear axis.

4.6.2 The Momentum Transfer Direction

Consider the diagram shown below:
The incident electron has momentum \( \mathbf{p}_0 \) along the z axis, and final momentum \( \mathbf{p}_1 \). The electron is scattered into the angle \( \theta_e \) (in the scattering plane). The momentum transfer vector \( \mathbf{k} \) is given by:

\[
\mathbf{k} = \mathbf{p}_0 - \mathbf{p}_1
\]

(4.6.2.1)

Now

\[
\mathbf{p}_0 = p_0 \hat{z} \\
\mathbf{p}_1 = p_1 \cos \theta_e \hat{z} + p_1 \sin \theta_e \hat{x} \\
\mathbf{k} = k \cos \theta_k \hat{z} - k \sin \theta_k \hat{x}
\]

Using these in equation 4.6.2.1 yields:

\[
p_0 = p_1 \cos \theta_e + k \cos \theta_k \\
0 = p_1 \sin \theta_e - k \sin \theta_k
\]

Multiplying the first equation by \( \sin \theta_k \) and the second by \( \cos \theta_k \) and subtracting yields the result:

\[
p_0 / p_1 = \cos \theta_k + \cot \theta_k \sin \theta_e
\]

Solving for \( \cot \theta_k \):

\[
\cot \theta_k = p_0 / (p_1 \sin \theta_e) - \cot \theta_e
\]

Now \( p_0 = (2mE_0)^{1/2} \) and \( p_1 = (2mE_1)^{1/2} \). Then the momentum transfer direction is given by:

\[
\cot \theta_k = \frac{1}{\sin \theta_e} \left( \frac{E_0}{E_1} \right)^{1/2} - \cot \theta_e
\]

(4.6.2.2)

Using conservation of energy,

\[
E_1 = E_0 - \Delta E
\]

where \( \Delta E \) is the amount of energy lost by the electron in the collision, the momentum transfer direction is:

\[
\tan \theta_k = \frac{(\sin \theta_e (1-\Delta E/E_0)^{1/2}) - \cot \theta_e}{(\sin \theta_e)^{-1}}
\]

(4.6.2.3)
REFERENCES

1 Brunt, J.N.H. Ph.D. Thesis 1975
   Univ. of Manchester, Manchester, England

2 Rea, F.R., Comer, J., Imhoff, R.E., Brunt, J.N.H. and Harting, E.

3 Brunt, J.N.H., Read, F.H. and King, G.C.

4 Harting, E. and Read, F.H.
   Electrostatic Lenses, Elsevier Press, 1976

5 Brunt, J.N.H., King, G.C. and Read, F.H.

6 Bolduc, E., Vuemenier, J.J. and Harnet, P.

7 Roy, D., Delage, A. and Cature, J.D.

8 Sanchez, L. and Schulz, G.J.

9 Grissos, J.T., Garrett, R.B. and Compton, R.N.

10 Spence, D.

11 Veilette, P. and Harnet, P.
    Can. J. Phys. 54(1976), p1268-75

12 Huard, D., Harnet, P. and Bolduc, E.

13 Roy, D. and Cature, J.D.

14 Roy, D., Delage, A. and Cature, J.D.

15 Delage, A., Roy, D. and Cature, J.D.

16 Nesbet, K.K.

17 Marchand, P. and Cardinal, J.

18 Dassen, R.W., Helbing, R.R.E., Huschilt, J.C. and McConkey, J.W.
    Abstracts XIII I.C.P.E.A.C. 1(1981), p196-7 (Gatlinburg)
19 Dassen, H.W., Gomes, R., King, G.C. and McConkey, J.W.

20 Taylor, J.R.
    Scattering Theory, Wiley and Sons, New York, 1972

21 Spence, D.

22 Heddle, D. in Electron and Photon Interactions with Atoms

23 Read, F.H.

24 Colling, K., Madden, R.P. and Ederer, D.L.

25 Colling, K. and Madden, R.P.

26 Colling, K. and Madden, R.P.

27 Madden, R.P., Ederer, D.L. and Colling, K.

28 Lin, C-D.

29 Roulay, M. and Marchand, F.

30 Read, F.H., Brunt, J.W.H. and King, G.C.

31 Valin, H. and Marmet, P.

32 Spence, D.

33 Spence, D.

34 Lefalivre, D. and Marmet, P.

35 Moore, C.E. 'Atomic Energy Levels' Vol. 1-3

36 Carbonneau, R., Bolduc, E. and Marmet, P.

37 Racek, J. and Jaecks, D.H.
38 Wykes, J.

39 Fano, U. and Macek, J.
Rev. Mod. Phys. 45(1973), p553-73

40 Blum, K. and Kleinpoppen, H.

41 Eminyan, M., MacAdam, K.B., Slevin, J. and Kleinpoppen, H.

42 Eminyan, M., MacAdam, K.B., Slevin, J. and Kleinpoppen, H.

43 Eminyan, M., MacAdam, K.B., Slevin, J., Standage, M.C.

44 Standage, M.C. and Kleinpoppen, H.

45 Tun, K.H., Fryar, J., Furano, E.S. and McConekey, J.W.

46 Ujzbabe, A., Teubner, P.J.C., Weigold, E. and Arriola, H.

47 Sutcliffe, V.C., Haddad, G.N., Steph, M.C. and Golden, D.E.

48 Arriola, H., Teubner, P.J.C., Ujzbabe, A. and Weigold, E.

49 Williams, J.F., in The Physics of Electronic and Atomic Collisions
p139-150, Univ. Wash. Press, Seattle, Wash., 1975

50 Dixon, A.J., Hood, S.T. and Weigold, E.

51 Hertel, L.V. and Stiel, W.

52 Macek, J. and Hertel, L.V.

53 Thomas, L.D., Csanak, G., Taylor, H.A. and Yarlagadda, B.S.

54 Flannery, M.R. and McCann, K.J.

55 Bransden, B.H. and Winters, K.H.

56 Scott, T. and McConnell, M.B.C.
57 Meneses, J.D., Padial, M.T. and Csatak, G.

58 Madison, D.H. and Shelton, W.N.

59 King, T.C.F., Williams, J.F. and Crowe, A.

60 Malcolm, I.C. and McConkey, J.W.

61 McConkey, J.W. and Malcolm, I.C. Coherence and Correlation in


64 McGregor, I., Hils, D., Höffler, R., Malik, N.A.,
Williams, J.F., Zaidi, A.A. and Kleinpoppen, H.

64 Bartschat, K., Blum, K., Hanne, G.P. and Kessler, J.

65 Slevin, J., Eminyan, M., Woolsey, J.M., Vassilev, G.,
Porter, H.Q. and Bach, C.

66 Zaidi, A.A., McGregor, I. and Kleinpoppen, H.

67 Blum, K. and Jakubowicz, P.

68 Blum, K. Density Matrix Theory and Applications

69 Blum, K. and Kleinpoppen, H.
Physics Reports 52(1979), p205-261

70 Blum, K. in Coherence and Correlation in Atomic Collisions

71 Dassch, H.W. and McConkey, J.W.

72 Footilov, P.P. The Physical Basis of Polarized Emission
Consultants' Bureau Enterprises, New York, 1961

73 Dassen, H.W. Master's Thesis
Univ. of Windsor, Windsor, Ont. 1980

eds K. Oda and K. Takanayagi, North Holland Pub., Amsterdam

75 Malcolm, I.C., Dassen, H.W. and McConkey, J.W.

76 Jette, A.K. and Cahill, E.
   Phys. Rev. 17b(1948), p186-

77 Baltayan, P. and Nedelec, C.

78 Baltayan, P. and Nedelec, C.
   J. Physique 36(1975), p125-

79 Dunn, G.H.

80 Macpherson, K.T., Simons, J.P., and Zare, R.N.

81 Heideman, H., van der Water, W., van Eck, J. and van
   Moorgestel, L., in Electronic and Atomic Collisions,
   eds K. Oda and K. Takanayagi, North Holland, Amsterdam, 1980

82 Kline, G.C., Adams, A. and Head, F.H.

83 Zuther, E.W., Pralha, A., Westervell, W.B. and McConkey, J.W.

84 Hertel, H.W. and Ross, K.J.

85 Huserlich, J.C., Dassen, H.W. and McConkey, J.W.

86 Hernandez, S.P., Dagdianian, R.J. and Doering, J.P.
   J. Chem. Phys. 83 in press

87 Haiz, A.U.

88 Stone, E.J. and Zipf, E.C.
   J. Chem. Phys. 56(1972), p4646-52
VITA AUCToris

I was born on October 18, 1955 in Tilburg, the Netherlands. My family came to Canada in 1959 and settled in Windsor, Ontario. After graduating from Assumption College School in 1974, I entered the University of Windsor, where I obtained an Honours B.Sc in Physics in 1978. During my four years as an undergraduate I was given the opportunity to gain research experience under the supervision of Dr. J.W. McConkey, whom I continued on with to obtain a Master's degree in Physics in 1980. I was funded by an NSERC Postgraduate Scholarship from 1978 to 1982, after which I received a University of Windsor Postgraduate Scholarship.