RECEIVED BY DTIC MAY 12 1969

Volume I

LOW-ENERGY, HIGH-RESOLUTION,
VARIABLE ANGLE ELECTRON IMPACT SPECTROSCOPY*

Thesis by
James Kinsey Rice

In Partial Fulfillment of the Requirements

For the Degree of
Doctor of Philosophy

There is no objection from the patent
standpoint to the publication or
dissemination of this document:

California Patent Group, USAEC

By

[Signature]
May 9 1969

California Institute of Technology

Pasadena, California

1969

(Submitted September 9, 1968)

*Work supported in part by the United States Atomic Energy Commission,
Reporting Code No. CALT-532-39

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LOW-ENERGY, HIGH-RESOLUTION,
VARIABLE ANGLE ELECTRON IMPACT SPECTROSCOPY

Thesis by
James Kinsey Rice

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

In Partial Fulfillment of the Requirements

For the Degree of
Doctor of Philosophy

California Institute of Technology

Pasadena, California

1969

(Submitted September 9, 1968)

leg

ACKNOWLEDGMENTS

I wish to express my sincere appreciation to Professor Aron Kuppermann for suggesting this research project and for the advice and encouragement which he generously offered throughout the course of this investigation.

The invaluable help of Sandor Trajmar in the initial stages of design and construction as well as his continuing collaboration is gratefully acknowledged.

Much of my insight into both the experimental and theoretical aspects of this project has been obtained through interactions with fellow students. In particular, I wish to thank Oakley Crawford and Lonne Lane for their instruction in mechanical engineering and high vacuum technology, Dave Cartwright and Merle Riley for their assistance in computer programming, and Don Truhlar for his help in many of the theoretical and computation aspects of this study.

Special thanks are extended to Bill Schuelke and Villy Jorgensen who, along with other machinists at the California Institute of Technology, made possible the construction of this apparatus. I am also indebted to Drs. J. Arol Simpson and Chris Kuyatt of the National Bureau of Standards for very helpful information about the design of their instruments.

Financial support from the Atomic Energy Commission and the National Science Foundation is gratefully acknowledged.

Finally, but with the most affection, I thank my wife, Linda, for her continuing enthusiasm and unfailing encouragement.

ABSTRACT

A low-energy, variable angle, high-resolution, electron-impact spectrometer has been designed, constructed, and put into operation. Its performance is discussed and is found to compare favorably with that of similar instruments^(24, 25, 35b).

The differential scattering cross sections (DCS) for the electron-impact excitation of helium and five molecules (N_2 , CO, H_2 , C_2H_2 , and C_2H_4) have been measured as a function of incident electron kinetic energy (from about 20 to 60 eV) and scattering angle (from about -30° to $+80^\circ$) with a resolution of 0.04 to 0.15 eV. These studies included the observation of twenty-nine electronically excited states, including 12 singlet $\rightarrow$ triplet transitions.

Comparisons of these results with presently available theoretical predictions have indicated the inadequacy of the latter. In addition, a theoretical calculation of the exchange excitation of ethylene ($\tilde{X}^1A_g - \tilde{a}^3B_{1u}$) by electron-impact is carried out via the Ochkur-Rudge approximation^(58, 62) and is compared with experiment.

The vibrational structure within several electronic bands has been resolved, and the relative vibrational intensities have been compared with optical and calculated relative Franck-Condon factors. Discrepancies, due to underlying forbidden transitions, have been noted in H_2 , acetylene, and ethylene.

Some general "spectroscopic rules" for the identification of spin-forbidden excitations observed by electron-impact are presented. These rules are derived from an examination of the angular dependencies of the differential cross sections for twenty-six known transitions. On this basis, one state in N_2 ($E^3 \Sigma_g^+$) has been unequivocally identified as a triplet, and two previously unknown low-lying triplet states in C_2H_2 at 5.2 eV and 6.1 eV have been detected and characterized.

TABLE OF CONTENTS

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
1.	INTRODUCTION	1
2.	HISTORICAL DEVELOPMENT	6
3.	THEORETICAL DESCRIPTION OF ELECTRON SCATTERING	12
3.1.	<u>Introduction</u>	12
3.2.	<u>Formal Description</u>	13
3.3.	<u>Approximations</u>	21
3.3.1.	Close-Coupling	21
3.3.2.	Two State	22
3.3.3.	Distorted Wave	23
3.3.4.	Born-Oppenheimer	25
	3.3.4.1. Scattering amplitude	25
	3.3.4.2. Spin statistics	27
	3.3.4.3. Ochkur-Rudge modifications	31
3.3.5.	Comparison of Methods	33
3.3.6.	Selection Rules	39
3.3.7.	Treatment of Molecules	41
	3.3.7.1. Diatomic molecules	41
	3.3.7.2. Ethylene	51
3.4.	<u>Partial Wave Analysis</u>	59
3.4.1.	Introduction	59

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
3.4.2.	Elastic Scattering by a Center of Force	62
3.4.3.	Data Expansion in Partial Waves	66
4.	EXPERIMENTAL	78
4.1.	<u>Design</u>	78
4.1.1.	Electron Energy Analyzer	78
4.1.1.1.	General considerations	78
4.1.1.2.	Hemispherical electro- static energy analyzer	80
4.1.1.2.1.	Trajectory equations	80
4.1.1.2.2.	Electron-optical properties	90
4.1.1.3.	Line shape	93
4.1.1.4.	Resolution	100
4.1.2.	Electron-Optics	103
4.1.2.1.	First stage electron- optics	103
4.1.2.1.1.	General require- ments	103
4.1.2.1.2.	Monochromator	105
4.1.2.1.3.	Lens system	108
4.1.2.1.4.	Electron gun	109
4.1.2.2.	Second stage electron optics	112

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
	4.1.2.2.1. General require- ments	112
	4.1.2.2.2. Selector	112
	4.1.2.2.3. Lens systems	113
4.1.3.	External Fields	114
	4.1.3.1. Introduction	114
	4.1.3.2. D. C. magnetic fields	115
	4.1.3.3. Radio-frequency (RF) fields	117
4.2.	<u>Construction</u>	120
	4.2.1. Vacuum System	120
	4.2.2. Shielding of External Fields	128
	4.2.2.1. Shielding of D. C. magnetic fields	128
	4.2.2.2. Shielding of RF fields	128
	4.2.3. Carriage	131
	4.2.4. Spectrometer Components	131
	4.2.4.1. General description	131
	4.2.4.2. Electron gun	134
	4.2.4.3. Monochromator and selector	136
	4.2.4.4. Lens system 1	139
	4.2.4.5. Scattering chamber	142
	4.2.4.6. Lens system 2	147

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
	4.2.4.7. Lens system 3	151
	4.2.4.8. Electron multiplier	151
4.2.5.	Support Structure	154
4.2.6.	Bakeout Heaters	160
4.2.7.	Rotary Motion	162
4.2.8.	Vacuum Feedthroughs	165
4.2.9.	Electrical Components	165
4.2.10.	Sample Inlet System	178
4.3.	<u>Procedure</u>	181
4.3.1.	Pump-Down and Bake-Out	181
4.3.2.	Magnetic Field Compensation	182
4.3.3.	Sample Introduction	182
4.3.4.	Spectrometer Operation	185
	4.3.4.1. Tuning	185
	4.3.4.2. Method of sweep	191
	4.3.4.3. Method of detection	193
	4.3.4.4. Sweep-signal correlation	195
4.3.5.	Obtaining a Spectrum	197
4.4.	<u>Performance</u>	198
4.4.1.	Vacuum Characteristics	198
4.4.2.	D. C. Collector Efficiency	199
4.4.3.	Electron Beam Characteristics	201

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
	4.4.3.1. Energy distribution from the gun	201
	4.4.3.2. Angular divergence	209
	4.4.3.3. Line shape	213
	4.4.3.4. Current versus resolution	214
	4.4.3.5. Contact potential	220
	4.4.3.6. Resolution versus analyzing energy	222
	4.4.4. Relation of the Differential Scattering Cross Section to the Scattered Signal	224
	4.4.4.1. Calculation	224
	4.4.4.2. Pressure dependence	229
	4.4.4.3. Energy-loss efficiency	234
	4.4.4.4. Volume correction	238
	4.4.5. Detector and Background Characteristics	241
	4.4.6. Energy-Loss Determination	245
5.	RESULTS AND DISCUSSION	247
	5.1. <u>Introduction</u>	247
	5.2. <u>Helium</u>	248

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
5.2.1.	Introduction	248
5.2.2.	Energy Scale Calibration	250
5.2.3.	Results and Discussion	250
5.2.4.	Further Discussion	285
5.3.	<u>Nitrogen</u>	
5.3.1.	Introduction	289
5.3.2.	Results and Discussion	295
5.4.	<u>Carbon Monoxide</u>	313
5.4.1.	Introduction	313
5.4.2.	Results and Discussion	319
5.5.	<u>Hydrogen</u>	335
5.5.1.	Introduction	335
5.5.2.	Results and Discussion	336
5.6.	<u>Acetylene</u>	346
5.6.1.	Introduction	346
5.6.2.	Additional Results and Discussion	348
5.7.	<u>Ethylene</u>	363
5.7.1.	Introduction	363
5.7.2.	Results and Discussion	367
6.	CONCLUSIONS	385
APPENDIX I	Overlap of Two Gaussians	391

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
APPENDIX II	Specifications of the 1024 Channel Nuclear Data Analyzer System	393
APPENDIX III	Angular Dependence of Low-Energy Electron Impact Excitation Cross Section of the Lowest Triplet States of H ₂	402
APPENDIX IV	Triplet States of Acetylene by Electron Impact	429
APPENDIX V	List of Vendors and/or Manufacturers	432
REFERENCES		440
PROPOSITIONS		458

1. INTRODUCTION

The collision of an electron with an isolated atom or molecule can have a number of outcomes. Among them are the transfer of translational energy, diffraction, electron exchange, excitation or deexcitation of internal states of the target, ionization, negative ion formation, molecular fragmentation, or a combination of several of these. For any case, the quantity which characterizes the scattering process is known as the cross section. Phenomenologically, the cross section for the occurrence of a certain type of event during a collision is equal to the number of these events per unit time per target particle divided by the current density (particles per unit time per unit area) of incident electrons relative to the target^(1a). As a consequence of this definition, the cross section has the units of area per target particle.

The cross section per unit solid angle for the particular process in which an electron collides with the target and then scatters into a given direction (defined by spherical polar angles θ , φ) is called the "differential scattering cross section" (hereafter abbreviated as DCS) and has the units of area per solid angle per target particle. The corresponding "total cross section" is the integral of the DCS over all scattering directions θ , φ . If we define a spherical polar coordinate system whose z axis lies along the incident beam direction, then the scattering angle θ is the colatitude of this coordinate system and φ is the azimuth (or longitude). If the target particles are randomly oriented with respect to the incident

beam direction (as is the case under our experimental conditions), then the DCS will not depend on φ .

There are two general classes of collision phenomena which can be studied by the detection of the scattered electrons:

(1) elastic scattering, in which the incident electron does not transfer any of its kinetic energy to internal energy states of the target, and

(2) inelastic scattering, in which it does.

In particular, the present investigation is concerned with the use of electron impact as a spectroscopic tool for the study of electronically excited states of atomic and molecular species in the gas phase.

In essence, the experimental method involves the production of a monochromatic beam of electrons (incident beam), the passage of this beam through a gaseous sample of the target particles (at a pressure of about 10^{-3} torr), and the measurement of the scattered electron intensity as a function of the incident electron energy, scattering angle, and energy-loss (the kinetic energy lost by the incident electron through an inelastic collision).

Under the experimental conditions employed here, each detected electron has been scattered by at most one target particle (over 90% of the incident beam is not scattered at all). Thus, each energy-loss is equal to one particular excitation energy of the target. Further, a measurement of the angular dependence of the intensity of scattered electrons with a given energy-loss (i. e. the distribution of scattered electrons which have caused a particular electronic

transition in the target) can provide the basis for an identification of the excited state.

The use of electrons to induce these transitions offers two significant advantages over the use of photons:

(1) It is no more difficult to measure energy-losses (and hence molecular excitations) corresponding to the extreme vacuum UV (wavelengths shorter than $500 \text{ \AA}$) than those in the visible region. This is certainly not the case for optical methods.

(2) Many of the normal optical selection rules⁽²⁾ governing the relative probability of observing different excitations can be broken by a judicious choice of incident electron energy and scattering angle. In particular, low-energy electrons (within a few tens of eV's of the excitation threshold) can be quite effective in causing transitions between states of different spin multiplicity (total spin angular momentum $S \rightarrow S \pm 1$) through the mechanism of electron exchange excitation. This exchange process involves the interchange of the incident electron and one of the bound ones. These transitions are highly forbidden under photon impact in the absence of appreciable spin-orbit coupling. In addition, the probability of producing transitions which are optically symmetry-forbidden can often be dramatically increased by the use of low-energy electrons.

To illustrate these marked differences, table 1. -1 presents a comparison of relative optical transition probabilities with ones obtained by electron impact for three transitions in helium. The

TABLE 1. -1

A comparison of some relative electron-impact excitation probabilities in helium with typical optical transition probabilities. $P_{\text{opt.}}$ is the relative optical excitation probability; $P_{\text{elec.}}^T$ is the relative electron-impact excitation probability for an incident energy of 35 eV; and $P_{\text{elec.}}(\theta)$ is the relative probability for electrons to scatter at an angle θ after causing the excitation for an incident energy of 35 eV.

Transition	Type	$P_{\text{opt.}}$	$P_{\text{elec.}}^T$	$P_{\text{elec.}}(\theta)^{(d)}$	
				$\theta = 0^\circ$	$\theta = 70^\circ$
$1^1S \rightarrow 2^1P$	electric dipole allowed	1(a)	1(a)	1(a)	1(a)
$1^1S \rightarrow 2^1S$	electric dipole forbidden, electric quad-rupole allowed.	$10^{-5} - 10^{-8} (b)$	.18(c)	0.40	.21
$1^1S \rightarrow 2^3P$	spin-forbidden, electric dipole allowed.	$< 10^{-8}$	.12(e)	.023	1.3

^a The relative probability of this transition is taken as unity.

^b Reference (2a), p 54. ^c Reference (42). ^d Present research, section 5.2. ^e Reference (43).

relative probability of exciting the 2^1P level (optically allowed transition) is taken as unity. The last two columns in the table give the relative probabilities for electrons which have caused a particular excitation to be scattered by a given angle θ .

To be sure, optical techniques offer some important advantages such as better resolution (about two or three orders of magnitude better in the visible region, but comparable in the vacuum UV), the ability to work with solid and liquid samples, and a well developed practical theory with which to interpret experimental results. It will become apparent that it is the lack of this latter feature in low-energy electron impact which seriously complicates its application.

The purpose of the research described here was to design, construct, and operate an electron-impact spectrometer which could use the electron-impact method of molecular excitation to obtain information about molecular excited states. A brief historical review of the experimental development of electron scattering is presented in section 2. A discussion of some of the more relevant aspects of scattering theory is given in section 3 along with an application to the electron-impact excitation of the $\tilde{a}^3\text{B}_{1u}$ state of ethylene. The design, construction, operation, and performance of the spectrometer is discussed in section 4. Section 5 contains the experimental results obtained for six systems--helium, molecular nitrogen, carbon monoxide, molecular hydrogen, acetylene, and ethylene. Finally, section 6 presents some empirical rules for the identification of states excited via electron impact.

2. HISTORICAL DEVELOPMENT

In 1914 Franck and Hertz⁽³⁾ initiated the field of electron-impact spectroscopy with their classic experiments on the measurement of energy-losses of electron swarms in atomic gases. However, it was not until 1927 that Dymond⁽⁴⁾ carried out the first measurements of the angular distribution of inelastically scattered electrons. At about this same time, Oppenheimer⁽⁵⁾ pointed out the possibility of an electron exchange mechanism whereby optically spin-forbidden transitions could be produced. During the next few years, until the middle 1930's, the study of electron-impact phenomena reached a peak only to be followed by two decades of relative inactivity. A comprehensive review of this early work has been presented by Massey and Burhop⁽⁶⁾.

Since the late 1950's, there has been a renewed and increasing interest in this field, due possibly to the development of more sophisticated experimental techniques and a heightened awareness of the importance of electron-molecule (atom) interactions in radiation chemistry, upper-atmosphere phenomena, and plasma physics. A more recent review of electron collision processes can be found in the book by McDaniel⁽⁷⁾.

At present there are essentially two methods used to study molecular excited states through electron-impact excitation and the detection of the scattered electrons. One method, introduced by Schulz⁽⁸⁾ and usually denoted the "trapped-electron" method, involves the use of an incident electron beam of variable kinetic energy E and

the detection of only those electrons which have lost nearly all of their kinetic energy through single collisions with the target particles. If W is a particular molecular excitation threshold, then a scattered signal is obtained for $E \approx W$. This signal, which contains contributions from electrons scattered at all angles, is proportional to the total excitation cross section in the vicinity of the excitation threshold. Since total cross sections for optically-forbidden transitions are usually steeper at threshold than those for allowed ones,^(6a) the "threshold excitation spectra" obtained by this method are often dominated by spin- and symmetry-forbidden transitions.

This method has been applied to several systems by Schulz⁽⁹⁾ and Bowman and Miller⁽¹⁰⁾. Recently, relatively high resolution data have been obtained by Brongersma and Oosterhoff⁽¹¹⁾, Dowell and Sharp⁽¹²⁾, and Compton, et al.⁽¹³⁾. However, the possibility of negative ion formation and the uncertainties in energy scale calibration and threshold behavior complicate the identification of the excited state.

The other electron scattering method involves the use of an incident electron beam of fixed (or variable) energy E and the detection of electrons which have been scattered by single collisions with the target in a particular θ, ϕ direction (or range of angles) after undergoing a particular energy-loss ($E - W$). Although it has been recognized for some time that the angular dependence of the scattered electron intensity for a particular energy-loss is sensitive to the nature of the transition giving rise to it^(6b), very little data

have yet been obtained about these distributions. Most of the experiments have been performed at fixed angles (or a fixed range of angles), usually near 0° or 90° .

Lassetre and coworkers⁽¹⁴⁾ were among the pioneers in the field of electron-impact spectroscopy. The bulk of their work has been on relatively small molecules with incident electron energies above 200 eV and scattering angles below about 20° . Rather than attempt a complete review of their work, we will summarize only those studies relevant to the systems studied here (He, N₂, H₂, CO, C₂H₂, C₂H₄). The results of their early work on these molecules^(14b) generally agreed with optical absorption measurements and indicated the validity of the Born approximation at low scattering angles and high incident energies. Of especial interest, Silverman and Lassetre⁽¹⁵⁾ showed that the ratio of the intensity of the $1^1S \rightarrow 2^1S$ transition (dipole-forbidden, quadrupole-allowed) to that of the $1^1S \rightarrow 2^1P$ transition (dipole-allowed) in helium varied from about .08 at $\theta = 3.8^\circ$ to 0.9 at $\theta = 15.3^\circ$ for 500 eV incident electrons. Also Lassetre and Krasnow⁽¹⁶⁾ verified the forbidden nature of the $X^1\Sigma_g^+ \rightarrow a^1\Pi_g$ transition (electric dipole-forbidden; magnetic dipole and electric quadrupole-allowed) in N₂ by the angular dependence ($\theta \leq 10^\circ$) of the scattered electrons at ~ 500 eV incident energy.

More detailed studies⁽¹⁷⁾ of N₂, at incident energies as low as 60 eV, revealed two additional electric-dipole forbidden transitions at 11.87 eV and 12.26 eV in addition to the $X \rightarrow a^1\Pi_g$ one. The upper states for both transitions were assigned as $^1\Sigma_g^+$. The one corres-

ponding to the 12.26 eV transition has also been assigned as $^1\Sigma_g^+$ by Dressler⁽¹⁸⁾ from optical absorption studies. While the assignment of the 11.87 eV transition agrees with the Penning ionization results of Cermák⁽¹⁹⁾, it disagrees with the $E\ ^3\Sigma_g^+$ assignment presented by Heideman, et al.⁽²⁰⁾ based on studies at lower electron-impact energies. We have resolved this controversy with the results given in section 5.3.

A study of CO at an incident energy of 200 eV and $\theta \leq 2^\circ$ has also been reported⁽²¹⁾. These results agreed quite well with UV absorption spectra except for an anomalously intense transition at 12.79 eV. At lower incident energies (30-60 eV) Skerbele, et al.⁽²²⁾ have resolved several singlet $\rightarrow$ triplet transitions in both N_2 and CO. However, they pointed out that in a survey of 16 additional polyatomic molecules at incident energies as low as 35 eV, they failed to observe any singlet $\rightarrow$ triplet transitions. The results of our research indicate that the restriction of their observations to small scattering angles was probably responsible for this failure.

In addition to the investigations mentioned above, Ross and Lassette⁽²³⁾ have obtained high resolution energy-loss spectra of C_2H_4 . Their results generally agreed with optical absorption measurements although the lowest singlet $\rightarrow$ triplet transition in ethylene was not observed while evidence of a quadrupole-allowed transition near 7.45 eV was obtained.

Several years ago, Simpson⁽²⁴⁾ constructed a high-resolution, $\theta = 0^\circ$, electron-impact spectrometer. This instrument and a later model⁽²⁵⁾ (variable angle) provided the basis for the design of the

spectrometer described here. The work of this group with the 0° instrument has been confined to impact energies below 100 eV. Although their early investigations of $\text{He}^{(26)}$, $\text{H}_2^{(27)}$, and $\text{C}_2\text{H}_4^{(26)}$ did not reveal any singlet $\rightarrow$ triplet transitions at impact energies as low as 30 eV, improvements in the apparatus led to the detection of several such transitions in $\text{He}^{(28)}$, $\text{N}_2^{(29)}$, and $\text{H}_2^{(30)}$. Their measurements of the forward scattering intensity ratios of several transitions in $\text{He}^{(28)}$ and the angular dependence⁽³¹⁾ ($0^\circ \rightarrow 60^\circ$) of electrons scattered after causing the $1^1\text{S} \rightarrow 2^3\text{S}$, 2^1S , and 2^1P transitions are compared with the results of this research in section 5.2. Recently, their variable angle instrument was also used to measure the scattered electron distributions ($0^\circ \leq \theta \leq 20^\circ$) for these same three excitations in He at impact energies of 100 eV to 400 eV⁽³²⁾. A large part of their work is presently directed toward the study of resonance phenomena⁽³³⁾ and instrument design⁽³⁴⁾.

Kuppermann and Raff⁽³⁵⁾ obtained energy-loss spectra for He, Ar, H_2 , and C_2H_4 with impact energies on the order of 50 eV and an instrument geometry which collected electrons scattered in the range $22^\circ \leq \theta \leq 112^\circ$ (with 90° favored), $0 \leq \varphi \leq 2\pi$. Under these conditions, singlet $\rightarrow$ triplet transitions were prominent features in the reported spectra. They were the first to detect triplet states by energy analysis of the scattered electrons. In particular, they observed the $\tilde{\text{X}}^1\text{A}_{1\text{g}} \rightarrow \tilde{\text{a}}^3\text{B}_{1\text{u}}$ transition in ethylene via electron impact for the first time.

Doering⁽³⁶⁾ has investigated the 90° scattering of low-energy electrons by He, N₂, C₂H₄, and C₆H₆. He confirmed the singlet $\rightarrow$ triplet transition in C₂H₄ mentioned above and observed spin-forbidden transitions in He, N₂, and C₆H₆ as well.

Recently, Ehrhardt and coworkers⁽³⁷⁾ have put into operation an elegant electron-impact spectrometer in which the target is a molecular beam. Although this instrument has been used primarily for the study of resonances, one measurement^(37b) of the angular distribution ($7^\circ \rightarrow 110^\circ$) of electrons causing the $1^1S \rightarrow 2^3S$ transition in helium can be compared with the present results (section 5.2).

Finally, the $\theta = 0^\circ$ energy-loss spectra of H₂⁽³⁸⁾, N₂⁽³⁹⁾, and C₂H₄⁽⁴⁰⁾ have been obtained at very high incident energies (~ 35 KeV) with good resolution (~ 0.03 eV). Under these conditions (high energy, low angle), the Born approximation seems quite reliable and, as expected, these spectra are nearly identical with UV absorption spectra.

It is quite interesting to note that in general the relative vibrational intensities within a given electronic excited state as determined via electron-impact have been found to be the same as those obtained by optical absorption studies (or accurate calculations)⁽⁴¹⁾. This includes the results of threshold excitation methods as well as energy-loss determinations--regardless of the molecular species, scattering angle, or incident energy (but excludes the cases in which excitation occurs via a temporary negative ion). The theoretical implications of this result are discussed in section 3.

3. THEORETICAL DESCRIPTION OF SCATTERING

3.1. Introduction

The cross section for a particular outcome of the collision of an electron and a complex "particle" CP has been defined in section 1. In this section, we present some of the methods which can be applied to the calculation of these quantities from first principles with particular emphasis on electronic excitation.

In the elastic or inelastic scattering of electrons, a small part δE of an electron's kinetic energy E_e in the laboratory system is transformed into laboratory kinetic energy of CP. Namely, for elastic scattering

$$\frac{\delta E}{E_e} \approx \frac{4m}{M} \sin^2 \frac{\theta}{2} \quad (3-1)$$

and for inelastic scattering events

$$\frac{\delta E}{E_e} \approx \frac{2m}{M} \left[1 - \frac{W}{2E_e} - \sqrt{1 - \frac{W}{E_e}} \cos \theta \right]. \quad (3-2)$$

m is the mass of the electron, M is the mass of CP, θ is the angle between the incident and scattered electron (scattering angle), and W is the energy lost by the incident electron to internal states of CP. Equations (3-1) and (3-2) can be derived from the conservation of total energy and momentum during the collision. For a single collision process, such as we study, $\frac{\delta E}{E_e}$ is $\sim 10^{-4}$ while the relative electron beam resolution is only $\sim 10^{-3}$. Neither translational energy transfer nor cooperative scattering phenomena, such as electron-diffraction^(6c), will be explicitly considered. In addition, only

those aspects of scattering theory which are particularly relevant to this investigation will be discussed in any detail. There are a number of good reference works available which review both the theoretical^(1, 44-47) and experimental^(6, 47) aspects of electron scattering phenomena.

3.2. Formal Description

The time evolution of a dynamical state $\Psi_I^T(t)$ of the electron-CP system is given by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi_I^T(t)}{\partial t} = \hat{H}_T \Psi_I^T(t) \quad (3-3)$$

where the subscript I specifies the initial conditions of this state, $\hat{H}_T$ is the total Hamiltonian operator, and $\hbar$ is Planck's constant divided by 2π . Since $\hat{H}_T$ is time-independent in the absence of any fields external to the electron-CP system, it is reasonable to use a time-independent formalism. Since the total energy E is conserved during the collision, $\Psi_I^T(t)$ must represent a state of constant $\langle E \rangle \equiv \langle \Psi_I^T(t) | \hat{H}_T | \Psi_I^T(t) \rangle$ (time is not included in this integration). $\Psi_I^T(t)$ can be factored into a time dependent part F(t) and a part Ψ_I , depending only on the coordinates of configuration space (since $\hat{H}_T$ is independent of time) as

$$\Psi_I^T(t) = \Psi_I F(t) \quad \text{where}$$

$$\langle \Psi_I^T(t) | \Psi_I^T(t) \rangle = \langle \Psi_I | \Psi_I \rangle |F(t)|^2 = 1, \quad ,$$

$$\langle E \rangle = \langle \Psi_I | \hat{H}_T | \Psi_I \rangle |F(t)|^2, \quad \text{and}$$

$$\frac{\hat{H}_T \Psi_I}{\Psi_I} = \frac{i\hbar}{F} \frac{\partial F(t)}{\partial t} = \text{const.}$$

Combining these relations yields the steady state Schrödinger equation for Ψ_I ,

$$(\hat{H}_T - \langle E \rangle) \Psi_I = 0. \quad (3-4)$$

As an example of the application of (3-4), we shall consider the case in which an electron collides with a stationary target CP containing $N-1$ electrons and N' nuclei.

The total Hamiltonian for this system is given by

$$\hat{H}_T = \hat{T}_a + \hat{T}_b + V_{aa} + V_{ab} + V_{bb} \quad (3-5)$$

in which

$$\hat{T}_a = -\frac{\hbar^2}{2m} \sum_{k=1}^N \nabla_k^2;$$

$$\hat{T}_b = -\frac{\hbar^2}{2} \sum_{j=1}^{N'} \nabla_j^2 / M_j;$$

$$V_{aa} = e^2 \sum_{\ell > k}^N \sum_{k=1}^N \frac{1}{r_{\ell k}};$$

$$V_{ab} = -e^2 \sum_{k=1}^N \sum_{j=1}^{N'} \frac{Z_j}{|\tilde{r}_k - \tilde{R}_j|};$$

$$V_{bb} = e^2 \sum_{j > i}^{N'} \sum_{i=1}^{N'} \frac{Z_j Z_i}{R_{ji}} ;$$

$$\begin{aligned} \nabla_k^2 = & \frac{1}{r_k^2} \frac{\partial}{\partial r_k} (r_k^2 \frac{\partial}{\partial r_k}) + \frac{1}{r_k^2 \sin \theta_k} \frac{\partial}{\partial \theta_k} (\sin \theta_k \frac{\partial}{\partial \theta_k}) \\ & + \frac{1}{r_k^2 \sin^2 \theta_k} \frac{\partial^2}{\partial \varphi_k^2} ; \end{aligned}$$

∇_j^2 is the same as ∇_k^2 except that $(r_k, \theta_k, \varphi_k)$ are replaced by $(R_k, \theta_j, \varphi_j)$; m and r_k are the mass and position, respectively, of the k^{th} electron; M_j , $|e|Z_j$, and R_j are the mass, charge, and position, respectively, of the j^{th} nucleus; $r_{lk} \equiv |r_l - r_k|$; and $R_{ji} \equiv |R_j - R_i|$. It will be assumed that the center of mass (CM) of the electron + CP system coincides with that of CP, that the CM of CP is the origin of the coordinates used above (and hence, the CM motion will be neglected), and that $\hat{H}_T$ does not depend on electron or nuclear spin.

$\hat{H}_T$ can be separated into two parts, one representing the bound system CP and another the free electron and its coulombic interactions with CP. One particular separation is

$$\hat{H}_T = \frac{\hbar^2}{2m} \nabla_1^2 + \hat{H}_{1CP} + V_{1CP} \quad (3-6)$$

where

$$V_{1CP} = e^2 \sum_{k=2}^N \frac{1}{r_{1k}} - e^2 \sum_{j=1}^{N'} \frac{Z_j}{|r_1 - R_j|} \quad \text{and}$$

$$\hat{H}_{1CP} = \hat{H}_T - V_{1CP} + \frac{\hbar^2}{2m} \nabla_1^2 .$$

There is nothing unique about the separation (3-6), i. e. any electron can be "free" and the remainder bound.

$\hat{H}_{1CP}$ has a set of eigenfunctions which can be factored into a spatial part times a spin part (since $\hat{H}_{1CP}$ is independent of spin). The spatial functions are given by the equation

$$\hat{H}_{1CP} \Phi_n(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) = \epsilon_n \Phi_n(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) \quad (3-7)$$

where ϵ_n is the energy of the state Φ_n (depending on the coordinates of all the nuclei $\underline{R}$ and electrons $\underline{r}$ except those of electron 1) and n represents the complete set of spatial quantum numbers which identifies this state.

We next construct a set of electronic spin wave functions $\mathcal{J}_{SS_z}(2, \dots, N)$ for the $N - 1$ electrons of CP. These functions satisfy the eigenvalue equations

$$\hat{S}^2 \mathcal{J}_{SS_z} = S(S + 1) \mathcal{J}_{SS_z} \quad (3-8a)$$

$$\hat{S}_z \mathcal{J}_{SS_z} = S_z \mathcal{J}_{SS_z} \quad (3-8b)$$

where S is the total spin angular momentum of these $N - 1$ electrons and S_z is the z component. The wave functions ψ_n which are simultaneous eigenfunctions of $\hat{H}_{1CP}$, $\hat{S}^2$, and $\hat{S}_z$ are obtained by multiplying Φ_n by $\mathcal{J}_{SS_z}^{(48)}$.

$$\begin{aligned} \psi_n(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) &= \Phi_n(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) \mathcal{J}_{S'S'_z}(2, \dots, N) \\ \hat{H}_{1CP} \psi_n &= E_n \psi_n \end{aligned} \quad (3-9)$$

where $\underline{n} = (n, s', s'_z)$ represents the required set of space and spin quantum numbers and $(\tau_2, \dots, \tau_N)$ are the electronic space and spin coordinates. The set of functions $\psi_{\underline{n}}$ will be constructed so that they satisfy the Pauli principle^(49a) (i. e., they are antisymmetric with respect to an interchange of all coordinates of any two electrons) and are orthonormal:

$$\langle \psi_{\underline{n}}^* (\tau_2, \dots, \tau_N; \underline{R}) \psi_{\underline{m}} (\tau_2, \dots, \tau_N; \underline{R}) \rangle_{(1)} = \delta_{\underline{n} \underline{m}}. \quad (3-10)$$

$\langle \rangle_{(1)}$ represents an integration over all space and spin coordinates except those of electron 1.

If the incident and scattered electron have momenta $\hbar \underline{k}_0$ and $\hbar \underline{k}_n$, respectively, the total energy E of equation (3-4) is given by

$$E = \frac{\hbar^2}{2m} k_0^2 + E_0 = \frac{\hbar^2}{2m} k_n^2 + E_n \quad (3-11)$$

where E_0 and E_n are the energies of CP before and after the collision, respectively. The scattering angle in this case is $\theta \equiv \arccos(\underline{k}_0 \cdot \underline{k}_n / k_0 k_n)$.

Thus, E of (3-4) is specified and the desired solutions $\Psi_I(\tau_1, \tau_2, \dots, \tau_N; \underline{R})$ will not only be eigenfunctions of $\hat{H}_T$ but must also satisfy certain boundary conditions dictated by the experimental arrangement.

For simplicity we shall consider an idealized experiment in which electrons of well defined momentum $\hbar \underline{k}_0$ strike the target molecules CP which are characterized by a specific initial state

$\psi_{\underline{0}}$. The electrons emanating from the scattering region, either unscattered or scattered leaving the molecules in one of their states $\psi_{\underline{n}}$, are detected after they have traveled a distance D which is large compared to the range d of V_{1CP} ($D/d \sim 10^7$). As a result, the asymptotic (near the detector) form of Ψ_I can be reasonably represented by a linear combination of solutions to (3-4) with $V_{1CP} = 0$, i. e., a plane wave times $\psi_{\underline{0}}$ to represent the unscattered beam, and outgoing spherical waves times the various $\psi_{\underline{n}}$'s to represent the scattered electrons. In addition, the antisymmetry requirement of the Pauli principle and the indistinguishability of the electrons should be included in the boundary condition for Ψ_I . One convenient way to accomplish this is to define a permutation operator $P_{1\ell}$ which, when operating on an N electron function, exchanges the ℓ^{th} electron with the first. The desired asymptotic form of Ψ_I , including electron exchange, is

$$\Psi_I \underset{D \rightarrow \infty}{\sim} \sum_{\underline{n}=0}^{\infty} (1 - \Sigma_{op}) \left\{ \left[e^{i \underline{k}_{\underline{0}} \cdot \underline{r}_1} \delta_{\underline{0}\underline{n}} + \zeta_{\underline{0}\underline{n}}(\theta_1, \varphi_1) \times \frac{e^{i \underline{k}_{\underline{n}} \cdot \underline{r}_1}}{r_1} \right] s_{\underline{n}}(1) \psi_{\underline{n}}(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) \right\}. \quad (3-12)$$

$\Sigma_{op} \equiv \sum_{\ell=2}^N P_{1\ell}$, $\sum_{\underline{n}=0}^{\infty}$ represents a sum over the discrete states

plus an integral over the continuum states of CP, $s_{\underline{n}}(\ell)$ is the normalized spin wavefunction (either α or β)^(49b) of the ℓ^{th} "free"

electron, and $\xi_{\underline{0}\underline{n}}(\theta_\ell, \varphi_\ell)$ is the scattering amplitude for each possible outcome of the collision (each $\underline{0} \rightarrow \underline{n}$ transition of CP). We will not explicitly consider ionization (two or more outgoing electrons) or negative ion formation (no outgoing electrons).

From (3-11) one notes that k_n is imaginary for $(E_n - E_0) > \frac{\hbar^2}{2m} k_0^2$. Consequently, the terms in (3-12) corresponding to the excitation of states which are not accessible by energy conservation decay exponentially with r and contribute negligibly to the detected scattering. Nevertheless, these terms must be included for mathematical completeness.

It can be shown^(1b) that the cross section per unit solid angle (DCS defined in section 1) for an electron to be scattered into the (θ, φ) direction leaving CP in its $\underline{n}^{\text{th}}$ state is

$$\sigma_{\text{on}}(k_0, \theta, \varphi) = \frac{k_n}{k_0} |\xi_{\underline{0}\underline{n}}(\theta, \varphi)|^2 \quad (3-13)$$

The total collision cross section $Q_{\text{on}}(k_0)$ for the $\underline{0} \rightarrow \underline{n}$ transition in CP is obtained by the integration of (3-13) over all θ and φ :

$$Q_{\text{on}}(k_0) = \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta \sigma_{\text{on}}(k_0, \theta, \varphi) d\theta \quad (3-14)$$

From an examination of the required asymptotic from (3-12), it appears that a simplification of the problem can be obtained by expanding Ψ_I in terms of the functions $\psi_{\underline{n}}$ (presumably known). This expansion must also be antisymmetric and can be written as

$$\Psi_I = \sum_{\underline{n}=0}^{\infty} (1 - \Sigma_{op}) \{ G_{\underline{n}}(\underline{r}_1) \psi_{\underline{n}}(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) \} \quad (3-15)$$

where $G_{\underline{n}}(\underline{r}_\ell)$ is an unknown function depending on the space and spin coordinates of the ℓ^{th} electron (see reference 50). Substitution of (3-15) into (3-4) yields

$$\sum_{\underline{n}=0}^{\infty} (\hat{H}_T - E) (1 - \Sigma_{op}) \{ G_{\underline{n}}(\underline{r}_1) \psi_{\underline{n}}(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) \} = 0. \quad (3-16)$$

Since $\hat{H}_T$ is completely symmetric in the coordinates of the electrons, $\hat{H}_T$ and Σ_{op} commute. If in addition one uses the separation of $\hat{H}_T$ indicated in (3-6) with conditions (3-9) and (3-11), (3-16) becomes

$$\begin{aligned} & \sum_{\underline{n}=0}^{\infty} (1 - \Sigma_{op}) \left\{ \left[\nabla_1^2 + k_n^2 - \frac{2m}{\hbar^2} V_{1CP} \right] \right. \\ & \quad \left. \times [G_{\underline{n}}(\underline{r}_1) \psi_{\underline{n}}(\underline{r}_2, \dots, \underline{r}_N; \underline{R})] \right\} = 0 \end{aligned} \quad (3-17)$$

After multiplying (3-17) by $\psi_{\underline{m}}^*(\underline{r}_2, \dots, \underline{r}_N; \underline{R})$ and integrating over all of the space and spin coordinates except those of electron 1, one obtains

$$(\nabla_1^2 + k_m^2) G_{\underline{m}}(\underline{r}_1) = \sum_{\underline{n}=0}^{\infty} U_{\underline{m}\underline{n}}(\underline{r}_1) G_{\underline{n}}(\underline{r}_1)$$

(3-18)

$$+ (N-1) \sum_{\underline{n}=0}^{\infty} \langle \psi_{\underline{m}}^*(\tau_2, \dots, \tau_N; \underline{R}) \psi_{\underline{n}}(\tau_1, \tau_3, \dots, \tau_N; \underline{R}) \hat{L}_2 G_{\underline{n}}(\tau_2) \rangle_{(1)},$$

where $\hat{L}_2 \equiv [\nabla_2^2 + k_n^2 - \frac{2m}{\hbar^2} V_{2CP}]$,

$$U_{\underline{m}\underline{n}}(\tau_1) \equiv \frac{2m}{\hbar^2} \langle \psi_{\underline{m}}^*(\tau_2, \dots, \tau_N; \underline{R}) V_{1CP} \psi_{\underline{n}}(\tau_2, \dots, \tau_N; \underline{R}) \rangle_{(1)},$$

and the operations indicated by Σ_{op} have been carried out. If this infinite set of coupled integro-differential equations can be solved for the $G_{\underline{n}}(\tau)$ with asymptotic forms

$$G_{\underline{n}}(\tau) \underset{r \rightarrow \infty}{\sim} e^{i \underline{k}_0 \cdot \underline{r}} \delta_{on} s_0 + \xi_{on}(\theta, \varphi) \frac{e^{i k_n r}}{r} s_n \quad (3-19)$$

then the scattering problem is solved.

3.3. Approximations

3.3.1. Close-Coupling

In practice, one cannot solve an infinite system of coupled equations without some sort of simplification. The least restrictive approximation which renders (3-18) soluble (in principle) is to confine the expansion (3-15) to a finite set of basis functions which are considered to be most important for the scattering process. This is known as the close-coupling approximation. However, the inclusion of many states is extremely laborious for even a relatively simple system in which CP is atomic hydrogen. The most extensive coupling scheme yet employed for this system⁽⁵¹⁾ included the 1s, 2s, 2p, 3s, 3p, and 3d atomic hydrogen states.

There is an additional complication for systems in which CP contains more than one electron since the exact wave functions $\psi_{\underline{n}}$ are not known analytically. Burke, et al.⁽⁵²⁾ have carried out the most complete close-coupling calculation for the case in which CP is helium. They used five states-- 1^1S , 2^1S , 2^3S , 2^1P , 2^3P --approximated by Hartree-Fock atomic wave functions.

3.3.2. Two State

A somewhat more drastic approximation that one may make is to assume that only the initial ($\psi_{\underline{o}}$) and final ($\psi_{\underline{n}}$) states of CP are important in expansion (3-15). In effect, one neglects all terms in (3-18) which do not directly couple $\underline{o} \leftrightarrow \underline{o}$, $\underline{n} \leftrightarrow \underline{n}$, or $\underline{o} \leftrightarrow \underline{n}$, assuming that the coupling between the $\underline{o}$, $\underline{n}$ states and all others is negligibly weak. For this case, (3-18) reduces to two coupled integro-differential equations

$$\begin{aligned}
 & [\nabla_1^2 + k_o^2 - U_{\underline{o}\underline{o}}] G_{\underline{o}}(\underline{\tau}_1) = U_{\underline{o}\underline{n}}(\underline{\tau}_1) G_{\underline{n}}(\underline{\tau}_1) \\
 & + (N-1) \langle \psi_{\underline{o}}^*(\underline{\tau}_2, \dots, \underline{\tau}_N; \underline{R}) \psi_{\underline{o}}(\underline{\tau}_1, \underline{\tau}_3, \dots, \underline{\tau}_N; \underline{R}) \hat{L}_2 G_{\underline{o}}(\underline{\tau}_2) \rangle_{(1)} \\
 & + (N-1) \langle \psi_{\underline{o}}^*(\underline{\tau}_2, \dots, \underline{\tau}_N; \underline{R}) \psi_{\underline{n}}(\underline{\tau}_1, \underline{\tau}_3, \dots, \underline{\tau}_N; \underline{R}) \hat{L}_2 G_{\underline{n}}(\underline{\tau}_2) \rangle_{(1)}
 \end{aligned} \tag{3-20a}$$

and

$$\begin{aligned}
 & [\nabla_1^2 + k_n^2 - U_{\underline{n}\underline{n}}] G_{\underline{n}}(\underline{\tau}_1) = U_{\underline{n}\underline{o}}(\underline{\tau}_1) G_{\underline{o}}(\underline{\tau}_1) \\
 & + (N-1) \langle \psi_{\underline{n}}^*(\underline{\tau}_2, \dots, \underline{\tau}_N; \underline{R}) \psi_{\underline{o}}(\underline{\tau}_1, \underline{\tau}_3, \dots, \underline{\tau}_N; \underline{R}) \hat{L}_2 G_{\underline{o}}(\underline{\tau}_2) \rangle_{(1)}
 \end{aligned} \tag{3-20b}$$

$$+ (N-1) \langle \psi_{\underline{n}}^*(\tau_2, \dots, \tau_N; \underline{R}) \psi_{\underline{n}}(\tau_1, \tau_3, \dots, \tau_N; \underline{R}) \hat{L}_2 G_{\underline{n}}(\tau_2) \rangle_{(1)} \quad .$$

This approach has been applied to a number of cases⁽⁵³⁾ and seems appropriate for transitions between states with a small energy difference (for example, the resonance $ns \rightarrow np$ transitions of alkali metals) at low impact energies.

3.3.3. Distorted Wave

If it is further assumed that the back coupling between the initial and final states is negligible (terms which couple $\underline{o} \leftarrow \underline{n}$ are dropped from (3-20), then (3-20a)) becomes

$$\begin{aligned} & [\nabla_1^2 + k_o^2 - U_{\underline{o}\underline{o}}] G_{\underline{o}}(\tau_1) \\ & = (N-1) \langle \psi_{\underline{o}}^*(\tau_2, \dots, \tau_N; \underline{R}) \psi_{\underline{o}}(\tau_1, \tau_3, \dots, \tau_N; \underline{R}) \hat{L}_2 G_{\underline{o}}(\tau_2) \rangle_{(1)} \end{aligned} \quad (3-21)$$

The solution $\tilde{G}_{\underline{o}}(\tau)$ of (3-21) with the asymptotic form

$$\tilde{G}_{\underline{o}}(\tau) \underset{r \rightarrow \infty}{\sim} (e^{i \underline{k}_o \cdot \underline{r}} + \tilde{\xi}_{\underline{o}\underline{o}}(\theta, \varphi) \frac{e^{i \underline{k}_o r}}{r}) s_o \quad (3-22)$$

is substituted into (3-20b) to give the inhomogeneous integro-differential equation

$$\begin{aligned} & [\nabla_1^2 + k_n^2 - U_{\underline{n}\underline{n}}] G_{\underline{n}}(\tau_1) = U_{\underline{n}\underline{o}}(\tau_1) \tilde{G}_{\underline{o}}(\tau_1) \\ & + (N-1) \langle \psi_{\underline{n}}^*(\tau_2, \dots, \tau_N; \underline{R}) \psi_{\underline{o}}(\tau_1, \tau_3, \dots, \tau_N; \underline{R}) \hat{L}_2 \tilde{G}_{\underline{o}}(\tau_2) \rangle_{(1)} \end{aligned} \quad (3-23)$$

$$+ (N - 1) \langle \psi_{\underline{n}}^*(\tau_2, \dots, \tau_N; \underline{R}) \psi_{\underline{n}}(\tau_1, \tau_3, \dots, \tau_N; \underline{R}) \hat{L}_2 G_{\underline{n}}(\tau_2) \rangle_{(1)} \quad (1)$$

If $\tilde{G}_{\underline{n}}(\tau_1)$ is the proper solution of the homogeneous equation corresponding to (3-23) (terms containing $\tilde{G}_{\underline{o}}$ are set equal to 0) with the asymptotic form

$$\tilde{G}_{\underline{n}}(\tau) \underset{r \rightarrow \infty}{\sim} (e^{i \underline{k}_{\underline{n}} \cdot \underline{r}} + \tilde{\zeta}_{\underline{o}\underline{n}}(\theta, \varphi) \frac{e^{i \underline{k}_{\underline{n}} r}}{r}) s_{\underline{n}}, \quad (3-24)$$

then it can be shown^(44a) that the scattering amplitude in the asymptotic form (3-19) of $G_{\underline{n}}(\tau)$ is given by

$$\begin{aligned} \zeta_{\underline{o}\underline{n}}(\theta, \varphi) = & -\frac{1}{4\pi} \int \{ \tilde{G}_{\underline{n}}(\tau_1, \pi - \Theta) [U_{\underline{n}\underline{o}}(\tau_1) \tilde{G}_{\underline{o}}(\tau_1) + \\ & + (N - 1) \langle \psi_{\underline{n}}^*(\tau_2, \dots, \tau_N; \underline{R}) \psi_{\underline{o}}(\tau_1, \tau_3, \dots, \tau_N; \underline{R}) \hat{L}_2 \tilde{G}_{\underline{o}}(\tau_2) \rangle_{(1)}] \} d\tau_1 \end{aligned} \quad (3-25)$$

where $\cos \Theta = \cos \theta \cos \theta_1 + \sin \theta \sin \theta_1 \cos(\varphi - \varphi_1)$.

This method is denoted as the distorted wave method since the free electron is represented by functions which are distorted by the static fields of CP before and after the excitation. In another sense, this procedure simply assumes that all inelastic processes are negligible compared to the elastic one (i. e., all $\zeta_{\underline{o}\underline{n}}(\underline{n} \neq \underline{o}) \ll \zeta_{\underline{o}\underline{o}}$ in (3-12) and hence only $G_{\underline{o}}$ is needed in (3-15). This situation is usually obtained at higher impact energies.

Calculations using this method have been performed for atomic hydrogen⁽⁵⁴⁾, helium⁽⁵⁵⁾, and a few other systems⁽⁵³⁾.

3.3.4. Born-Oppenheimer

3.3.4.1. Scattering amplitude

The Born-Oppenheimer approximation⁽⁵⁶⁾ results if, in addition to the previous approximations, we assume that all scattering (elastic and inelastic) is a small perturbation on the incident and scattered plane waves (i. e., that $\tilde{\xi}_{\underline{0}\underline{0}}$ and $\tilde{\xi}_{\underline{0}\underline{n}}$ can be neglected in equations (3-22) and (3-24)). If $\tilde{G}_{\underline{0}}$ and $\tilde{G}_{\underline{n}}$ in equation (3-25) are replaced by undistorted plane waves times one electron spin wave functions, then the scattering amplitude is given by

$$\begin{aligned} \xi_{\underline{0}\underline{n}}(\theta, \varphi) = & -\frac{1}{4\pi} \int \left\{ e^{i(\underline{k}_{\underline{0}} - \underline{k}_{\underline{n}}) \cdot \underline{r}_1} s_{\underline{0}}(1) s_{\underline{n}}^*(1) U_{\underline{n}\underline{0}}(\underline{r}_1) \right. \\ & + (N-1) e^{-i\underline{k}_{\underline{n}} \cdot \underline{r}_1} s_{\underline{n}}^*(1) \langle \psi_{\underline{n}}^*(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) \psi_{\underline{0}}(\underline{r}_1, \underline{r}_3, \dots, \underline{r}_N; \underline{R}) \\ & \times [\hat{L}_2 e^{i\underline{k}_{\underline{0}} \cdot \underline{r}_2} s_{\underline{0}}(2)] \rangle_{(1)} \left. \right\} d\underline{r}_1 \end{aligned} \quad (3-26)$$

This equation can be rewritten, using the definitions of $U_{\underline{n}\underline{0}}$, $\psi_{\underline{n}}$, and $\hat{L}_2$ as

$$\begin{aligned} \xi_{\underline{0}\underline{n}}(\theta, \varphi) = & \langle s_{\underline{0}}(1) \int_{SS_Z} (2, \dots, N) s_{\underline{n}}^*(1) \int_{S'S'_Z}^* (2, \dots, N) \rangle_{\text{spin}} f_{\text{on}}^B(\theta, \varphi) \\ & - (N-1) \langle s_{\underline{0}}(2) \int_{SS_Z} (1, 3, \dots, N) s_{\underline{n}}^*(1) \int_{S'S'_Z}^* (2, \dots, N) \rangle_{\text{spin}} g_{\text{on}}^{\text{BO}}(\theta, \varphi) \end{aligned} \quad (3-27)$$

where

$$\begin{aligned} & f_{\text{on}}^B(\theta, \varphi) \\ & \equiv -\frac{2\pi m}{h^2} \langle e^{i(\underline{k}_{\underline{0}} - \underline{k}_{\underline{n}}) \cdot \underline{r}_1} \Phi_{\underline{n}}^*(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) V_{1CP} \Phi_{\underline{0}}(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) \rangle_{\text{space}}; \end{aligned} \quad (3-28a)$$

$$\begin{aligned}
& g_{\text{on}}^{\text{BO}}(\theta, \varphi) \\
& \equiv -\frac{2\pi m}{h^2} \langle e^{-i\mathbf{k}_n \cdot \mathbf{r}_1} \Phi_n^*(\mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}) V_{2\text{CP}} \Phi_0(\mathbf{r}_1, \mathbf{r}_3, \dots, \mathbf{r}_N; \mathbf{R}) \\
& \quad \times [e^{i\mathbf{k}_0 \cdot \mathbf{r}_2}] \rangle_{\text{space}} ;
\end{aligned} \tag{3-28b}$$

$\oint_{S'S'_z}$ and Φ_n are the normalized space and spin wave functions, respectively, associated with each ψ_n ; and $\langle \rangle_{\text{spin}}$ and $\langle \rangle_{\text{space}}$ represent an integration over all spin and space coordinates, respectively, of the N electrons and N' nuclei. (3-28a) and (3-28b) correspond to the usual definitions of the Born direct and Born-Oppenheimer exchange scattering amplitudes, respectively.

The Born-Oppenheimer approximation is expected to be valid at relatively high incident energies (a few times the excitation threshold) since it is based on the assumption that there is only a weak interaction between the incident electron and the target (i. e., the probability per collision for excitation is small). Detailed discussions of the applicability of this approximation can be found elsewhere^(42, 53, 57). Usually it overestimates total cross sections within a few eV of the excitation threshold by about a factor of 10. At higher impact energies (where the probability of exchange processes approaches zero) it seems to agree with more exact calculations⁽⁵⁷⁾.

3.3.4.2. Spin statistics

The spin state of the N electron system (in the absence of appreciable spin-orbit coupling) before the collision ($s_0(1)\mathcal{J}_0(2,\dots,N)$) is denoted by $\mathcal{S}_{\Sigma\mu}(1,\dots,N)$ and is an eigenfunction of total spin $\hat{S}_T^2 = (\hat{S}_1 + \hat{S}_2 + \dots + \hat{S}_N)^2$ with eigenvalue Σ and of the z component $\hat{S}_{zT} = (\hat{S}_{z1} + \dots + \hat{S}_{zN})$ with eigenvalue μ . Since the interaction giving rise to the excitation is assumed independent of spin, Σ and μ are conserved. Thus, the spin state after collision ($s_n(1)\mathcal{J}_n(2,\dots,N)$) is denoted $\mathcal{S}'_{\Sigma\mu}(1,\dots,N)$ (with the same Σ and μ). There is a scattering amplitude $\xi_{\underset{\sim}{O}\underset{\sim}{N}}^{\Sigma\mu}$ associated with each value of (Σ, μ) which is computed by averaging over the experimentally accessible initial states $\mathcal{S}_{\Sigma\mu}$ and summing over the final ones $\mathcal{S}'_{\Sigma\mu}$ with the same values of Σ and μ . Since we have specifically excluded the possibility of a state with a given (Σ, μ) evolving into any state with a different (Σ, μ) , the amplitudes $\xi_{\underset{\sim}{O}\underset{\sim}{N}}^{\Sigma\mu}$ cannot interfere and the DCS is given by

$$\sigma_{on}(k_o, \theta, \varphi) = \frac{k_n}{k_o} \sum_{\Sigma, \mu} p(\Sigma, \mu) |\xi_{\underset{\sim}{O}\underset{\sim}{N}}^{\Sigma\mu}|^2. \quad (3-29)$$

$p(\Sigma, \mu)$ is the probability per collision for a spin state with Σ and μ and the sum extends over all Σ and μ which correspond to the same excitation energy of the target.

From (3-27) $\xi_{\underset{\sim}{O}\underset{\sim}{N}}^{\Sigma\mu}$ is given by

$$\begin{aligned} \xi_{\underset{\sim}{O}\underset{\sim}{N}}^{\Sigma\mu} &= \langle \mathcal{S}_{\Sigma\mu}(1,\dots,N) \mathcal{S}'_{\Sigma\mu}^*(1,\dots,N) \rangle_{\text{spin}_{on}^B} \\ &- (N-1) \langle \mathcal{S}_{\Sigma\mu}(2,1,\dots,N) \mathcal{S}'_{\Sigma\mu}^*(1,\dots,N) \rangle_{\text{spin}_{on}^{BO}} \end{aligned} \quad (3-30)$$

As specific examples for the application of (3-29) and (3-30), the scattering of electrons by atomic hydrogen and helium will be considered.

For a two electron system (electron + hydrogen atom), Σ may have the values 0 (singlet state) and 1 (triplet state) with μ values of 0 and 1, 0, -1, respectively. For each value of (Σ, μ) , there is only one two-electron spin state so that $\mathcal{S}_{\Sigma\mu} = \mathcal{S}'_{\Sigma\mu}$. In this case (3-30) reduces to the simple form:

$$\begin{aligned} \zeta_{\text{on}}^{\Sigma\mu} &= \langle \mathcal{S}_{\Sigma\mu}(1,2) \mathcal{S}_{\Sigma\mu}^*(1,2) \rangle_{\text{spin}} f_{\text{on}}^{\text{B}} \\ &\quad - \langle \mathcal{S}_{\Sigma\mu}(2,1) \mathcal{S}_{\Sigma\mu}^*(1,2) \rangle_{\text{spin}} g_{\text{on}}^{\text{BO}} \\ &= f_{\text{on}}^{\text{B}} \pm g_{\text{on}}^{\text{BO}} \end{aligned} \quad (3-31)$$

where the - or + is used depending on whether $\mathcal{S}_{\Sigma\mu}$ is symmetric or antisymmetric. Since the states $(\Sigma, \mu) = (0, 0)$ are antisymmetric while those with $(\Sigma, \mu) = (1, 1), (1, 0),$ or $(1, -1)$ are symmetric, it is easy to see from (3-31) that

$$\begin{aligned} \zeta_{\text{on}}^{0,0} &= f_{\text{on}}^{\text{B}} - g_{\text{on}}^{\text{BO}} \quad \text{and} \\ \zeta_{\text{on}}^{1,1} &= \zeta_{\text{on}}^{1,0} = \zeta_{\text{on}}^{1,-1} = f_{\text{on}}^{\text{B}} + g_{\text{on}}^{\text{BO}} \end{aligned} \quad (3-32)$$

The four $(\Sigma\mu)$ states mentioned above are all equally probable since we use an unpolarized electron beam, and no other $(\Sigma\mu)$ combinations are possible. Thus, the differential cross section as given by (3-29) is

$$\sigma_{\text{on}}(k_0, \theta, \varphi) = \frac{k_n}{k_0} \left\{ \frac{1}{4} |f_{\text{on}}^{\text{B}} - g_{\text{on}}^{\text{BO}}|^2 + \frac{3}{4} |f_{\text{on}}^{\text{B}} + g_{\text{on}}^{\text{BO}}|^2 \right\} \quad (3-33)$$

within the framework of the Born-Oppenheimer approximation.

For a three electron system (electron + helium), Σ may have the values $\frac{1}{2}$ (doublet state) and $\frac{3}{2}$ (quartet state) with μ values of $\frac{1}{2}$, $-\frac{1}{2}$ and $\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{3}{2}$, respectively. Since essentially all of the helium atoms are in their singlet ground state (two electrons paired) the initial configuration (and also the final one) of the electron plus helium system must be a doublet. However, the final helium configuration can be either singlet or triplet. These two possible outcomes are observable as different events and, therefore, there are two amplitudes $\zeta_{\underset{\sim}{\underset{\sim}{\text{on}}}_1}$ and $\zeta_{\underset{\sim}{\underset{\sim}{\text{on}}}_3}$ corresponding to the singlet - singlet and singlet - triplet transitions, respectively. For helium in a singlet state and one free electron there are two possible spin states (with equal probability)

$$\mathcal{S}_{\frac{1}{2}\frac{1}{2}}(1, 2, 3) = \frac{1}{\sqrt{2}} \alpha_1 (\alpha_2 \beta_3 - \beta_2 \alpha_3) \quad \text{and}$$

$$\mathcal{S}_{\frac{1}{2}-\frac{1}{2}}(1, 2, 3) = \frac{1}{\sqrt{2}} \beta_1 (\alpha_2 \beta_3 - \beta_2 \alpha_3).$$

If the final helium configuration is singlet, these same states are also the final ones. Then one obtains $\zeta_{\underset{\sim}{\underset{\sim}{\text{on}}}_1}^{\frac{1}{2}, \frac{1}{2}}$ and $\zeta_{\underset{\sim}{\underset{\sim}{\text{on}}}_1}^{\frac{1}{2}, -\frac{1}{2}}$ from (3-30):

$$\begin{aligned} \zeta_{\underset{\sim}{\underset{\sim}{\text{on}}}_1}^{\frac{1}{2}, \frac{1}{2}} &= \frac{1}{2} \langle (\alpha_1 \alpha_2 \beta_3 - \alpha_1 \beta_2 \alpha_3) (\alpha_1 \alpha_2 \beta_3 - \alpha_1 \beta_2 \alpha_3) \rangle_{\text{spin } f_{\text{on}}^{\text{B}}} \\ &\quad - \langle (\alpha_2 \alpha_1 \beta_3 - \alpha_2 \beta_1 \alpha_3) (\alpha_1 \alpha_2 \beta_3 - \alpha_1 \beta_2 \alpha_3) \rangle_{\text{spin } g_{\text{on}}^{\text{BO}}} \end{aligned}$$

$$= f_{on_1}^B - g_{on_1}^{BO} \text{ and similarly,}$$

$$\zeta_{on_1}^{\frac{1}{2}, -\frac{1}{2}} = f_{on_1}^B - g_{on_1}^{BO}.$$

Thus, the differential cross section is given by (3-29) as

$$\begin{aligned} \sigma_{on_1}(k_O, \theta, \varphi) &= \frac{k_{n_1}}{k_O} \left\{ \frac{1}{2} \left| \zeta_{on_1}^{\frac{1}{2}, \frac{1}{2}} \right|^2 + \frac{1}{2} \left| \zeta_{on_1}^{\frac{1}{2}, -\frac{1}{2}} \right|^2 \right\} \\ &= \frac{k_{n_1}}{k_O} \left| f_{on_1}^B - g_{on_1}^{BO} \right|^2. \end{aligned} \quad (3-34)$$

For helium in a triplet state and one free electron there are six possible spin functions, two of which have $\Sigma = \frac{1}{2}$ as required.

They are

$$S'_{\frac{1}{2}\frac{1}{2}}(1, 2, 3) = \frac{1}{\sqrt{6}}(\alpha_1\beta_2\alpha_3 + \alpha_1\alpha_2\beta_3 - 2\beta_1\alpha_2\alpha_3)$$

$$S'_{\frac{1}{2}-\frac{1}{2}}(1, 2, 3) = \frac{1}{\sqrt{6}}(\beta_1\beta_2\alpha_3 + \beta_1\alpha_2\beta_3 - 2\alpha_1\beta_2\beta_3).$$

Then using the correct $S_{\Sigma\mu}$ for each $S'_{\Sigma\mu}$ (the same values of $(\Sigma\mu)$ in each), $\zeta_{on_3}^{\frac{1}{2}, \pm\frac{1}{2}}$ can be obtained from (30).

$$\begin{aligned} \zeta_{on_3}^{\frac{1}{2}, \frac{1}{2}} &= \frac{1}{\sqrt{12}} \langle (\alpha_1\alpha_2\beta_3 - \alpha_1\beta_2\alpha_3) (\alpha_1\beta_2\alpha_3 + \alpha_1\alpha_2\beta_3 - 2\beta_1\alpha_2\alpha_3) \rangle_{\text{spin } f_{on_3}^B} \\ &\quad - \frac{2}{\sqrt{12}} \langle (\alpha_2\alpha_1\beta_3 - \alpha_2\beta_1\alpha_3) (\alpha_1\beta_2\alpha_3 + \alpha_1\alpha_2\beta_3 - 2\beta_1\alpha_2\alpha_3) \rangle_{\text{spin } g_{on_3}^{BO}} \\ &= -\sqrt{3} g_{on_3}^{BO}, \text{ and} \end{aligned}$$

$$\zeta_{\tilde{0}\tilde{n}_3}^{\frac{1}{2}, -\frac{1}{2}} = \sqrt{3} g_{\text{on}_3}^{\text{BO}} \text{ in a similar manner.}$$

Thus, the cross section as given by (3-29) is

$$\begin{aligned} \sigma_{\text{on}_3}(k_0, \theta, \varphi) &= \frac{k_{n_3}}{k_0} \left\{ \frac{1}{2} |-\sqrt{3} g_{\text{on}_3}^{\text{BO}}|^2 + \frac{1}{2} |\sqrt{3} g_{\text{on}_3}^{\text{BO}}|^2 \right\} \\ &= 3 \frac{k_n}{k_0} |g_{\text{on}_3}^{\text{BO}}|^2. \end{aligned} \quad (3-35)$$

3.3.4.3. Ochkur-Rudge modifications

In 1963 Ochkur⁽⁵⁸⁾ made a significant improvement in the Born-Oppenheimer approximation. He expanded $g_{\text{on}}^{\text{BO}}$ in powers of $\frac{1}{k_0}$ and retained only the leading term, which varied as $\frac{1}{k_0^2}$ (the next term is of order $\frac{1}{k_0^3}$)⁽⁵⁹⁾. The deletion of these higher order terms was justified by the fact that the Born direct amplitude f_{on}^{B} does not contain these higher order terms. The leading term can be readily obtained⁽⁵³⁾ and is given by

$$g_{\text{on}}^{\text{O}} = -\frac{2me^2}{\hbar^2 k_0^2} \langle e^{i\mathbf{q} \cdot \mathbf{r}_2} \Phi_n^*(\mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}) \Phi_0(\mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}) \rangle_1, \quad (3-36)$$

where $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_n$.

At this point, we note also that f_{on}^{B} (equation 3-27) can be simplified. Substitution of $V_{1\text{CP}}$ by its explicit form (3-6) and integration⁽⁶⁰⁾ over the coordinates of the incident electron yields

$$f_{\text{on}}^{\text{B}} = -\frac{2me^2}{\hbar^2 q^2} \langle \Phi_n^*(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) [\sum_{\ell=2}^N e^{i\mathbf{q} \cdot \underline{r}_\ell} - \sum_{j=1}^{N'} e^{i\mathbf{q} \cdot \underline{R}_j}] \Phi_0(\underline{r}_2, \dots, \underline{r}_N; \underline{R}) \rangle_{(1)} \quad (3-37a)$$

If we assume that Φ can be factored into a product of an electronic and nuclear wave function⁽⁶¹⁾, then for $n \neq 0$,

$$f_{\text{on}}^{\text{B}} = -\frac{2me^2}{\hbar^2 q^2} (N-1) \langle \Phi_n^* e^{i\mathbf{q} \cdot \underline{r}_2} \Phi_0 \rangle_{(1)} \quad (3-37b)$$

since all of the terms in the first sum give equal contributions and the terms of the second sum (core interaction) vanish because the electronic parts of Φ_n and Φ_0 are orthogonal. It is worth noting that for elastic scattering ($n = 0$), the core interaction terms must be retained in (3-37a) but that they do not appear in (3-36).

The expectation values of (3-36) and (3-37b) are the same and the scattering amplitudes differ only in the replacement of $\frac{1}{k_0^2}$ in (3-36) by $\frac{(N-1)}{q^2}$ in (3-37b). This difference leads to quite different angular dependencies as will be seen later.

Rudge⁽⁶²⁾ has pointed out that the Ochkur result is not consistent with certain variational principles. He obtained an improvement of the Ochkur result which differs only in the pre-integral factor and is given by

$$g_{\text{on}}^{\text{OR}} = -\frac{k_0^2}{[k_n - iA]^2} g_{\text{on}}^{\text{O}} \quad (3-38)$$

where $A = [2mI_1]^{1/2}/\hbar$ and I_1 is the ionization energy of the initial bound state. The Rudge result is also expected to be superior to the Ochkur one since the former is complex--a necessary⁽⁶³⁾ but not sufficient^(64, 57) condition for the conservation of particle flux. However, $\xi_{\underline{on}}$ computed using $g_{\underline{on}}^{\text{OR}}$ does not satisfy the principle of detailed balance ($|\xi_{\underline{on}}|^2 \neq |\xi_{\underline{no}}|^2$) if the final state can be reached by a direct process. (Both the Ochkur and Born-Oppenheimer approximations satisfy this principle^(65a).) Bely⁽⁶⁴⁾ has shown that this failure can be corrected if $g_{\underline{on}}^{\text{OR}}$ is replaced by its absolute value $|g_{\underline{on}}^{\text{OR}}|$.

3.3.5. Comparison of Methods

Truhlar, et al.⁽⁵⁷⁾ have recently presented an excellent comparison of the methods discussed above (and several others) for the special case of atomic hydrogen. They included a comparison of differential as well as total scattering cross sections. In addition, calculated differential cross sections are available for the $1^1\text{S} \rightarrow 2^3\text{S}$ ^(32, 66, 67), $1^1\text{S} \rightarrow 2^3\text{P}$ ⁽⁶⁶⁾ transitions in helium and the $1^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$, $a^3\Sigma_g^+$ ones of H_2 ^(66, 68). We know of no other inelastic differential cross section calculations apart from those using only the direct Born amplitude f_{on}^{B} ⁽⁶⁹⁾.

It is of interest to compare the results of some of these methods with experiment for two specific cases in helium. Tables 3.3-1 and 3.3-2 present some experimental and theoretical total cross sections for the $1^1\text{S} \rightarrow 2^3\text{P}$ and $1^1\text{S} \rightarrow 2^3\text{S}$ transitions, respectively. Table 3.3-3 shows a comparison of differential cross

TABLE 3.3-1

Total cross sections for the $1^1\text{S} \rightarrow 2^3\text{P}$ excitation of helium in units of $10^{-2} \pi a_0^2$. The excitation threshold is 20.96 eV.

Incident Electron Energy (eV)	Experiment JS ^(a)	Theory				
		MM ^(b)	BEM ^(c)	OB ^(d)	MR ^(e)	C ^(f)
(max) ^(g)	2.7(23)	15(24)	30(21)	6.8(25)	4.6(24)	4.4(25)
30	2.4	11	14	6.0	3.5	3.5
50	1.3	2.7	3.0	2.2	1.0	1.0
100	0.23	0.26	0.36	0.35	0.14	-
225	($\lesssim .01$)	0.01	0.02	0.03	-	-

^a Experimental results, reference (43).

^b Distorted wave method, reference (55b).

^c Born-Oppenheimer approximation, reference (70).

^d Ochkur approximation, reference (58b)

^e Rudge modification of Ochkur result, reference (71).

^f Ochkur-Rudge method, reference (66).

^g The number in parentheses is the incident energy at which the maximum cross section is obtained.

TABLE 3.3-2

Total cross sections for the $1^1S - 2^3S$ transition of helium in units of $10^{-2} \pi a_0^2$. The excitation threshold is 19.82 eV.

Incident Electron Energy (eV)	Experiment VSM ^(a)	Theory				
		MM ^(b)	BEM ^(c)	OB ^(d)	MR ^(e)	C ^(f)
30	-	1.50	85	6.0	6.0 ₅	4.7
50	-	.60	21	2.2	2.5	1.9
100	.090 ₅	-	1.6	.35	.43	-
150	.024 ₃	-	0.28	.11	.14	-
200	.010 ₁	-	0.058	.047	-	-

^a Experimental results, reference (67b).

^b Distorted wave approximation, reference (55a).

^c Born-Oppenheimer approximation, reference (70).

^d Ochkur approximation, reference (58b).

^e Rudge modification, reference (71).

^f Ochkur-Rudge approximation, reference (66).

TABLE 3. 3-3

DCS for the $1^1S \rightarrow 2^3S$ excitation of helium in units of $10^{-2} \pi a_0^2$ per steradian. The incident electron energy is 100 eV.

Scattering Angle	Experiment VSM ^(a)	Theory	
		MK ^(b)	C ^(c)
5°	0.19	.0045	.0019
10°	0.15	.020	.0075
15°	0.12	.051	.019
20°	0.057	.095	.038

^a Experimental results, reference (67b).

^b Born-Oppenheimer approximation, reference (67a).

^c Ochkur-Rudge approximation, reference (66).

sections for the $1^1S \rightarrow 2^3S$ transition. Although the Ochkur (and Ochkur-Rudge) approximation seems to afford a remarkable improvement over the distorted wave and Born-Oppenheimer approximations for total cross sections at low energy, it fails to adequately describe the differential cross sections, either in magnitude or variation. All first order theories (Born-Oppenheimer, Ochkur-Rudge, etc.) predict a differential cross section which is peaked off 0° at sufficiently high energies for the case of the $1s \rightarrow 2s$ exchange transition in atomic hydrogen⁽⁵⁷⁾. It is interesting to note, however, that the Born-Oppenheimer approximation predicts significant forward peaking of the $1s \rightarrow 2s$ differential cross section at lower energies for which the Ochkur approximation does not.

In the cases for which g_{on} provides a negligible contribution to ξ_{on} (high incident energy, low scattering angles, and no spin multiplicity change in the target⁽⁷²⁾), the Born approximation (f_{on}^B) has been successful⁽⁵³⁾ in predicting differential cross sections as well as total ones. This is somewhat surprising since the Born amplitude is real and as a result cross sections derived from it necessarily violate the so called optical theorem or Born-Peierls-Placzek relation (conservation of particle flux). It can be shown^(1c) simply from the Hermitian character of the Hamiltonian governing the scattering process that

$$Q_o^{\text{total}} = \frac{4\pi}{k_o} \text{Im} \{ \xi_{oo}(0^\circ, 0^\circ) \} \quad (3-39)$$

where Q_o^{total} is the total cross section for all processes with the initial state o and $\xi_{oo}(0^\circ, 0^\circ)$ is the forward scattering amplitude for the elastic process. If $\xi_{oo}(0^\circ, 0^\circ)$ is replaced by $f_{oo}^B(0^\circ, 0^\circ)$, then (3-39) implies that $Q_o^{\text{total}} = 0$ which is certainly not true. While (3-39) shows that the Born approximation is fundamentally incorrect at $(\theta, \varphi) \equiv (0^\circ, 0^\circ)$, (3-14) indicates that its value there does not contribute to the total cross section. Further, $f_{oo}^B(\theta, \varphi)$ can be modified in a trivial way to satisfy (3-39), without altering the total cross section or differential ones except at $(\theta, \varphi) \equiv (0^\circ, 0^\circ)$, by defining

$$f_{on}^{B'}(\theta, \varphi) = f_{on}^B(\theta, \varphi) \left[1 + i \frac{k_o Q_o^{\text{total}}}{4\pi f_{oo}^B(0^\circ, 0^\circ)} \delta(\theta) \delta(\varphi) \right]. \quad (3-40)$$

Then, from (3-13) the DCS at 0° for this modification is

$$\begin{aligned} \sigma'_{on}(k_o, 0^\circ, 0^\circ) \\ = \frac{k_n}{k_o} |f_{on}^B(0^\circ, 0^\circ)|^2 \left\{ 1 + \frac{k_o^2}{16\pi^2} \frac{(Q_o^{\text{total}})^2}{[f_{oo}^B(0^\circ, 0^\circ)]^2} \right\}. \end{aligned} \quad (3-41)$$

But $\sigma_{oo}(k_o, 0^\circ, 0^\circ) \cong |f_{oo}^B(0^\circ, 0^\circ)|^2$ and at high incident energy $Q_o^{\text{total}} \cong Q_{oo}$ (total elastic). Since $\sigma_{oo}(k_o, 0^\circ, 0^\circ)$ is independent of k_o and $Q_{oo} \propto \frac{1}{k_o^2}$ at sufficiently high energy^(44b),

$k_o^2 (Q_o^{\text{total}})^2 / (f_{oo}^B(0^\circ, 0^\circ))^2 \rightarrow 0$ as $\frac{1}{k_o^2}$ for large k_o . However,

calculations of forward differential scattering cross sections based on f_{on}^B at relatively low energies seem of doubtful value⁽⁷³⁾.

3.3.6. Selection Rules

General selection rules concerning electron impact excitation are quite difficult to define since all excited states are in principle coupled with the initial state (see equation (3-18)). However, at energies for which first order approximations are valid (in particular equation (3-27)), some meaningful "selection rules" can be obtained. We will consider the excitation of helium from its ground state as a specific example in order to simplify the discussion.

The DCS for transitions which do not involve a spin multiplicity change ($1^1S \rightarrow n^1L$, where $L = S, P, \dots$ and $n = 2, 3, \dots$), is given (from equation (3-34)) approximately by

$$\begin{aligned} & \sigma_{on_1}(k_0, \theta, \varphi) \\ & \cong \frac{k_{n_1}}{k_0} [|f_{on_1}^B|^2 + |g_{on_1}^O|^2 - 2 \cos \varphi_{on_1} (f_{on_1}^B g_{on_1}^O)] \end{aligned} \quad (3-42)$$

where φ_{on_1} is the relative phase angle between the direct and exchange amplitudes. φ_{on_1} is a function of k_0 but not (θ, φ) . From a comparison of (3-36) and (3-37) for helium, we obtain

$$g_{on_1}^O = \frac{q^2}{2k_0^2} f_{on_1}^B \quad (3-43)$$

which implies from (3-42) that

$$\sigma_{on_1}(k_0, \theta, \varphi) \cong \frac{k_{n_1}}{k_0} |f_{on_1}^B|^2 \left[1 - \frac{q^2}{k_0^2} \cos \varphi_{on_1} + \frac{q^4}{4k_0^4} \right]. \quad (3-44)$$

Thus, in this approximation, the behavior of $f_{on_1}^B$ (equation 3-37) will determine that of σ_{on_1} .

Without loss of generality, the z_2 axis for the $\underline{r}_2$ integration in (3-37) can be chosen along $\underline{q}$. Further,

$$e^{i q z_2} = \sum_{\ell=0}^{\infty} \frac{(i q z_2)^\ell}{\ell!} \quad \text{if } (q z_2)^2 < \infty. \quad (74a) \quad (3-45)$$

Substitution of (3-45) into (3-37) yields

$$f_{on_1}^B = \frac{-4me^2}{\hbar^2 q^2} \sum_{\ell=1}^{\infty} \frac{(i q)^\ell}{\ell!} z_{on_1}^\ell \quad (3-46)$$

where $z_{on_1}^\ell \equiv \int \phi_{n_1}^*(\underline{r}_2, \underline{r}_3) (z_2)^\ell \phi_0(\underline{r}_2, \underline{r}_3) d\underline{r}_2 d\underline{r}_3$.

The $z_{on_1}^\ell$ are the z components of the electric dipole ($\ell = 1$), quadrupole ($\ell = 2$), etc., transition moments encountered in optical spectroscopy⁽⁷⁵⁾. If $\frac{\hbar^2 k_o^2}{2m} \gg E_n - E_o$, and θ^2 small, equation (3-44) becomes

$$\sigma_{on_1}(k_o, \theta, \varphi) \cong C \left\{ \frac{(z_{on_1}^1)^2}{q^2} + \frac{7}{12} (z_{on_1}^2)^2 + \dots \right\} \{1 - O(\theta^2)\}, \quad (3-47)$$

where $C = \left(\frac{4me^2}{\hbar^2} \right)^2$.

For dipole-allowed transitions ($1^1S \rightarrow 2^1P$ in helium for example) $z_{on_1}^1$ is dominant. In this case, electron impact excitation cross sections obey the usual electric-dipole selection rules of optical spectroscopy.

If a transition is electric-dipole forbidden ($z_{on_1}^1 = 0$) but electric-quadrupole allowed ($z_{on_1}^2 \neq 0$), then the transition is "allowed" to this same order by electron impact. The $1^1S \rightarrow n^1S$ transitions in helium are examples of this case. Note that to

$O(\theta^2)$ (and the neglect of $(z_{on_1}^3)^2$, etc.) the differential cross section does not depend on either k_0 or θ . It has recently been shown⁽³²⁾ that the $1^1S \rightarrow 2^1S$ differential cross section from 5° to 20° is relatively independent of k_0 from 150 eV to 400 eV but decreases sharply with increasing θ .

We next consider the case of exchange excitation in helium ($1^1S \rightarrow n^3L$). Equation (3-35) and the preceding analysis which led to equation (3-47) lead to

$$\begin{aligned} \sigma_{on_3}(k_0, \theta, \varphi) \\ \cong 3C \left\{ \frac{q^2}{k_0^4} (z_{on_3}^1)^2 + \frac{7}{12} \frac{q^4}{k_0^4} (z_{on_3}^2)^2 + \dots \right\}. \end{aligned} \quad (3-48)$$

Note that σ_{on_3} is predicted to increase with increasing θ (for small angles) for both $S \rightarrow S$ and $S \rightarrow P$ transitions. This seems to be in direct contradiction to the observed⁽³²⁾ behavior of the $1^1S \rightarrow 2^3S$ transition at large energies. It is also worth noting that as θ increases from 0° , the DCS for optically forbidden (spin and symmetry) transitions are enhanced relative to the allowed ones (compare equations (3-48) and (3-47)).

3.3.7. Treatment of Molecules

3.3.7.1. Diatomic molecules

The principles discussed above can be applied equally well to molecules if we continue to neglect such interactions as spin-orbit and spin-spin coupling, and magnetic and relativistic effects in the

Hamiltonian $\hat{H}_T$. This will generally be the case for small molecules containing atoms of low atomic number.

We will discuss the special case of the electron-impact excitation of diatomic molecules since it serves to illustrate most of the additional complications.

Let o, o, J , and M be the electronic, vibrational, and rotational quantum numbers for the initial molecular state (the ground electronic and vibrational state), and n, ν, J' , and M' the corresponding final ones. The molecular wave function can be written as⁽⁶¹⁾

$$\psi_{\left(\begin{smallmatrix} n \\ o \end{smallmatrix}\right)}(\tau_2, \dots, \tau_N; R) = \Phi_{\left(\begin{smallmatrix} n \\ o \end{smallmatrix}\right)}(\tau_2, \dots, \tau_N; R) \mathcal{J}_{\left(\begin{smallmatrix} S'S'_Z \\ SS_Z \end{smallmatrix}\right)}(2, \dots, N) \quad (3-49)$$

$$\Phi_{\left(\begin{smallmatrix} n \\ o \end{smallmatrix}\right)} = \phi_{\left(\begin{smallmatrix} n \\ o \end{smallmatrix}\right)}(\tau_2, \dots, \tau_N; R) \eta_{\left(\begin{smallmatrix} n\nu J' \\ ooJ \end{smallmatrix}\right)}(R) Y_{\left(\begin{smallmatrix} J'M' \\ JM \end{smallmatrix}\right)}(\chi, \theta). \quad (3-50)$$

ϕ_o and ϕ_n are the ground and excited state electronic wave functions for a particular internuclear distance R ; η_{ooJ} and $\eta_{n\nu J'}$ are the ground and excited state vibrational wave functions; Y_{JM} and $Y_{J'M'}$ are the rotational wave functions (spherical harmonics^(1d)) of the initial and final rotational states; χ, θ are the spherical polar angles defining the molecular orientation with respect to a space fixed axis; and the $\mathcal{J}_{\left(\begin{smallmatrix} S'S'_Z \\ SS_Z \end{smallmatrix}\right)}$ are the $N-1$ electron spin wave functions

for each state.

The Born direct scattering amplitude (f_{on}^B of equation (3-37)) and the Ochkur approximation (g_{on}^O of equation (3-36)) to the Born-

Oppenheimer exchange scattering amplitude are given by

$$f_{\text{on}}^B(\theta, \varphi) = \frac{-2me^2}{\hbar^2 q} (N-1) \int \Phi_n^* e^{i\mathbf{q} \cdot \mathbf{r}_2} \Phi_0 d\mathbf{r}_2 \dots d\mathbf{r}_N d\mathbf{R} \quad (3-51)$$

and

$$g_{\text{on}}^O(\theta, \varphi) = \frac{-2me^2}{\hbar^2 k_0} \int \Phi_n^* e^{i\mathbf{q} \cdot \mathbf{r}_2} \Phi_0 d\mathbf{r}_2 \dots d\mathbf{r}_N d\mathbf{R} \quad (3-52)$$

where $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}'$

$$k' = \left[k_0^2 - \frac{2m}{\hbar^2} (E_{n\nu J' M'} - E_{00JM}) \right]^{\frac{1}{2}}$$

$E_{n\nu J' M'}$ and E_{00JM} are the energies of the final and initial molecular states, respectively. If $\mathcal{S}_{\Sigma\mu}$ and $\mathcal{S}'_{\Sigma\mu}$ are the initial and final total spin wave functions for the N electrons ($N-1$ bound and one free), then the scattering amplitude, in direct analogy to (3-30), is

$$\begin{aligned} \zeta_{\text{on}}^{\Sigma\mu} &= \langle \mathcal{S}'_{\Sigma\mu}(1, \dots, N) \mathcal{S}_{\Sigma\mu}(1, \dots, N) \rangle_{\text{spin}} f_{\text{on}}^B \\ &- (N-1) \langle \mathcal{S}'_{\Sigma\mu}(2, 1, \dots, N) \mathcal{S}_{\Sigma\mu}(1, \dots, N) \rangle_{\text{spin}} g_{\text{on}}^O \end{aligned} \quad (3-53)$$

The differential cross section for a particular $(o, o, J, M) \rightarrow (n, \nu, J', M')$ transition in analogy to (3-29) is

$$\sigma_{\text{on}}(k_0, \theta, \varphi) = \frac{k'}{k_0} \sum_{2\Sigma=0}^{\infty} \sum_{\mu=-\Sigma}^{\Sigma} p(\Sigma, \mu) |\zeta_{\text{on}}^{\Sigma\mu}|^2 \quad (3-54)$$

If $\mathcal{S}_{SS_Z} \neq \mathcal{S}_{S'S'_Z}$, f_{on}^B will not contribute to $\xi_{on}^{\Sigma\mu}$ since the spin integral multiplying f_{on}^B in (3-53) will be zero.

Define:

$$\begin{aligned} T_{on}(k_o, \theta, \varphi; R, \chi, \emptyset) \\ \equiv \int \phi_n^*(\underline{r}_2, \dots, \underline{r}_N; R) e^{i \underline{q} \cdot \underline{r}_2} \phi_o(\underline{r}_2, \dots, \underline{r}_N; R) d\underline{r}_2 \dots d\underline{r}_N, \end{aligned} \quad (3-55)$$

$$\begin{aligned} \Lambda_{ooJ}^{n\nu J'}(k_o, \theta, \varphi; \chi, \emptyset) \\ \equiv \int \eta_{n\nu J'}^*(R) T_{on} \eta_{ooJ}(R) R^2 dR, \end{aligned} \quad (3-56)$$

$$\begin{aligned} \mathcal{S} &\equiv \langle \mathcal{S}_{\Sigma\mu}^{*'}(1, \dots, N) \mathcal{S}_{\Sigma\mu}(1, \dots, N) \rangle_{\text{spin}}, \\ \text{and} \\ \tilde{\mathcal{S}} &\equiv \langle \mathcal{S}_{\Sigma\mu}^{*'}(2, 1, \dots, N) \mathcal{S}_{\Sigma\mu}(1, \dots, N) \rangle_{\text{spin}}. \end{aligned} \quad (3-57)$$

Then, $|\xi_{on}^{\Sigma\mu}|^2$ can be written as

$$|\xi_{on}^{\Sigma\mu}|^2 = \left(\frac{2me^2(N-1)}{\hbar^2} \right)^2 \left(\frac{\mathcal{S}}{q^2} - \frac{\tilde{\mathcal{S}}}{k_o^2} \right)^2 |\Gamma_{ooJM}^{n\nu J'M'}|^2 \quad (3-58)$$

where

$$\begin{aligned} \Gamma_{ooJM}^{n\nu J'M'}(k_o, \theta, \varphi) \\ \equiv \int Y_{J'M'}^*(\chi, \emptyset) \Lambda_{ooJ}^{n\nu J'} Y_{JM}(\chi, \emptyset) \sin \chi d\chi d\emptyset. \end{aligned} \quad (3-59)$$

Under the present experimental conditions, the target molecules are initially in their ground electronic and vibrational states with room temperature ($\sim 300^\circ\text{K}$) Boltzmann distributions of rotational ones. Since we do not resolve rotational excitation and since each molecule (in a particular o, o, J, M state) scatters independently of all the others, the observed DCS for a particular $o, o \rightarrow n, \nu$ transition is proportional to $I_{oo}^{n\nu}(k_o, \theta, \varphi)$ where

$$I_{oo}^{n\nu} \equiv \left\langle \sum_{J'=0}^{J'_{\max}} \sum_{M'=-J'}^{J'} |\Gamma_{ooJM}^{n\nu J'M'}|^2 \right\rangle_{JM}. \quad (3-60)$$

$\langle \rangle_{JM}$ indicates a statistical-mechanical average over the initial rotational states J, M . $J'_{\max}$ is the maximum J' for which k' of (3-52) remains real. The mathematical details and the assumptions involved in evaluating (3-60) are given by Cartwright and Kuppermann⁽⁷⁶⁾. Their result is

$$I_{oo}^{n\nu} \cong \frac{1}{4\pi} \int |\Lambda_{oo}^{n\nu}|^2 \sin \chi \, d\chi \, d\theta \quad (3-61)$$

where k' is replaced by

$$k'' = \left\{ k_o^2 - \frac{2m}{\hbar^2} [E_{n\nu oo} - E_{oooo}] \right\}^{\frac{1}{2}} \quad (3-62)$$

and the vibrational wave functions are assumed independent of J' and J . The orientationally and rotationally averaged scattering amplitude from equation (3-58) is then

$$|\xi_{\underset{\sim}{o}\underset{\sim}{n}}^{\Sigma\mu}|_{\text{AVG}}^2 = \left[\frac{2me^2(N-1)}{\hbar^2} \right]^2 \left[\frac{\mathcal{S}''}{q^2} - \frac{\tilde{\mathcal{S}}}{k_o^2} \right]^2 I_{oo}^{n\nu}. \quad (3-63)$$

If T_{on} is a slowly varying function of R ⁽¹⁶⁾, it may be evaluated at R equal to the equilibrium internuclear separation R_e of the ground state and removed from the R integral of (3-56).

Then,

$$I_{oo}^{n\nu} = G_{oo}^{n\nu} |T_{on}(k_o, \theta, \varphi; R_e)|_{AVG}^2 \quad (3-64)$$

where

$$\begin{aligned} & |T_{on}(k_o, \theta, \varphi; R)|_{AVG}^2 \\ &= \frac{1}{4\pi} \int |T_{on}(k_o, \theta, \varphi; R, \chi, \emptyset)|^2 \sin \chi d\chi d\emptyset \end{aligned} \quad (3-65)$$

and

$$G_{oo}^{n\nu} \equiv \int \eta_{n\nu}^*(R) \eta_{oo}(R) R^2 dR \quad (3-66)$$

$G_{oo}^{n\nu}$ is the Franck-Condon factor⁽⁷⁷⁾ for the $(oo) \rightarrow (n\nu)$ electronic-vibrational transition. If the vibrational structure of the excited state is not resolved, $I_{oo}^{n\nu}$ must be summed over all vibrational states ν .

Since

$$\sum_{\nu=0}^{\infty} G_{oo}^{n\nu} = 1 \quad (3-67)$$

(Franck-Condon factor sum rule⁽⁷⁸⁾),

$$I_{oo}^n \equiv \sum_{\nu=0}^{\infty} I_{oo}^{n\nu} \cong |T_{on}(k_o, \theta, \varphi; R_e)|_{AVG}^2 \quad (3-68)$$

where k'' is replaced by

$$k''' = \left\{ k_0^2 - \frac{2m}{\hbar^2} [E_{n\nu'00} - E_{000}] \right\}^{\frac{1}{2}} \quad (3-69)$$

and ν' is the value of ν for which $G_{00}^{n\nu}$ is a maximum. The validity of (3-68) depends on k_0^2 being large enough so that k'' doesn't change appreciably over the range of ν for which $G_{00}^{n\nu}$ is not negligibly small.

It is worth emphasizing that there are three basic approximations inherent in the derivation of (3-64).

1) The ground and excited state wave functions can be factored into a product of electronic, vibrational, rotational, and electron spin parts. This is called the Born-Oppenheimer separability approximation and is an excellent approximation in cases for which spin-orbit coupling is negligible.

2) The electronic transition occurs on a time scale that is short compared to vibrational periods. This is called the Franck-Condon principle⁽⁷⁹⁾ and provides the justification for using the same R in both the ground and excited state wave functions. It should be a good approximation provided the excitation does not occur via a long lived negative ion.

3) The electronic transition amplitude T_{on} is a slowly varying function of R . This is a more subtle point which in general requires either empirical or numerical verification. If the vibrational structure (or overall envelope) of an electronic excitation can be observed, then the relative intensities of the vibrational transitions

can be compared with the $G_{00}^{n\nu}$ obtained from calculations or optical spectroscopy. For all reported cases, the electron-impact and optical absorption measurements of relative intensities have agreed⁽⁴¹⁾ (except for transitions occurring through negative ion formation).

Since we can clearly resolve vibrational structure in the energy-loss spectra of H_2 , N_2 , and CO , it is worthwhile to examine more closely the relative vibrational level peak intensities to be expected from the above Franck-Condon factor considerations. For a three electron system within the framework of the Born approximation (no exchange), the differential cross section for excitation of the n^{th} electronic and ν^{th} vibrational state from the ground electronic and vibrational state is

$$\begin{aligned} \sigma_{n\nu}(k_0, \theta) \\ = \frac{k_\nu}{k_0} \frac{16}{q^4} G_{00}^{n\nu} |T_{\text{on}}(k_0, \theta, \varphi; R_e)|_{\text{AVG}}^2 \end{aligned} \quad (3-70)$$

in Hartree atomic units. $|T_{\text{on}}(k_0, \theta, \varphi; R_e)|_{\text{AVG}}^2$ is defined by equation (3-65), k_0 and k_ν are the wave numbers of the incident and scattered electrons, respectively, and

$$q^2 = k_0^2 + k_\nu^2 - 2k_0 k_\nu \cos \theta$$

For small q , $e^{i\mathbf{q} \cdot \mathbf{r}_2}$ appearing in equation (3-55) can be expanded as in equation (3-45). In this way the energy and scattering angle dependence in $|T_{\text{on}}|_{\text{AVG}}^2$ can be factored out term by term.

For an electronic transition which is dipole allowed, equation (3-70) becomes approximately

$$\sigma_{n\nu}(k_o, \theta) \cong \frac{k_\nu}{k_o} \frac{16}{q^2} G_{oo}^{n\nu} (z_1)^2 \quad (3-71)$$

where z_1 is the properly averaged dipole-matrix element⁽¹²⁸⁾ in analogy to equation (3-46). Since we measure the energy-loss spectrum at constant resolution and with a collection efficiency that is independent of energy (see section 4.4.4.3.), the ratio of the peak intensities $I_\nu/I_{\nu o}$ for two vibrational levels ν and νo is

$$\begin{aligned} \left(\frac{I_\nu}{I_{\nu o}} \right) & \begin{matrix} \text{DIR.} \\ \text{DIPOLE} \end{matrix} \\ &= \frac{\sigma_{n\nu}(k_o, \theta)}{\sigma_{n\nu o}(k_o, \theta)} = C_{\nu\nu o}^{DD} \frac{G_{oo}^{n\nu}}{G_{oo}^{n\nu o}} \end{aligned} \quad (3-72)$$

with

$$C_{\nu\nu o}^{DD} = \frac{k_\nu}{k_{\nu o}} \frac{q_o^2}{q^2}$$

and

$$k_\nu^2 = k_o^2 - 2W_\nu$$

$$k_{\nu o}^2 = k_o^2 - 2W_{\nu o}$$

$$q_o^2 = k_o^2 + k_{\nu o}^2 - 2k_o k_{\nu o} \cos \theta$$

where W_ν and $W_{\nu o}$ are the excitation energies (in hartrees) of the ν^{th} and νo^{th} vibrational states of the upper electronic state (n), respectively.

In an analogous way, this analysis can be performed for a dipole-forbidden but quadrupole-allowed transition with the result

$$\left(\frac{I_\nu}{I_{\nu 0}}\right)_{\text{DIR. QUAD}} = C_{\nu\nu 0}^{\text{DQ}} \frac{G_{00}^{n\nu}}{G_{00}^{n\nu 0}} \quad (3-73)$$

where

$$C_{\nu\nu 0}^{\text{DQ}} = \frac{k_\nu}{k_{\nu 0}}$$

For the case of exchange scattering, the Ochkur approximation and the same high-energy approximations used to derive equation (3-72) yield (assuming z_1 is dominant),

$$\left(\frac{I_\nu}{I_{\nu 0}}\right)_{\text{EX DIPOLE}} = C_{\nu\nu 0}^{\text{ED}} \frac{G_{00}^{n\nu}}{G_{00}^{n\nu 0}} \quad (3-74)$$

with

$$C_{\nu\nu 0}^{\text{ED}} = \frac{k_\nu}{k_{\nu 0}} \frac{q^2}{q_0^2}$$

If $z_1 = 0$ and z_2 is dominant,

$$\left(\frac{I_\nu}{I_{\nu 0}}\right)_{\text{EX QUAD}} = C_{\nu\nu 0}^{\text{EQ}} \frac{G_{00}^{n\nu}}{G_{00}^{n\nu 0}} \quad (3-75)$$

with

$$C_{\nu\nu 0}^{\text{EQ}} = \frac{k_\nu}{k_{\nu 0}} \frac{q^4}{q_0^4}$$

The factors multiplying the Franck-Condon factor ratios in equations (3-72), (3-73), and (3-74) have been calculated for some specific cases and are given in the discussions of N_2 (section 5.3) and CO (section 5.4).

From the failure of both the Born and Ochkur approximations to reliably predict low-energy differential cross sections, it is of doubtful value to use them in determining the relation of relative peak heights to relative Franck-Condon factors.

3.3.7.2 Ethylene

In this section we apply the Ochkur approximation to the spin-forbidden $\tilde{X}^1A_{1g} \rightarrow \tilde{a}^3B_{1u}$ ($\pi \rightarrow \pi^*$) transition^(80,81a) of ethylene. This transition has been observed by both optical methods^(82,83) and electron impact⁽⁸⁴⁾.

Within the framework of the Born-Oppenheimer separability approximation, the π electron approximation^(81b) and the LCAO method⁽⁸⁵⁾, the ground and excited state wave functions for this transition can be written as

$$\begin{aligned} \psi_{\tilde{X}} \\ = \phi_{\tilde{X}\pi}(\mathbf{r}_2, \mathbf{r}_3; \mathbf{R}) \phi_{\tilde{X}\sigma}(\mathbf{r}_4, \dots, \mathbf{r}_{17}; \mathbf{R}) \phi_{\tilde{X}}(\mathbf{R}) \int_{00}(2, \dots, 17) \end{aligned} \quad (3-76)$$

and

$$\begin{aligned} \psi_{\tilde{a}} \\ = \phi_{\tilde{a}\pi}(\mathbf{r}_2, \mathbf{r}_3; \mathbf{R}) \phi_{\tilde{a}\sigma}(\mathbf{r}_4, \dots, \mathbf{r}_{17}; \mathbf{R}) \phi_{\tilde{a}}(\mathbf{R}) \int_{1S'_Z}(2, \dots, 17) \end{aligned} \quad (3-77)$$

$\phi_{\tilde{x}\pi}$ and $\phi_{\tilde{a}\pi}$ are the ground and excited state wave functions for the two π electrons at fixed nuclear geometry $\tilde{R}$. $\phi_{\tilde{x}\sigma}$ and $\phi_{\tilde{a}\sigma}$ are the corresponding wave functions for the remaining electrons. $\phi_{\tilde{x}}(\tilde{R})$ and $\phi_{\tilde{a}}(\tilde{R})$ are the vibrational-rotational wave functions, and $\int_{00}$ and $\int_{1S'_Z}$ are the normalized spin wave functions for the ground and excited states. We assume that only the two π electrons are involved in the transition so that

$$\phi_{\tilde{x}\sigma} = \phi_{\tilde{a}\sigma} \quad (3-78)$$

and the N in equation (3-58) is 3. The ground state spin wave function is a singlet ($S = 0$) while the excited state is a triplet ($S' = 1$). In analogy with helium, the DCS for the spin forbidden transition in the Ochkur approximation is

$$\sigma_{\tilde{x}\tilde{a}}^O(k_O, \theta, \varphi) = \frac{3k'''}{k_O} |g_{\tilde{x}\tilde{a}}^O|^2 \quad (3-79)$$

where

$$|g_{\tilde{x}\tilde{a}}^O|^2 \cong \left(\frac{2me^2}{\hbar^2 k_O^2}\right)^2 |T_{\tilde{x}\tilde{a}}(k_O, \theta, \varphi; R_e)|_{\text{AVG}}^2, \quad (3-80)$$

$$k''' = \left\{ k_O^2 - \frac{2m}{\hbar^2} W \right\}^{\frac{1}{2}}, \quad (3-81)$$

$|T_{\tilde{x}\tilde{a}}(k_O, \theta, \varphi; R_e)|_{\text{AVG}}^2$ is given by equation (3-65) with

$$\begin{aligned} & T_{\tilde{x}\tilde{a}}(k_O, \theta, \varphi; R, \chi, \emptyset) \\ &= \int \phi_{\tilde{a}\pi}^*(\underline{r}_2, \underline{r}_3, R) e^{i\mathbf{q} \cdot \underline{r}_2} \phi_{\tilde{x}\pi}(\underline{r}_2, \underline{r}_3, R) d\underline{r}_2 d\underline{r}_3, \end{aligned} \quad (3-82)$$

$$\underline{q} = \underline{k}_0 - \underline{k}''',$$

$$q^2 = k_0^2 + (k''')^2 - 2k_0 k''' \cos \theta.$$

$\hbar \underline{k}_0$ is the initial electron momentum and $\hbar \underline{k}'''$ is the final one. R_e is the C-C equilibrium internuclear distance, $\frac{\hbar^2}{2m} k_0^2$ is the incident electron kinetic energy, $\frac{\hbar^2}{2m} k'''^2$ is the scattered electron kinetic energy, and W is the excitation energy for the peak of the transition (~ 4.6 eV). We have assumed that ethylene can be treated as a diatomic molecule and that the cross section (3-79) has been summed over all rotational and vibrational states (since neither is resolved). The π electron spatial wave functions for electrons 2 and 3 can be approximated by⁽⁸⁶⁾

$$\phi_{\tilde{x}\pi} = h_1(\underline{r}_2) h_1(\underline{r}_3) \quad (3-83)$$

$$\phi_{\tilde{a}\pi} = \frac{1}{\sqrt{2}} \{ h_1(\underline{r}_2) h_2(\underline{r}_3) - h_1(\underline{r}_3) h_2(\underline{r}_2) \}$$

where

$$h_1 = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{1 + S_{ab}}} (\chi_a + \chi_b),$$

$$h_2 = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{1 - S_{ab}}} (\chi_a - \chi_b), \quad (3-84)$$

χ_a and χ_b are P_z orbitals^(49c) centered on carbon a and b, respectively;

$$\chi_{(b)}^{(a)} = \left(\frac{\gamma^5}{\pi}\right)^{\frac{1}{2}} \cos \theta_{(b)}^{(a)} r_{(b)}^{(a)} e^{-\gamma r_{(b)}^{(a)}}, \quad (3-85)$$

and S_{ab} is the overlap of the two orbitals for an internuclear $(C_a - C_b)$ distance R_e ,

$$S_{ab} \equiv \int \chi_a \chi_b d\mathbf{r} \quad (3-86)$$

Substitution of (3-83) into (3-82) yields

$$T_{\tilde{x}\tilde{a}} = -\frac{1}{2\sqrt{2}} \int \{(\chi_a(\mathbf{r}_a))^2 - (\chi_b(\mathbf{r}_b))^2\} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \quad (3-87)$$

where the origin of $\mathbf{r}$ is centered on a line joining the two carbons and the origins of $\mathbf{r}_a$ and $\mathbf{r}_b$ are carbons a and b. If $\mathbf{R}_a$ and $\mathbf{R}_b$ are the fixed vector positions of carbons a and b with respect to the origin of $\mathbf{r}$, then

$$\mathbf{R}_b + \mathbf{r}_b = \mathbf{r}$$

$$\mathbf{R}_a + \mathbf{r}_a = \mathbf{r} \quad (3-88)$$

$$\mathbf{R}_a = -\mathbf{R}_b \equiv \mathbf{R}_e/2$$

Substitution of (3-88) into (3-87) yields

$$T_{\tilde{x}\tilde{a}} = \left(\frac{-i\gamma^5}{\sqrt{2\pi}} \right) \frac{\sin(\mathbf{q}\cdot\mathbf{R}_e/2)}{\sqrt{1 - S_{ab}^2}} \int \cos^2 \theta \, r^2 \, e^{-2\gamma r} e^{i\mathbf{q}\cdot\mathbf{r} \cos \theta} r^2 dr d(\cos \theta) d\varphi \quad (3-89)$$

where the z axis for the $\mathbf{r}$ integration has been chosen along $\mathbf{q}$.

The integration of (3-89) is straightforward^(74b), and we obtain

$$T_{\tilde{x}\tilde{a}} = -i \frac{64\gamma^6}{\sqrt{2}} \frac{1}{\sqrt{1-S_{ab}^2}} \frac{(4\gamma^2 - 5q^2)}{(4\gamma^2 + q^2)^4} \sin(q \cdot R_e/2) \quad (3-90)$$

Substitution of (3-90) into (3-65) and integration over all molecular orientations gives

$$|T_{\tilde{x}\tilde{a}}|_{\text{AVG}}^2 = A^2 \left(\frac{4\gamma^2 - 5q^2}{[4\gamma^2 + q^2]^4} \right)^2 \left[1 - \frac{\sin q R_e}{q R_e} \right] \quad (3-91)$$

where

$$A = \frac{32\gamma^6}{\sqrt{1-S_{ab}^2}}$$

The differential cross section is then obtained by substituting (3-91) into (3-80) and (3-80) into (3-79).

$$\sigma_{\tilde{x}\tilde{a}}^O(k_o, \theta) = B^2 \frac{k_o'''}{k_o^5} \left(\frac{4\gamma^2 - 5q^2}{[4\gamma^2 + q^2]^4} \right)^2 \left[1 - \frac{\sin q R_e}{q R_e} \right] \quad (3-92a)$$

where

$$B = \frac{2\sqrt{3} A m e^2}{\hbar^2}$$

The expression for the DCS of (3-92a) can be converted to the more accurate Ochkur-Rudge expression by

$$\sigma_{\tilde{x}\tilde{a}}^{\text{OR}}(k_o, \theta) = \frac{k_o^4}{[k_o''' - iA]^4} \sigma_{\tilde{x}\tilde{a}}^O(k_o, \theta) \quad (3-92b)$$

(see equation 3-38)). The total cross section is given by

$$Q_{\tilde{x}\tilde{a}}(k_o) = 2\pi \int_{-1}^1 \sigma_{\tilde{x}\tilde{a}}^{\text{OR}} d(\cos \theta) \quad (3-93)$$

Both the differential and total cross sections have been calculated (via equations (3-92b) and (3-93)) for

$$W = 4.6 \text{ eV}$$

$$R_e = 1.33 \text{ \AA} \text{ (reference 81c)}$$

$$\gamma = 3.07 \text{ \AA}^{-1} \quad (81d)$$

$$S_{ab} = .28 \quad (81e)$$

The results obtained for the total cross section are compared in figure 3.3-1 with the results of Ochkur and Bratsev^(58b) for excitation of the 2^3P state of helium. The shapes of the cross section curves are quite similar. Figure 3.3-2 shows the threshold region of the $\tilde{x}^1A_{1g} - \tilde{a}^3B_{1u}$ total excitation cross section along with the experimental results of Brongersma⁽⁸⁷⁾. The experimental and theoretical cross section curves have similar shapes, while the discrepancies in the magnitudes are not at all unreasonable considering the approximations involved in the calculation. The angular distributions (DCS) obtained by this calculation are compared with our experimental results in section 5.7.

Figure 3.3-1. The total cross section Q for the $\tilde{X}^1A_{1g} - \tilde{a}^3B_{1u}$ transition in ethylene by electron impact (solid line). E is the kinetic energy of the incident electron minus the excitation energy $W = 4.6$ eV. The dashed line is the calculated^(58b) total cross section $\times 10$ for excitation of the 2^3P state of helium.

Figure 3.3-2. The total cross section Q near threshold for the $\tilde{x}^1A'_{1g} \rightarrow \tilde{a}^3B'_{1u}$ transition in ethylene by electron impact. The solid line is the calculated behavior, and the circles are the experimental results of Brongersma⁽⁸⁷⁾ times $\frac{1}{2}$. The calculated slope is $0.13\pi a_0^2/\text{eV}$ while the experimental one is $0.34\pi a_0^2/\text{eV}$. E is the energy above threshold.

3.4. Partial Wave Analysis

3.4.1 Introduction

The approximate first order methods discussed above are expected to be valid only at relatively high impact energies. Thus, some other approach is needed to provide at least a qualitative understanding of the angular distribution of scattered electrons for low impact energies. The method of partial waves^(44c) is one such approach which has proved useful in the treatment of scattering by spherically symmetric potentials. The method involves the expansion of the total wave function in radial functions (functions of r) times spherical harmonics (functions of θ, ϕ). If the possibility of exchange excitation is included, the desired radial functions are solutions of an infinite set of coupled integro-differential equations similar in form to equation (3-18) for even the simplest system of an electron plus atomic hydrogen⁽⁸⁸⁾.

A more fruitful qualitative approach (though certainly less rigorous) is to treat the electron plus target scattering problem as if it were spherically symmetric. The differences between the direct and exchange excitation mechanisms are then included through the use of different effective electron-target interaction potentials.

For example, in a three electron system, the "potential"^(44d) leading to direct excitation is in some sense proportional to the electronic matrix element

$$M_D(r_1) \propto \int \phi_n^*(\underline{r}_2, \underline{r}_3) \frac{1}{r_{12}} \phi_0(\underline{r}_2, \underline{r}_3) d\underline{r}_2 d\underline{r}_3 \quad (3-94)$$

while that for exchange is

$$M_{EX}(r_1) \propto \int \phi_n^*(\underline{r}_1, \underline{r}_2) \frac{1}{r_{12}} \phi_0(\underline{r}_2, \underline{r}_3) d\underline{r}_2 d\underline{r}_3 \quad (3-95)$$

$\underline{r}_3$, $\underline{r}_2$, and $\underline{r}_1$ are the respective coordinates of the two initially bound electrons and the incoming one. ϕ_n and ϕ_0 are the final and initial bound state spatial wave functions, respectively, of the target.

$$r_{12} \equiv |\underline{r}_1 - \underline{r}_2|.$$

The potentials M_D and M_{EX} have quite different effective ranges as indicated by their behavior for $r_1 \gg r_2, r_3$ (a case in which the incoming electron is relatively far from the target).

$\frac{1}{r_{12}}$ can be expanded as

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \frac{r_2^\ell}{r_1^{\ell+1}} P_\ell(\cos\theta_{12}) \quad \text{for } r_1 > r_2. \quad (3-96)$$

The $P_\ell(\cos\theta_{12})$ are Legendre polynomials and $\cos\theta_{12} = \frac{\underline{r}_1 \cdot \underline{r}_2}{r_1 r_2}$.

Substitution of (3-96) into (3-94) and (3-95) yields

$$M_D(r_1) \underset{r_1 \gg r_2, r_3}{\sim} \frac{\hat{r}_1}{(r_1)^2} \cdot \int \phi_n^*(\underline{r}_2, \underline{r}_3) \underline{r}_1 \phi_0(\underline{r}_2, \underline{r}_3) d\underline{r}_2 d\underline{r}_3 \quad (3-97)$$

$$+ O\left(\frac{1}{(r_1)^3}\right).$$

and

$$\begin{aligned}
 M_{EX}(r_1) \sim & \frac{1}{r_1} \int \phi_n^*(\underline{r}_1, \underline{r}_2) \phi_0(\underline{r}_2, \underline{r}_3) d\underline{r}_2 d\underline{r}_3 \\
 & + \frac{\hat{r}_1}{(r_1)^2} \cdot \int \phi_n^*(\underline{r}_1, \underline{r}_2) \underline{r}_2 \phi_0(\underline{r}_2, \underline{r}_3) d\underline{r}_2 d\underline{r}_3 \\
 & + O\left(\frac{1}{r_1^3}\right),
 \end{aligned} \tag{3-98}$$

respectively, where $\hat{r}_1$ is a unit vector in the $\underline{r}_1$ direction. However,

$$\phi_n^*(\underline{r}_1, \underline{r}_2) \sim r_1^m e^{-\alpha n r_1} \chi^*(\underline{r}_2; \theta_1, \varphi_1) \tag{3-99}$$

since $\underline{r}_1$ is the coordinate of a bound electron in the excited state.

Substitution of (3-99) into (3-98) yields

$$\begin{aligned}
 M_{EX}(r_1) \sim & r_1^{m-1} e^{-\alpha n r_1} \int \chi^*(\underline{r}_2; \theta_1, \varphi_1) \phi_0(\underline{r}_2, \underline{r}_3) d\underline{r}_2 d\underline{r}_3 \\
 & + O(r_1^{m-2} e^{-\alpha n r_1}).
 \end{aligned} \tag{3-100}$$

As a result, $M_{EX}(r_1)$ is of much shorter range than $M_D(r_1)$ since the former decays exponentially while the latter decreases only as $\frac{1}{r_1^2}$.

Thus, we will apply the partial wave method rigorously to the problem of elastic scattering from a central potential. Then the angular dependence of the direct and exchange differential cross sections can be qualitatively explained in terms of the different effective ranges of the direct and exchange "potentials."

3.4.2. Elastic Scattering by a Center of Force.

The steady state Schrödinger equation for an electron of kinetic energy $\frac{\hbar^2}{2m} k^2$ (at $r = \infty$) in a potential field $V(r)$ is

$$[\nabla^2 + (k^2 - U(r))]\psi(r) = 0 \quad (3-101)$$

where $U(r) = \frac{2m}{\hbar^2} V(r)$.

If the electron is assumed to be incoming along the z axis of the $\underline{r}$ coordinate system with a momentum $\hbar \underline{k}$ (at $r \rightarrow \infty$), then the desired solutions of (3-101) have an asymptotic form

$$\psi(r, \theta) \underset{r \rightarrow \infty}{\sim} e^{i k z} + f(\theta) \frac{e^{i k r}}{r} \quad (3-102)$$

(ψ is not a function of φ since $V(r)$ is spherically symmetric.)

The general solution of (3-101) is

$$\psi(r, \theta) = \frac{1}{r} \sum_{\ell=0}^{\infty} R_{\ell}(r) P_{\ell}(\cos \theta) \quad (3-103)$$

where $R_{\ell}(r)$ is a solution of

$$\frac{d^2 R_{\ell}(r)}{dr^2} + [k^2 - U(r) - \frac{\ell(\ell+1)}{r^2}] R_{\ell}(r) = 0 \quad (3-104)$$

If $U(r)$ tends to zero faster than $\frac{1}{r}$ as $r \rightarrow \infty$, then

$$R_{\ell}(r) \underset{r \rightarrow \infty}{\sim} A_{\ell} \sin(kr + \epsilon_{\ell}) \quad (3-105)$$

where A_ℓ and ϵ_ℓ are constants.

If $U(r) = 0$, the solutions $R_\ell^0(r)$ to (3-104) which are bounded at the origin, are

$$R_\ell^0(r) = B_\ell \sqrt{\frac{\pi k r}{2}} J_{\ell + \frac{1}{2}}(kr) \quad (3-106)$$

where B_ℓ is a constant and $J_{\ell + \frac{1}{2}}(kr)$ is a Bessels' function of the first kind. $R_\ell^0(r)$ has the asymptotic form

$$R_\ell^0(r) \underset{r \rightarrow \infty}{\sim} B_\ell \sin(kr - \frac{1}{2} \ell \pi) \quad (3-107)$$

Thus, for $U(r) \neq 0$, we require

$$R_\ell(r) \underset{r \rightarrow \infty}{\sim} A_\ell \sin(kr - \frac{1}{2} \ell \pi + \eta_\ell) \quad (3-108)$$

so that the phase shift η_ℓ is zero for $U(r) = 0$. η_ℓ depends on k and $U(r)$.

A_ℓ is determined by first substituting (3-108) into (3-103) to obtain

$$\begin{aligned} \psi(r, \theta) \underset{r \rightarrow \infty}{\sim} \frac{1}{2ir} \sum_{\ell=0}^{\infty} [(e^{-i\ell\pi/2} e^{i\eta_\ell}) e^{ikr} - (e^{i\ell\pi/2} e^{-i\eta_\ell}) e^{-ikr}] \\ \times A_\ell P_\ell(\cos \theta) \end{aligned} \quad (3-109)$$

Then (3-102) is expanded in Legendre polynomials:

$$\begin{aligned} \psi(r, \theta) \underset{r \rightarrow \infty}{\sim} \frac{1}{2ir} \sum_{\ell=0}^{\infty} [(\frac{2\ell+1}{k} + 2iC_\ell) e^{ikr} - (\frac{(2\ell+1)e^{i\ell\pi}}{k}) e^{-ikr}] \\ \times P_\ell(\cos \theta) \end{aligned} \quad (3-110)$$

where

$$f(\theta) = \sum_{\ell=0}^{\infty} C_{\ell} P_{\ell}(\cos \theta) \quad (3-111)$$

Since (3-109) and (3-110) are asymptotic forms of the same function, they must be equivalent. A comparison of the coefficients of $e^{\pm i k r}$ requires

$$C_{\ell} = \frac{(2\ell+1)}{2ik} (e^{2i\eta_{\ell}} - 1) \quad (3-112)$$

The differential cross section is given by

$$\sigma(k, \theta) = |f(\theta)|^2 \quad (3-113)$$

and, thus,

$$\sigma(k, \theta) = \frac{1}{4k^2} \left| \sum_{\ell=0}^{\infty} (2\ell+1) [e^{2i\eta_{\ell}} - 1] P_{\ell}(\cos \theta) \right|^2 \quad (3-114)$$

The phase shifts are obtained in general by numerical integration of (3-104).

It can be shown^(44e), however, that

$$\eta_{\ell} \cong -\frac{\pi}{2} \int_0^{\infty} U(r) [J_{\ell+\frac{1}{2}}(kr)]^2 r \, dr \quad (3-115)$$

if the right hand side is small. This is a form of the Born approximation for potential scattering.

Suppose that $r^2 U(r)$ has an effective range $r_{\max}$ and that within that range it never exceeds some finite value, i. e.

$$\begin{aligned}
 r^2 |U(r)| &\leq a & 0 < r \leq r_{\max} \\
 &= 0 & r_{\max} < r
 \end{aligned}
 \tag{3-116}$$

If the impact energy is low enough so that $\frac{kr_{\max}}{2} \ll 1$, then the small argument form⁽⁸⁹⁾ of $J_{\ell + \frac{1}{2}}$ can be used and

$$\begin{aligned}
 |\eta_{\ell}| &\leq \left(\frac{\pi}{2}\right) \frac{a}{(\Gamma(\ell + \frac{3}{2}))^2} \int_0^{r_{\max}} \left(\frac{kr}{2}\right)^{2\ell+1} \frac{dr}{r} \\
 &= \frac{2\pi a}{(2\ell+1)^3} \left(\frac{kr_{\max}}{2}\right)^{2\ell+1} \frac{1}{[\Gamma(\ell + \frac{1}{2})]^2}
 \end{aligned}
 \tag{3-117}$$

If η_{ℓ} is small then (3-114) implies that

$$\sigma(k, \theta) \cong \frac{1}{k^2} \left| \sum_{\ell=0}^{\infty} (2\ell+1) \eta_{\ell} P_{\ell}(\cos \theta) \right|^2. \tag{3-118}$$

Each term in the expansion is called a "partial wave" and is often designated as an S, P, D, etc. wave depending on whether $\ell = 0, 1, 2$, etc.

Since the range ($r_{\max}$) of the interaction leading to direct scattering is much larger than that leading to exchange, the number of η_{ℓ} 's needed in (3-118) is greater. From the nature of Legendre polynomials, the more of them which are included in (3-118), the more sharply peaked toward $\theta = 0^\circ$ can be the differential cross section. Thus, we expect the angular distribution of electrons scattered after causing exchange excitations to be relatively more

isotropic than that of electrons causing excitations via a direct mechanism. Indeed, this has been found to be the case⁽⁹⁰⁾.

Notice also that if k is lowered (lower impact energy) fewer η_ℓ 's are required and both direct and exchange cross sections should become more isotropic. This also has been observed⁽⁹¹⁾.

3.4.3. Data Expansion in Partial Waves

In this research we actually measure several inelastic differential cross sections, corresponding to excitation via direct and/or exchange mechanisms, over an angular range of $10^\circ \lesssim \theta \lesssim 80^\circ$. It would be of interest to expand these measured distributions in Legendre polynomials in an attempt to determine the c_ℓ 's of an expansion such as (3-111). For a general inelastic process, the c_ℓ 's do not have the simple form of (3-112) in which η_ℓ is real. This form can be preserved for the general case if

$$\eta_\ell \equiv \lambda_\ell + i\mu_\ell \quad (3-119)$$

where λ_ℓ and μ_ℓ are real^(44f). For our purposes, we assume

$$c_\ell \equiv a'_\ell e^{ib'_\ell} \quad (3-120)$$

in which a'_ℓ and b'_ℓ are real. The differential cross section for any particular inelastic process ($o \rightarrow n$) can be written as

$$\sigma_{on}(k_o, \theta) = \frac{k_n}{k_o} |A_{on}|^2 \quad (3-121)$$

where $\frac{\hbar^2 k_o^2}{2m}$ is the energy of the incident electron, $\frac{\hbar^2 k_n^2}{2m}$ is the energy of the scattered electron, and A_{on} is the complete scattering amplitude associated with the observed process (a suitable linear combination of ζ_{on}^{S, S_z} , as discussed previously). We have neglected any φ dependence in (3-121) since we do not measure it nor do we expect it under our experimental conditions. The amplitude A_{on} can be expanded in Legendre polynomials as

$$A_{on} = \sum_{\ell=0}^{\infty} c_{\ell} P_{\ell}(\cos \theta). \quad (3-122)$$

The substitution of (3-120) into (3-122) and the result into (3-121) yields

$$\begin{aligned} & \frac{\sigma_{on}(k_o, \theta)}{(a'_o)^2} \\ &= \frac{k_n}{k_o} \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} a_{\ell} a_m e^{i(b_{\ell} - b_m)} P_{\ell}(\cos \theta) P_m(\cos \theta), \end{aligned} \quad (3-123)$$

where $a_{\ell} \equiv a'_{\ell}/a'_o$ and $b_{\ell} \equiv b'_{\ell} - b'_o$. These last two definitions are introduced since: (1) the experimental cross section in this case (σ_{on}^{EXP}) is related to the theoretical one (3-123) by an unknown multiplicative constant and; (2) a knowledge of σ_{on} leaves A_{on} indeterminate to within an arbitrary phase factor $e^{i\theta}$.

The product of Legendre polynomials in (3-123) can also be expanded as

$$P_\ell(\cos\theta) P_m(\cos\theta) = \sum_{p=0}^{\infty} D_{\ell m}^p P_p(\cos\theta) \quad (3-124)$$

where

$$D_{\ell m}^p \equiv \frac{2p+1}{2} \int_{-1}^1 P_p(\cos\theta) P_\ell(\cos\theta) P_m(\cos\theta) d(\cos\theta) .$$

Notice that $D_{\ell m}^p = D_{m\ell}^p$. It can be shown^(65b) that

$$\int_{-1}^1 P_{\ell_1}(\mu) P_{\ell_2}(\mu) P_{\ell_3}(\mu) d\mu = 2 \begin{pmatrix} \ell_1 \ell_2 \ell_3 \\ 0 0 0 \end{pmatrix}^2 \quad (3-125)$$

where $\begin{pmatrix} \ell_1 \ell_2 \ell_3 \\ 0 0 0 \end{pmatrix}$ is the usual Wigner 3_j symbol⁽⁹²⁾.

Thus,

$$D_{\ell m}^p = (2p+1) \begin{pmatrix} p \ell m \\ 0 0 0 \end{pmatrix}^2 . \quad (3-126)$$

Substitution of (3-124) into (3-123) and a rearrangement of terms yields

$$\frac{\sigma_{\text{on}}(k_o, \theta)}{(a'_o)^2} = \frac{k_n}{k_o} \sum_{p=0}^{\infty} F_p P_p(\cos\theta) \quad (3-127)$$

where

$$F_p \equiv \sum_{\ell=0}^{\infty} a_\ell^2 D_{\ell\ell}^p + 4 \sum_{\ell>0} \sum_{m=0}^{\infty} a_\ell a_m \cos(b_\ell - b_m) D_{\ell m}^p . \quad (3-128)$$

The experimentally determined differential cross section at each angle θ_i is related to the theoretical one by

$$\sigma_{\text{on}}^{\text{EXP}}(k_o, \theta_i) \cong C' \sigma_{\text{on}}(k_o, \theta_i) \quad (3-129)$$

where C' is an unknown positive constant, depending on k_0 , but not θ . In principle, the F_p 's of (3-127) (and hence the a_ℓ 's and b_ℓ 's of (3-128)) can be determined by a least squares fit of the data to the theoretical expression (3-127). In particular, we wish to minimize the quantity

$$\gamma \equiv \sum_{s=1}^M [\sigma_{\text{on}}^{\text{EXP}}(k_0, \theta_s) - C' \sigma_{\text{on}}(k_0, \theta_s)]^2 \left(\frac{1}{\epsilon_s} \right)^2 \quad (3-130)$$

where ϵ_s is the relative error in the measurement at the angle θ_s , and M is the number of experimental points. It is clear that the expansion (3-127) must be truncated so that there are fewer unknowns than data points. If the number of terms retained in (3-127) is $N + 1$, then

$$\gamma = \sum_{s=1}^M [\sigma_{\text{on}}^{\text{EXP}}(k_0, \theta_s) - C \sum_{p=0}^N F_p P_p(\cos \theta_s)]^2 \left(\frac{1}{\epsilon_s} \right)^2 \quad (3-131)$$

where $C = C' (a'_0)^2 \frac{k_n}{k_0}$.

The minimization of (3-131) was attempted in two ways.

I. γ was minimized with respect to a variation in $F'_p = CF_p$.

In other words, we require

$$\frac{\partial \gamma}{\partial F'_p} = 0 \quad \text{for } p = 0, \dots, N.$$

This implies from (3-131) that

$$\sum_{s=1}^M \left(\frac{1}{\epsilon_s} \right)^2 [\sigma_{\text{on}}^{\text{EXP}}(\theta_s) - \sum_{p=0}^N F'_p P_p(\cos \theta_s) P_q(\cos \theta)] = 0 \quad (3-132)$$

for $q = 0, \dots, N$.

The solutions F'_p to the system of equations (3-132) can be written in matrix notation as

$$\underline{F'} = (\underline{IP} \underline{IE} \underline{IP}^T)^{-1} (\underline{IP} \underline{IE} \underline{g}) \quad (3-133)$$

where $\underline{F'}$ and $\underline{g}$ are column vectors with elements F'_p and $\sigma_{on}^{EXP}(\theta_s)$, respectively;

$$(\underline{IP})_{ij} = P_i(\cos \theta_j); \quad (\underline{IE})_{kl} = \left(\frac{1}{\epsilon_k}\right)^2 \delta_{kl};$$

and the various indices have ranges: $(p, i) \rightarrow (0, \dots, N)$; $(j, k, \ell, s) \rightarrow (1, \dots, M)$. The matrix inversion and multiplications indicated in (3-133) were first carried out in double-precision arithmetic on an IBM 7094 computer for two test cases.

Test case (1): A set of ten "data-points" (value of the differential cross section at ten angles $\theta_s = n \times 10^\circ$, $n = 0, \dots, 9$) was generated by assuming

$$\sigma_{on}^{EXP}(\theta_s) = \sum_{\ell=0}^2 x_\ell P_\ell(\cos \theta_s) \quad (3-134)$$

where x_ℓ is given.

These values of $\sigma_{on}^{EXP}(\theta_s)$, each with the same relative error, were substituted into (3-133). (3-133) was then solved to obtain the F'_p 's for $N = 2$ and 4. Table 3.4-1 summarizes the results for one set of x_ℓ 's. Notice that the "data" are fit with the correct coefficients for $N = 2$ and that the inclusion of higher-order P_ℓ 's does not affect the coefficients of the first three terms. This ideal

TABLE 3.4-1

Least squares fit of "data" from test case (1). $N + 1$ is the number of terms included in the expansion (3-127). x_ℓ is the "true" coefficient of the ℓ^{th} order Legendre polynomial while F'_ℓ is the one calculated according to equation (3-133). RMS is the root-mean-square deviation of the fit from the "data."

	x_0	x_1	x_2	x_3	x_4	RMS
$N + 1$	.5550	.3330	.1110	.0	.0	
	F'_0	F'_1	F'_2	F'_3	F'_4	
3	.5550	.3330	.1110	-	-	1.1×10^{-6}
5	.5550	.3330	.1110	-5.7×10^{-6}	1.1×10^{-6}	1.0×10^{-6}

behavior is to be expected.

Test case (2): In this case, a random percentage error, $-5\% \leq \epsilon_s \leq +5\%$, was added to each "data-point" of test case (1). (3-133) was solved in this case for $N = 2, 4$, and 6. Table 3.4-2 summarizes the results for the same set of x_ℓ 's used in Table 3.4-1. Notice that in this case the addition of higher-order polynomials drastically affects the coefficients of lower-order ones.

Unfortunately, an analysis of the real data according to this method (equation (3-133)) yielded the results indicated by test case (2). Therefore, we do not feel that meaningful coefficients can be obtained in this way from our experimental data. Nevertheless, we can estimate the minimum number of terms needed in (3-122) to explain the observed angular distribution. We simply determine the minimum even value of N for which the least-squares fit (according to (3-133)) lies within the range of error in the data. The minimum number of terms this requires in (3-122) is $\frac{N}{2} + 1$.

II. Recently, Hooper, et. al.⁽⁹³⁾ have been successful in fitting the observed low-energy elastic differential scattering cross sections of several rare gases to an expansion of the type (3-111) with c_ℓ given by (3-112). Their neglect of the imaginary part of η_ℓ (equation (3-119)) was justifiable since the electron impact energies were below the lowest inelastic threshold. Even though the extension of their method into the realm of inelastic scattering doubles the number of unknowns for the same maximum value of ℓ , it was felt that a consistent set of coefficients might be obtained

TABLE 3.4-2

Least squares fit of "data" from test case (2). Refer to the legend of table 3.4-1.

	x_0	x_1	x_2	x_3	x_4	x_5	x_6	RMS
	.5550	.3330	.1110	0.0	0.0	0.0	0.0	
	F'_0	F'_1	F'_2	F'_3	F'_4	F'_5	F'_6	
3	.5687	.2805	.1402	-	-	-	-	.025
5	4.697	-9.029	8.636	-4.376	1.079	-	-	.021
7	12.26	-35.24	53.60	-53.38	35.30	-14.34	2.811	.020

(i. e., the expansion (3-127) might converge).

The method, as outlined below, is based on the expansion of F_p (equations (3-127), (3-128)) in a Taylor series about some initial "guesses" for the a_ℓ 's and b_m 's (denote these by a_ℓ^0 and b_m^0).

$$F_p \cong F_p^0 + \sum_{\ell=1}^N \left(\frac{\partial F_p}{\partial a_\ell} \right)_0 \Delta a_\ell + \sum_{m=1}^N \left(\frac{\partial F_p}{\partial b_m} \right)_0 \Delta b_m \quad (3-135)$$

where F_p^0 is F_p (equation (3-128)) evaluated at a_ℓ^0 , b_m^0 ; $(\)_0$ represents the derivative evaluated at a_ℓ^0 , b_m^0 ; and $N+1$ is the number of terms to be included in the expansion (3-127). Note that

$$\left(\frac{\partial F_p}{\partial a_\ell} \right)_0 = 2 \sum_{m=0}^N a_m D_{m\ell}^p \cos(b_\ell - b_m) \quad (3-136a)$$

and

$$\left(\frac{\partial F_p}{\partial b_\ell} \right)_0 = 2 \sum_{m=0}^N a_m a_\ell D_{m\ell}^p \sin(b_m - b_\ell) \quad (3-136b)$$

F_p (as given by 3-135) is substituted into (3-131) and γ is minimized with respect to variations in C and the Δa_ℓ 's and Δb_m 's (except, of course for $\ell = m = 0$ for which $a_0 = 1$ and $b_0 = 0$).

The best initial C (labelled C_0) is determined from the requirement that

$$\frac{\partial \gamma}{\partial C} = 0 \text{ for } \Delta a_\ell = \Delta b_\ell = 0 \text{ for } \ell = 1, \dots, N. \text{ It can be}$$

shown in a straightforward way that

$$C_0 = \frac{\tilde{F}^{0T} \mathbf{I}^p \mathbf{I}^E \tilde{g}}{\tilde{F}^{0T} \mathbf{I}^p \mathbf{I}^E \mathbf{I}^{pT} \tilde{F}^0} \quad (3-137)$$

where the matrix definitions are the same as before and $\tilde{F}^0$ is a column vector of elements F_p^0 .

This value of C_0 is substituted back into equation (3-131) and the Δa_ℓ 's and Δb_ℓ 's are determined from the requirements that

$$\left(\frac{\partial \gamma}{\partial \Delta a_\ell}\right) = 0; \quad \left(\frac{\partial \gamma}{\partial \Delta b_\ell}\right) = 0 \quad \text{for } \ell = 1, \dots, N.$$

Again, after a little matrix algebra, we obtain

$$\begin{aligned} \Delta \tilde{x} = & (IF^{0T} IP IE IP^T IF^0)^{-1} \left\{ \frac{1}{C_0} IF^{0T} IP IE g \right. \\ & \left. - IF^{0T} IP IE IP^T \tilde{F}^0 \right\}. \end{aligned} \quad (3-138)$$

where $\Delta \tilde{x}$ is a column vector with $2N$ elements $(\Delta a_1, \dots, \Delta a_N, \Delta b_1, \dots, \Delta b_N)$ and IF^0 is a matrix in which

$$(IF^0)_{ij} = \left(\frac{\partial F_i}{\partial \Delta x_j} \right)_0.$$

The solution $\Delta \tilde{x}$ of (3-138) is used to correct the initial values a_ℓ^0, b_ℓ^0 as

$$a_\ell(\text{new}) = a_\ell^0(\text{initial}) + \Delta a_\ell$$

and

$$b_\ell(\text{new}) = b_\ell^0(\text{initial}) + \Delta b_\ell.$$

These improved values are substituted back into equation (3-135) and the entire procedure is repeated. Thus, by successive iterations, the required a_ℓ 's and b_ℓ 's can in principle be determined from the data.

The method was first applied to a set of test "data" similar to that of test case (1) mentioned previously. In this case, however, the values of a_ℓ and b_ℓ , as determined by successive iterations of equations (3-137) and (3-138), would not converge very rapidly to the "true" values even for initial guesses which were within 1/100 of these values. Table 3.4-3 summarizes one such test case. If the initial "guess" was not within about 1/10 of the correct value, the method would not converge at all. These initial attempts were discouraging enough to forestall the further application of this method.

TABLE 3.4-3

Iterative least-squares determination of the a_ℓ 's and b_ℓ 's from initial "guesses" a_ℓ^0 , b_ℓ^0 . a_0 and b_0 are not varied, as discussed in the text. The value of a_ℓ (b_ℓ) obtained after the n^{th} iteration is labelled a_ℓ^n (b_ℓ^n). The "true" values are labelled a_ℓ^T (b_ℓ^T). RMS is defined in the legend of table 3.4-1.

n	a_1^n	b_1^n	RMS
0	.8710	.5010	
1	.8730	.4928	.00026
2	.8730	.4927	.00026
9	.8729	.4929	.00025
$a_1^T = .8700$		$b_1^T = .5000$	

4. EXPERIMENTAL

4.1 Design

4.1.1. Electron Energy Analyzer

4.1.1.1 General considerations

It is essential to the aim of these experiments to distinguish between electrons that have scattered after causing molecular excitations to an energy level W_n from those causing excitations to another level W_m (n and m represent the set of quantum numbers which identifies a molecular state). Since the scattered electrons are identical except for their energy, one must provide an incident beam of kinetic energy $E_0 \pm \Delta E/2$ and must resolve the energy of the scattered beam to within $\pm \Delta E/2$ where

$$\Delta E \lesssim |W_n - W_m| \quad (4-1)$$

in order to distinguish the two excitations.

The energy distribution of electrons emitted from a thermionic cathode is given approximately by the Boltzmann equation (see section 4.4.1),

$$I(E, T) = \frac{I_0(T)}{(kT)^2} E e^{-E/kT} \quad (4-2)$$

in which $I(E, T)$ is the current carried by electrons with kinetic energy E per unit energy, $I_0(T)$ is the total current at cathode temperature T , and k is the Boltzmann constant. The full-width at half-maximum (FWHM) $\Delta E_{\frac{1}{2}}$ of this distribution is $2.54 kT$. The maximum current that can be drawn from a cathode of area A and

work function ϕ_W is given by the well known Richardson-Dushman equation^(94a),

$$I_{\text{MAX}}(T) \approx 120 \text{ A T}^2 e^{-(\phi_W/kT)} \quad (4-3)$$

If T is lowered in order to decrease $\Delta E_{\frac{1}{2}}$, the maximum available current $I_{\text{MAX}}(T)$ falls faster than exponentially. Even with low work function oxide coated cathodes ($\phi_W \approx 1$ to 2 eV) the lower temperature limit for suitable currents is approximately 1000°K , for which $\Delta E_{\frac{1}{2}} = 0.22$ eV. While electronic energy level spacings in molecules are of the order of 1 to 10 eV, vibrational spacings are $\sim .01$ to 0.1 eV and rotational spacings are ~ 0.001 to 0.0001 eV. Consequently, to resolve higher electronic states and vibrational states, some sort of electron energy analyzer is required to provide an incident beam of sufficiently narrow energy spread and to determine the energy of the scattered electrons.

Although any device whose transmission varies with electron energy can in principle be used as an analyzer, the most common arrangement is to use an electric and/or magnetic field configuration so that the electron trajectory through the system is a function of energy. Systems which have been successfully employed include those based on uniform magnetic fields⁽⁹⁵⁾; crossed electric and magnetic fields^(96,97); and electrostatic fields between parallel plates⁽⁹⁸⁾, coaxial cylinders^(9,99,100,101), and concentric hemispheres^(21,24). Our choice of the last type of analyzer resulted from several considerations. First, magnetic fields, which are

difficult to effectively shield from other parts of the apparatus, are not required; second, the hemispherical analyzer focuses in two directions so that axially symmetric lens systems can be used for beam propagation and control; and third, it is easy to construct, simple to operate, and has given satisfactory performance in other laboratories^(24,25).

4.1.1.2. Hemispherical electrostatic energy analyzer

4.1.1.2.1. Trajectory equations

Although Purcell⁽¹⁰²⁾ has described the spherical sector analyzer, it is necessary to carry out a more detailed analysis for our present application. The analyzer system is shown in Figure 4.1-1. The field matching elements, denoted as Herzog numbers 1 and 2, are equipotential with the center of the gap between the concentric outer and inner hemispheres of radii R_2 and R_1 , respectively. The potential field $V(R, \theta, \varphi)$ in the space between the spheres can be determined by solving Laplace's equation,

$$\nabla^2 V(R, \theta, \varphi) = 0, \quad (4-4)$$

with the boundary conditions

$$V(R_0, \theta, \varphi) = V_0, \quad (4-5)$$

$$V(R_1, \theta, \varphi) - V(R_2, \theta, \varphi) = \Delta V$$

in which $R_0 = (R_1 + R_2)/2$, V_0 is the Herzog potential, and ΔV is the potential difference between the spheres. Equation (4-4) can be easily solved to yield

Figure 4.1-1. Diagram of the analyzer system and the coordinate system chosen for the derivation of section 4.1.1.2. The symbols are defined in the text.

$$V(R_1, \theta, \phi) = V(R) = G \Delta V (1/R - 1/R_0) + V_0 \quad (4-6)$$

where

$$G = R_1 R_2 / (R_2 - R_1).$$

Note from (4-6) that the potentials of the inner and outer sphere with respect to the Herzogs are $R_2 \Delta V / (R_2 + R_1)$ and $-R_1 \Delta V / (R_2 + R_1)$, respectively. Consequently, the dividing resistors in figure 4.1-1 must obey the relation

$$\Omega_1 / \Omega_0 = R_2 / R_1 \quad (4-7)$$

In the absence of "fringe-field" effects, space charge, and magnetic or extraneous electric fields, the electron-optical properties of this analyzer can be derived from the trajectory of an electron subject to $V(R)$. The Lagrangian equations of motion for an electron between the spheres are

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{X}_i} \right) = \frac{\partial L}{\partial X_i} \quad (4-8)$$

where $X_i = R, \theta, \text{ or } \phi$

$$\dot{X}_i = \frac{dX_i}{dt}$$

$$L = \left(\frac{m}{2} \right) [\dot{R}^2 + (R\dot{\theta})^2 + (R\dot{\phi} \sin \theta)^2] + qV(R),$$

m = electron mass ,

q = absolute value of electron charge.

Consider an electron of initial velocity v_i' coming from Herzog 1 and entering the gap between the spheres at a point P_i whose distance

from their center O is R_i . In crossing the boundary between Herzog 1 and the spheres, the electron velocity will in general change, both in magnitude and direction, to $\underline{v}_i$ at time $t = 0$. Let us choose a coordinate system centered on O with the z axis containing P_i and the yz plane containing $\underline{v}_i$. Then, if

$$\underline{v}_i = \hat{j} v_{iy} + \hat{k} v_{iz}$$

(where $\hat{j}$ and $\hat{k}$ are the unit vectors in the O_y and O_z directions, respectively), the six initial conditions required to solve (4-8) are

$$\begin{aligned} R(t=0) &= R_i & \dot{R}(t=0) &= v_{iz} \\ \theta(t=0) &= 0 & \dot{\theta}(t=0) &= v_{iy}/R_i \\ \varphi(t=0) &= \pi/2 & \dot{\varphi}(t=0) &= 0 \end{aligned} \quad (4-9)$$

φ - equation

With $X_i = \varphi$, (4-8) yields

$$\varphi m R^2 \sin^2 \theta = C \quad (4-10)$$

at any time $t \geq 0$ in which C is a time-independent constant (constant of the motion). The initial conditions require $C = 0$, hence, $\varphi m R^2 \sin^2 \theta = 0$ for all $t \geq 0$. Thus,

$$\varphi(t) = 0, \quad (4-11)$$

(i. e. the electron remains in the same φ plane throughout its trajectory).

θ - equation

With $X_i = \theta$, (4-8) and (4-11) yield

$$m R^2 \dot{\theta} = A \quad (4-12)$$

in which A is a time-independent constant. Applying the initial conditions, we find that

$$A = m R_i v_i \cos \alpha \quad (4-13)$$

where $\cos \alpha = v_{iy}/v_i$. α (which we will denote as the entrance angle) is the angle between $\underline{v}_i$ and $\hat{j}$.

 R - equation

With $X_i = R$, (4-8), (4-11), and (4-12) yield

$$\frac{d^2 R}{dt^2} = \frac{2}{m} \frac{R_i^2}{R^3} E_i \cos^2 \alpha - \frac{q}{m} G \frac{\Delta V}{R^2} \quad (4-14)$$

where $E_i = \frac{1}{2} m v_i^2$ is the kinetic energy of the electron just after entering the analyzer at point P_i . The substitution of $R = \frac{1}{U}$ and a change from t to θ as the independent variable gives

$$\frac{d^2 U}{d\theta^2} + U = \frac{q \Delta V G}{2 E_i R_i^2 \cos^2 \alpha} \quad (4-15)$$

After integration and application of the remaining boundary conditions, $R(\theta)$ can be expressed as

$$R(\theta) = R_i \left[\frac{q G \Delta V (1 - \cos \theta)}{2 E_i R_i \cos^2 \alpha} + \cos \theta - \tan \alpha \sin \theta \right]^{-1} \quad (4-16)$$

Note, however, that E_i is a function of R_i . The total electron energy before entering the analyzer is equal to its kinetic energy $E = \frac{1}{2} m(v_i')^2$ plus its potential energy $-qV_0$ in Herzog 1. This total energy is conserved through its trajectory. In particular, the electron's total energy in Herzog 1 is equal to its total energy immediately after entering the analyzer at P_i . Mathematically, this implies

$$E - qV_0 = E_i - qV(R_i) . \quad (4-17)$$

Substitution of E_i in (4-16) by (4-17) with (4-6) yields

$$R(\theta) = R_i \left[\frac{G(1 - \cos \theta)}{2R_i \cos^2 \alpha} \left(\frac{E}{q\Delta V} + \frac{G}{R_i} - \frac{G}{R_0} \right)^{-1} + \cos \theta - \tan \alpha \sin \theta \right]^{-1} . \quad (4-18)$$

ΔV is chosen so that an electron of kinetic energy E_0 in Herzog 1 entering the analyzer so that $R_i = R_0$ and $\alpha = 0$ describes a circular orbit of radius R_0 . Solving (4-18) for $q\Delta V$ under these conditions yields

$$q\Delta V = \frac{2E_0 R_0}{G} . \quad (4-19)$$

Substitution of this result into (4-18) yields

$$R(\theta) = R_i \left[\frac{R_0(1 - \cos \theta)}{2R_i \cos^2 \alpha} \left(\frac{E}{2E_0} + \frac{R_0}{R_i} - 1 \right)^{-1} + \cos \theta - \tan \alpha \sin \theta \right]^{-1} . \quad (4-20)$$

If $R_i = R_0$ and $E = E_0$ in (4-20), we obtain

$$R(\theta) = R_o \left[\frac{1 - \cos \theta \sin^2 \alpha}{\cos^2 \alpha} - \tan \alpha \sin \theta \right]^{-1} \quad (4-21)$$

Since we use a cylindrically symmetric electron beam, α can have a range of values centered on 0. Expanding (4-21) for small α , we obtain

$$R(\theta) = R_o [1 - \alpha \sin \theta + O(\alpha^2)]^{-1} \quad (4-22)$$

Thus, if $\theta = \pi$, $R(\theta = \pi)$ will be independent of the entrance angle α to order α^2 . For this reason, the analyzer is chosen to be hemispherical.

At $\theta = \pi$ the electron leaves the analyzer at a distance $R_f = R(\theta = \pi)$ from the center with an exit angle α' with respect to the negative y axis. R_f and α' are given by

$$R_f = \frac{R_i \cos^2 \alpha [1 - \eta \frac{R_i}{R_o}]}{1 - \cos^2 \alpha [1 - \eta \frac{R_i}{R_o}]} \quad (4-23)$$

and

$$\tan \alpha' = \frac{1}{R} \left(\frac{dR}{d\theta} \right)_{\theta = \pi} = \frac{R_f}{R_i} \tan \alpha \quad (4-24)$$

where $\eta \equiv 1 - E/2E_o$.

Typical electron trajectories calculated from (4-20) are shown in figures 4.1-2, -3, and -4. Note from (4-23) that:

(1) Electrons with the same E and R_i entering with entrance

Figure 4.1-2. Electron trajectories in the yz plane (fig. 4.1-1) according to equation (4-20) for $\alpha = 0^\circ$, $R_0 = 1.00$, and $E = E_0$. The curves are for the indicated values of R_1 .

Figure 4.1-3. Electron trajectories in the yz plane (fig. 4.1-1) according to equation (4-20) for $R_0 = R_1$ and $E = E_0$. The curves are for the indicated values of α .

Figure 4.1-4. Electron trajectories in the yz plane (fig. 4.1-1) according to equation (4-20) for $\alpha = 0$, $E_0 = 2.0$, and $R_1 = R_0$. The curves are for the indicated values of E.

angles of the same absolute value (i. e. , α and $-\alpha$) exit at the same point,

(2) For small α , R_f is independent of α to order α^2 , indicating first order focusing in α ,

(3) Electrons with the same E , R_i , and $|\alpha|$ but which enter the analyzer in different φ planes for which $0 < \varphi < \pi$ will leave the analyzer at the same point R_f (i. e. , focusing occurs in φ as well as in α).

4.1.1.2.2 Electron-optical properties

The electron-optical properties of this analyzer can be obtained from the total differential relation

$$dR_f = \frac{\partial R_f}{\partial R_i} dR_i + \frac{\partial R_f}{\partial E} dE + \frac{\partial R_f}{\partial \alpha} d\alpha \quad (4-25)$$

in which $\frac{\partial R_f}{\partial R_i}$, $\frac{\partial R_f}{\partial E}$, and $\frac{\partial R_f}{\partial \alpha}$ represent the magnification, energy dispersion, and angular aberration, respectively. For small α , (4-23) reduces to

$$R_f = \frac{R_o}{\eta} \left[1 + \alpha^2 \left(1 - \frac{R_o}{\eta R_i} \right) \right] - R_i \quad (4-26)$$

Since the maximum value of α is approximately .07 radians in the present apparatus, this is a relatively good approximation. After carrying out the indicated partial differentiation in (4-25) using (4-26), we obtain

$$\begin{aligned}
\frac{dR_f}{R_o} = & \left[-1 + \frac{\alpha^2 R_o^2}{\eta^2 R_i^2} \right] \frac{dR_i}{R_o} \\
& + \left[\frac{1 + \alpha^2}{2\eta^2} - \frac{\alpha^2 R_o}{\eta^3 R_i} \right] \frac{dE}{E_o} \\
& + \frac{2\alpha}{\eta} \left[1 - \frac{R_o}{\eta R_i} \right] d\alpha .
\end{aligned} \tag{4-27}$$

The change in R_f , ΔR_f , for a finite change in entrance conditions from those for which the hemispheres are tuned ($R_i \rightarrow R_o \pm \Delta R_i/2$, $E \rightarrow E_o \pm \Delta E/2$, $\alpha \rightarrow 0 + \alpha$) is given by the integration of (4-27) over the indicated ranges.

$$\begin{aligned}
\frac{\Delta R_f}{R_o} = & \left[-1 + \frac{\alpha^2}{\eta^2 (1 - \Delta R_i/2R_o)^2} \right] \frac{\Delta R_i}{R_o} \\
& + \left[\frac{2}{1 - (\frac{\Delta E}{2E_o})^2} \right] \left[1 + \alpha^2 + \frac{4\alpha^2 R_o}{R_i [1 - (\frac{\Delta E}{2E_o})^2]} \right] \frac{\Delta E}{E_o} \\
& + \left(\frac{1}{\eta} - \frac{R_o}{R_i \eta^2} \right) \alpha^2 .
\end{aligned} \tag{4-28}$$

An electron beam entering the analyzer with a conical divergence angle equal to α , a diameter of ΔR_i centered at R_o , and a broad range of kinetic energies, will be dispersed so that the portion of the beam of diameter ΔR_f centered at R_o leaving the analyzer will have a maximum energy spread of ΔE as given by relation (4-28). Note that ΔE is not the same as the FWHM $\Delta E_{\frac{1}{2}}$, but is approximately the base width of the transmission line shape. The actual line

shape (and hence $\Delta E_{\frac{1}{2}}$) depends on the energy and geometrical distribution of the beam entering the analyzer as well as the exit electron optics. On the basis of experimental observations, $\Delta E_{\frac{1}{2}} \approx \Delta E/2$ and line shapes are generally Gaussian⁽²⁴⁾. In section 4.1.1.3 a mathematical verification of these observations will be carried out.

Since the experimental conditions require $\Delta R_f/R_o$, $\Delta R_i/R_o$, and α^2 all $\ll 1$, $\Delta E/E_o$ must also be small. Rewriting (4-28) under these conditions and requiring equal entrance and exit apertures, either real or virtual, yields

$$\frac{\Delta E_{\frac{1}{2}}}{E_o} = \frac{\Delta R}{2R_o} + \frac{\alpha^2}{2} \quad (4-29)$$

where $\Delta R = \Delta R_i = \Delta R_f$.

Another property of the analyzer which is of interest is the maximum deviation $r_{\max}$ of the beam from the central trajectory of radius R_o . For small deviations of E , R_i , and α from E_o , R_o , and 0, respectively,

$$r_{\max} \approx |R(\theta = \pi/2) - R_o|. \quad (4-30)$$

Thus, from (4-20) and (4-30) with $E = E_o \pm \Delta E/2$, $R_i = R_o \pm \Delta R/2$, and $\alpha^2 \ll 1$,

$$r_{\max}/R_o = \Delta E/E_o + \sqrt{\alpha^2 + (\Delta R/2R_o + \Delta E/E_o)^2} \quad (4-31)$$

+ higher order terms.

4.1.1.3. Line shape

In order to assess the performance of the analyzer system and interpret the energy-loss spectrum peaks in terms of a DCS, it is important to know the characteristic instrumental line shape. Refer to figure 4.1-5 for the definitions of the coordinates associated with the following derivation. In addition, we define the quantities

$\underline{I_0} \equiv$ the total number of electrons per second entering the analyzer;

$\underline{F(E, R, \phi, \alpha)} \equiv$ the fraction of I_0 entering at the coordinate position (R, ϕ) per unit area with kinetic energy E per unit energy range and an entrance angle α per unit range of α .

E is the kinetic energy of the electrons when they are in Herzog 1 (at potential V_0). F is called the input function;

$\underline{N(K, R', \phi', \alpha')} \equiv$ the number of these electrons per second leaving the analyzer at (R', ϕ') per unit area with kinetic energy K per unit energy range and an exit angle α' per unit range of α' . K is the kinetic energy of the electrons when they are in Herzog 2 (also at potential V_0).

$\underline{i(K)} \equiv$ the total number of electrons per second leaving the analyzer through a particular area with a given range of α' (determined by the electron optics at the exit of the analyzer) and with a kinetic energy K per unit energy range. This is the definition of the line shape function of a single analyzer.

Figure 4.1-5. Front view of the analyzer (xz plane of figure 4.1-1) showing the coordinate definitions used in section 4.1.1.3. The angles ϕ and ϕ' are shown in a positive sense. The other symbols are discussed in the text.

$F(E, R, \varphi, \alpha)$ is normalized so that

$$\int_{E=0}^{\infty} \int_{R=R_1}^{R_2} \int_{\varphi=-\pi/2}^{\pi/2} \int_{\alpha=-\pi/2}^{\pi/2} F(E, R, \varphi, \alpha) R dE dR d\varphi d\alpha = 1. \quad (4-32)$$

An electron entering the analyzer at (R, φ) with kinetic energy E and a small entrance angle α will exit at (R', φ') with kinetic energy K and exit angle α' if and only if:

- (1) $R = R(R', E, \alpha)$ in which R is given by (4-26) ($R \equiv R_i$, $R' \equiv R_f$),
- (2) $E = K$ (conservation of energy),
- (3) $\varphi = \varphi'$ (consequence of (4-11)),
- (4) $\alpha = R\alpha' / R'$ (small α approximation to (4-24)).

From these conditions, it follows directly that

$$\begin{aligned} & N(K, R', \varphi', \alpha') \\ = & \int_{E=0}^{\infty} \int_{R=R_1}^{R_2} \int_{\varphi=-\pi/2}^{\pi/2} \int_{\alpha=-\pi/2}^{\pi/2} \{ I_0 F(E, R, \varphi, \alpha) \\ & \times \delta[E - K] \frac{\delta[R - R(R', E, \alpha)]}{R} \delta[\varphi - \varphi'] \delta[\alpha - \frac{R}{R'} \alpha'] \} R dE dR d\varphi d\alpha. \end{aligned} \quad (4-33)$$

Performing the E, φ , and α integrals leaves a delta function in the integrand of the form $\delta[R - R(R', K, R\alpha' / R')]$. This function is converted to $\delta[R - R(R', K, \alpha')]$ by solving the equation $R = R(R', K, R\alpha' / R')$ for R . After performing the final R integral one obtains

$$N(K, R', \phi', \alpha') = I_0 F(K; R(R', K, \alpha'); \phi', \frac{R(R', K, \alpha')}{R'} \alpha') \quad (4-34)$$

from (4-33). Then, the line shape function is

$$i(K) = \int_{R' = R'_{\min}}^{R'_{\max}} \int_{\phi' = \phi'_{\min}}^{\phi'_{\max}} \int_{\alpha' = \alpha'_{\min}}^{\alpha'_{\max}} N(K, R', \phi', \alpha') R' dR' d\phi' d\alpha' \quad (4-35)$$

in which the integrations are carried out over the range of beam angles (α') and area (R', ϕ') sampled by the exit electron optics. If the input function F were known, it would be a straightforward, albeit tedious, exercise to calculate $i(K)$. In order to arrive at an approximate expression for $i(K)$ that will be applicable to the present case, we will consider the following input function describing the initial electron beam (beam leaving the electron gun and entering the monochromator):

$$F(E, R, \phi, \alpha) = A f(E) g(R, \phi) \delta(\alpha) \quad (4-36)$$

in which (1) $\alpha = 0$ for all electrons (parallel beam),

$$(2) \quad f(E) = \begin{cases} \left(\frac{E-V}{kT} \right) \exp [- (E-V)/kT] & E \geq V \\ 0 & E < V \end{cases},$$

(T is the cathode temperature and k is Boltzmann's constant),

$$(3) \quad g(R, \varphi) = \begin{cases} e^{-(R-R_0)^2/a^2} e^{-R_0^2 \varphi^2/a^2} & R_1 < R < R_2 \\ & -\pi/2 < \varphi < \pi/2 \\ 0 & \text{otherwise} \end{cases}$$

$$(4) \quad A \cong \frac{2}{a \pi (kT)^2}$$

$f(E)$ represents the expected kinetic energy distribution of the electrons in Herzog 1 due to a Boltzmann distribution of energies from a thermionic cathode after acceleration by V . The peak of $f(E)$ occurs at $E' = V + kT$. We shall assume that the analyzer is "tuned" so that E_0 (of equation (4-19) and following) equals E' .

$g(R, \varphi)$ is the geometrical beam distribution peaked at R_0 and $\varphi = 0$. "a" characterizes the entrance beam diameter. We actually expect the incoming beam to be cylindrically symmetric, which $g(R, \varphi)$ is not. A symmetric distribution could be of the form,

$$\exp \left\{ - [R_0^2 + R^2 - 2RR_0 \cos \varphi] / a^2 \right\}$$

But, for small values of φ this becomes

$$\exp \left[- (R - R_0)^2 / a^2 \right] \exp \left[- RR_0 \varphi^2 / a^2 \right] \quad (4-37)$$

Since the real beam is relatively narrow, an accurate mathematical representation would require that the characteristic beam radius "a" be much smaller than R_0 . Only values of R in the region $R_0 \pm a$,

for which $RR_0/a^2 \approx R_0^2/a^2$, will contribute significantly to the integral over $g(R, \phi)$.

A is simply the normalization constant required by (4-32).

It has also been assumed that the incoming beam exhibits no correlation between its kinetic energy and geometry. This is not strictly true since the focal properties of the lenses used to form the beam are energy dependent. These approximations are quite good compared to the more fundamental assumption that all electrons obey the trajectory equation (4-20) (negligible "fringe-fields", space charge, and magnetic or electric disturbances).

From (4-26) and the preceding conditions, one obtains

$$R = R_0/(1 - K/2E_0) - R' = R(R', K, \alpha'). \quad (4-38)$$

We obtain the line shape function $i(K)$ from (4-34), (4-35), (4-36), and (4-38).

$$i(K) = C f(K) X(K) \quad (4-39)$$

in which the ranges of integration for (4-35) were chosen to be

$R'_{\min} = R_0 - b$, $R'_{\max} = R_0 + b$, $\phi'_{\min} = -\beta$, and $\phi'_{\max} = +\beta$. (b and β define the area of the beam collected by the exit electron optics.)

C is given by

$$C = \frac{I_0}{KT} \operatorname{erf} \left(\frac{R_0 \beta}{a} \right)$$

and $X(K)$ by

$$X(K) = \frac{\sqrt{\pi} (K/2E_0)}{(1 - K/2E_0)} [\operatorname{erf} \epsilon_+ - \operatorname{erf} \epsilon_-]$$

$$+ \frac{a}{R_o} [e^{-\epsilon_+^2} - e^{-\epsilon_-^2}]$$

where

$$\epsilon_{\pm} = \frac{R_o(K/E_o - 1)}{a(1 - K/2E_o)} \pm \frac{b}{a}$$

and

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

In the present system the electron beam diameter entering the analyzer (characterized by "a") and that collected by the exit optics (characterized by "b") are nearly the same ($a/b \sim 1$). Also R_o is about 100 times the beam diameter (i. e. , $R_o/a \sim 10^2$). Equation (4-39) can be simplified somewhat under these conditions if we consider only the "tails" of the $i(K)$ distribution. If $K \geq 1.02 E_o$ (note that $i(K)$ peaks at $K = E_o$), (4-39) can be written to a good approximation as

$$i(K) \cong C G_-(K) e^{-\left\{ \frac{[K - E_o(1 + b/2R_o)]^2}{(aE_o/2R_o)^2} \right\}} \quad (4-40)$$

which for $K \leq 0.98 E_o$

$$i(K) \cong C G_+(K) e^{-\left\{ \frac{[K - E_o(1 + b/2R_o)]^2}{(aE_o/2R_o)^2} \right\}} \quad (4-41)$$

where

$$G_{\pm}(K) = f(K) \left[\frac{(1/\epsilon_{\pm}^3 - 1/\epsilon_{\pm})}{(1 - 2E_o/K)} - \frac{a}{R_o} \right]$$

The behavior of $i(K)$ is dominated by the exponential in these regions, and as a consequence, $i(K)$ "tails" off approximately as a Gaussian with a FWHM of $\Delta K_{\frac{1}{2}} \approx aE_0\sqrt{\ell n2}/R_0$. If ΔR is the geometrical FWHM of the incident beam, $\Delta R = 2a\sqrt{\ell n2}$ and

$$\frac{\Delta E_{\frac{1}{2}}}{E_0} \cong \frac{\Delta R}{2R_0} \quad , \quad (4-42)$$

which is identical to (4-29) with $\alpha = 0$.

A comparison of the line shape calculated according to (4-39) with a Gaussian and the experimental peak shape is given in section 4.4.5.3.

4.1.1.4. Resolution

Since the energy-loss spectra obtained from the spectrometer are to be interpreted in terms of relative differential scattering cross sections, it is extremely important to assess the effects of the finite resolving power of the analyzer on these spectra.

Consider a simple target "atom" with two electronic excited states of energies $E_b > E_a$ above the ground state. It is assumed that the inherent energy width of these states is much smaller than any achievable resolution in the present instrument. Let the electron beam striking the target have a Gaussian energy distribution centered at $E_0 > E_a$ or E_b and a FWHM of $\Delta E_{\frac{1}{2}}^m$. After scattering and passing through the selector with a FWHM of $\Delta E_{\frac{1}{2}}^s$, the electron beam will produce a signal I at the detector which is a function of the energy-loss E . If we assume the analyzer

has a Gaussian line shape (see section 4.1.1.3), then the observed spectrum will be a superposition of Gaussians, centered at 0, E_a , and E_b , with FWHM which are determined by the resolution of the analyzers. The detected signal at each energy-loss can then be represented mathematically as

$$I(E) = \frac{I_0}{D\sqrt{\pi}} \left\{ f_e e^{-E^2/D^2} + f_a e^{-(E-E_a)^2/D^2} + f_b e^{-(E-E_b)^2/D^2} \right\} \quad (4-43)$$

$D^2 = \frac{(\Delta E_{\frac{1}{2}}^s)^2 + (\Delta E_{\frac{1}{2}}^m)^2}{4 \ln 2}$; I_0 is the total electron current reaching the detector; and f_e , f_a , and f_b are the fractions of I_0 scattered elastically and inelastically leaving the "atom" in states E_a and E_b , respectively. Suppose that $E_b - E_a = W$ and that E_a^2/D^2 is so large that there is no significant overlap of the elastic peak with the inelastic ones. That portion of the energy-loss spectrum in which we are interested can be represented by an equation of the form

$$I(E) = C \left\{ f_a \exp\left(-\frac{E^2}{D^2}\right) + f_b \exp\left[-\frac{(E-W)^2}{D^2}\right] \right\} \quad (4-44)$$

in which the elastic peak has been neglected, E_a has been taken as the energy-loss origin, and C is an energy-loss independent constant.

The slope of (4-44) is given by

$$S(E) = -\frac{2C}{D^2} [f_a e^{-E^2/D^2} + f_b (E - W) e^{-(E - W)^2/D^2}] \quad (4-45)$$

If the two peaks (at energy-losses E_a and E_b) are resolved, $S(E)$ will have three distinct zeros in the range $0 \leq E \leq W$ given by the transcendental equation

$$x e^{-2a^2 x} = (1 - x) \frac{f_b}{f_a} e^{-a^2} \quad (4-46)$$

in which $x = \frac{E}{W}$ and $a = \frac{W}{D}$.

A careful analysis of relation (4-46) reveals the following:

(1) If $W^2 < 2D^2$, then the peaks will not be resolved (i. e., only two zeros in equation (4-45)) regardless of the value of $\frac{f_b}{f_a}$. We assume $W^2 > 2D^2$ for the remainder of this discussion.

(2) If

$$\frac{f_b}{f_a} < \frac{1 + p}{1 - p} e^{-W^2 p/D^2} \quad (4-47)$$

where $p = (1 - \frac{2D^2}{W^2})^{\frac{1}{2}}$, the smaller feature is buried under the tail of the larger one.

(3) The range of parameters (f_a, f_b, D , and W) for which the spectrum is considered resolved (i. e., three zeros in $S(E)$) is given by the inequality

$$\frac{1 + p}{1 - p} e^{-W^2 p/D^2} < \frac{f_b}{f_a} < \frac{1 - p}{1 + p} e^{W^2 p/D^2} \quad (4-48)$$

As a specific example, we shall consider the problem of resolving the transitions from the ground 1^1S state of helium to

the 3^1S (state a) and 3^1P (state b) ones at an incident energy of 35 eV and a 25° scattering angle. From the data of section 5.2 (figure 5.2-1 in particular) we note that $f_b/f_a \cong 5.5$ and $W = 0.16$ eV (we will ignore the effect of the underlying $1^1S \rightarrow 3^3P$ transition). Then, (4-48) implies that the maximum allowable $\Delta E_{\frac{1}{2}} \approx 0.11$ eV which is approximately the case in this example (figure 5.2-1). State a will be shifted in apparent energy-loss by ≈ 0.01 eV due to the overlap with state b, while b will be shifted only by $\approx .001$ eV. The peak height of a will be increased by $\sim 5\%$ due to b while the increase of b is completely negligible.

4.1.2. Electron-Optics

4.1.2.1. First stage electron-optics

4.1.2.1.1. General requirements

The design criteria for an electron gun to generate the electron beam and for the optics to transport the beam through the monochromator and into the scattering chamber are obtained by specifying the required beam conditions at the scattering chamber entrance. In turn, the optimum entrance or "incident beam" conditions are determined by the nature of the present experimental investigation.

There are five parameters which appropriately characterize the incident beam--kinetic energy, energy spread, angular divergence, diameter, and intensity. Unfortunately, they are not independently adjustable, and the final result will be a compromise

between two basically incompatible requirements at fixed energy-- high current density and low angular divergence.

The electron beam kinetic energy and FWHM are to be ~ 30 eV and $\sim .03$ eV, respectively. An incident energy of 30 eV is chosen since it is within a few tens of eV's of the excitation threshold for most atomic and molecular electronically excited states. This is just the energy region in which forbidden transitions are most likely to occur (recall the discussions in section 3.). The FWHM of .03 eV is desired so that we may readily resolve vibrational structure in electronic transitions.

Since we wish to measure differential scattering cross sections, which are functions of the angle between the incident and scattered beam, the incident beam must have a relatively well defined direction. It need not be as narrow in this case as experiments at higher (> 100 eV) impact energy require since low energy differential cross sections are not peaked so sharply in the forward ($\theta = 0^\circ$) direction^(6d). An angular divergence (incident beam cone angle) of $\sim .03$ radians and diameter of ~ 0.5 mm are assumed as reasonable values since this choice can provide an angular resolution of about 2° . Finally, the optimum beam intensity is the highest value compatible with the four other restrictions.

4.1.2.1.2. Monochromator

Since the monochromator is the current-limiting element in this case, we consider its optimal parameters first. $\Delta E_{\frac{1}{2}}$ has already been specified. Assume that the size of the monochromator (R_O) has also been fixed. Then, the electron kinetic energy in the analyzer for maximum current is determined to a certain extent by space charge^(103a).

The space-charge-limited current I_S which can be transmitted through a cylindrical volume defined by two apertures of diameter d separated by a length ℓ is ^(104a)

$$I_S = K E^{3/2} (d/\ell)^2 \mu A , \quad (4-49)$$

in which E is the electron kinetic energy in eV and $K = 38.5$. The beam must be launched so that in the absence of space charge it would focus to a point at the center of the volume. Figure 4.1-2 shows an example of this type of focus for the present analyzer. If that portion of the analyzer in which the beam is confined is treated as a volume of diameter ΔR and length $\ell = \pi R_O$, then from (4-49) the space-charge-limited current which can be transmitted by the analyzer is

$$I_S = (K/\pi^2) E^{3/2} (\Delta R/R_O)^2 . \quad (4-50)$$

α of the relation (4-29) should equal 0 to satisfy the launching condition. Then (4-29) becomes

$$\frac{\Delta E_{\frac{1}{2}}}{E} = \frac{\Delta R}{2R_0} \quad (4-51)$$

Combining (4-50) and (4-51) yields

$$I_s \approx \frac{4K}{\pi} \frac{(\Delta E_{\frac{1}{2}})^2}{\sqrt{E}} \quad (4-52)$$

(4-52) indicates that the greatest space charge limited current can be obtained at the lowest mean kinetic energy (E).

This oversimplified model ignores some of the internal focusing of the monochromator. A significantly more sophisticated point of view has been taken recently by Kuyatt and Simpson⁽²⁵⁾. In this approach, space charge spreading is considered to be the result of a negative lens in the vicinity of the minimum beam cross section, i. e. , at the exit focal plane of the analyzer. After space charge spreading, the electron beam appears to come from a source smaller than the actual minimum beam diameter. Acceleration of the beam reduces the degree of space charge and allows one to obtain a real image of the apparently small source. As a result, the "effective" aperture size (ΔR) and angular spread (α) can be chosen independently⁽²⁵⁾. (4-49) can be rewritten in terms of the beam angle $\alpha = d/\ell$ as

$$I_s = K E^{3/2} \alpha^2 \quad (4-53)$$

The maximum allowable α^2 is determined from (4-29) and is proportional to $\Delta E_{\frac{1}{2}}/E$. If $\alpha^2 = C \Delta E_{\frac{1}{2}}/E$, then

$$I_S = KC E^{\frac{1}{2}} \Delta E_{\frac{1}{2}}. \quad (4-54)$$

(4-54) differs from (4-52) in one very significant way--increasing the mean kinetic energy in the monochromator should increase the space charge limited current. Note, however, that to maintain constant resolution with increasing E , ΔR and α must decrease. For a fixed analyzer size (R_0), and resolution ($\Delta E_{\frac{1}{2}}$), the required aperture size (ΔR) to satisfy (4-29) varies inversely with the first power of the electron kinetic energy. However, the susceptibility of the electron beam to stray magnetic fields drops off only as the inverse one-half power of the energy (refer to section 4.1.3.2.). As a result, at higher analyzing energies, the effect of magnetic disturbances becomes more severe.

In studying this space charge lens⁽²⁵⁾ model, it was found that an empirically determined anomalous energy spread factor limited the analyzer performance. Dense electron beams exhibit energy widths which are current dependent and much greater than those characterized by the cathode temperature⁽²⁵⁾. Consequently, an optimum monochromator design must take into consideration this new factor. Since its dependence on analyzer or electron-optics geometry is not known, an "a priori" monochromator design is not possible.

Aside from these maximum current considerations, (4-29) can be used to obtain approximate design parameters. An empirical adjustment of voltages and lens elements can then be used to optimize the analyzer performance.

If ΔR is on the order of 0.05 cm and $\Delta E_{\frac{1}{2}} \sim .03$ eV, (4-29) requires

$$E_0 \sim R_0 \quad (4-55)$$

for E_0 in eV, R_0 in cm and provided that

$$\alpha^2 \ll (\Delta R / 2R_0). \quad (4-56)$$

The choice of R_0 (or E_0) is still arbitrary. We have chosen $R_0 = 2.5$ cm primarily because the apparatus is then reasonably compact, adequate magnetic field compensation (section 4.3.2.) is more easily obtained, and analyzers of this same dimension have been successfully employed elsewhere^(24,25). With this choice of R_0 , (4-55) requires $E_0 \sim 2.5$ eV.

4.1.2.1.3. Lens system

Since the electron kinetic energy E_s at the scattering chamber is to be ~ 30 eV while E_0 (the kinetic energy in the analyzer) is only ~ 2 to 3 eV, some sort of accelerating lens system is required to image the exit plane of the monochromator onto the physical aperture at the scattering chamber entrance. In this way, the low-energy electrons leaving the analyzer do not pass through any physical apertures until they have been accelerated to a much higher energy. It is believed that this will eliminate aperture scattering effects and secondary electron production at the focal planes of the analyzer. Double-aperture lenses described by Spangenberg⁽¹⁰⁵⁾ are used for this purpose because of their ease of construction and operation.

Let P be the object distance; Q the image distance; A and D the aperture separation and diameter, respectively; R_a the acceleration ratio ($R_a = E_s/E_o$); and M the magnification. We choose $M = 1$, $A/D = 1$, and require $R_a \approx 10$. This implies⁽¹⁰⁵⁾ That $P/A = Q/A = 4.4$. With A taken to be 3.2 mm, $P = Q = 14.1$ mm. The choice of A is predicated upon two considerations:

(1) the lens should be reasonably short but (2) not narrow enough to intercept any appreciable portion of the beam.

As a consequence of accelerating the beam, α_s , the beam half-angle at the scattering chamber, will differ from α , the beam half-angle at the monochromator. The beam angles and energies at these image-object planes are related by the Abbe-Helmholtz sine law⁽¹⁰⁶⁾

$$E_s^{\frac{1}{2}} \sin \alpha_s = M E_o^{\frac{1}{2}} \sin \alpha, \quad (4-57)$$

in which M is the Gaussian magnification. Substituting the appropriate values that have been previously determined, we find that the maximum allowable α is 0.1 radians.

Two pairs of parallel plate electrostatic deflectors were installed at the entrance to the scattering chamber to aid in "threading" the beam through this aperture.

4.1.2.1.4. Electron gun

It has been pointed out⁽¹⁰⁶⁾ that for unipotential electron guns (a cathode-anode structure with a single accelerating potential)

of axial symmetry derived from space charge limited diodes there exist both a minimum voltage and maximum width-to-length ratio γ of the space that can be saturated with electrons. If a unipotential gun is to be used for this research, it must operate at ~ 2 to 3 eV (since this is the mean electron kinetic energy required in the analyzer) and saturate a space approximately defined by $\gamma = \alpha = 6^\circ$ (since this is the maximum desired beam divergence at the analyzer). From reference (106) it is apparent that this cannot be done. This limitation can be circumvented⁽¹⁰⁷⁾ by using a two-stage gun in which an extraction stage, based upon the immersion objective of Soa⁽¹⁰⁸⁾ and operated at a higher voltage to overcome space charge at the cathode, is followed by a deceleration stage based on the double-aperture lenses characterized by Spangenberg⁽¹⁰⁵⁾. The design of this type of gun has been thoroughly discussed in reference (107), and we have followed the procedure outlined there.

The gun should saturate with electrons a space defined by an angle of $\sim 6^\circ$ with a beam energy of ~ 2.5 eV and a diameter of $\sim .05$ cm (conditions on the beam at the entrance of the monochromator). From (4-53) the space charge limited current is found to be $\sim 1.5 \mu\text{A}$. The maximum achievable current density J_{max} in an electron beam at energy E with respect to the cathode is related to the current density J_{cathode} at the cathode by the Langmuir equation^(104b, 109)

$$J_{\text{max}}/J_{\text{cathode}} = (1 + 11,600 E/T) \sin^2 \gamma \quad (4-58)$$

for E in eV and T in $^{\circ}\text{K}$. In this case $J_{\text{max}} \approx 10^3 \mu\text{A}/\text{cm}^2$, and as a result J_{cathode} must exceed $3 \times 10^3 \mu\text{A}/\text{cm}^2$ for a cathode temperature of 1160°K . This value of the cathode loading is well within the capabilities of most cathode materials^(103b).

The required perveance ($I/V^{3/2}$) is $\sim .009 \mu\text{A}/\text{V}^{3/2}$ for an extraction voltage of 30 V. The extraction stage is followed by a 10:1 deceleration stage identical in design to the double-aperture lens system described in section 4.1.2.1.3.

From the design graph of reference (107) this value of the perveance requires M_G (magnification of the gun) to be ~ 2 .

Q/d_k can be estimated by extrapolation to be ~ 22 . (Q is the anode-gun image distance; d_k is the cathode-grid distance.) A grid bias ($V_{\text{grid}}/V_{\text{anode}}$) of $\sim .023$ is also necessary according to reference (107). Since the diameter of the emitting area of the cathode is approximately $1/2$ the grid bore D_q , the final image size at the analyzer ΔR , is given by the relation

$$\Delta R = 1/2 D_q M_G \quad (4-59)$$

With $\Delta R = .05 \text{ cm}$ and $M_G = 2$, we obtain $D_q = .05 \text{ cm}$. Once D_q has been determined, all other spacings in the Soa gun are fixed⁽¹⁰⁷⁾.

Two pairs of electrostatic deflectors have been incorporated into the gun structure to facilitate the correction of any misalignment in the beam.

4.1.2.2. Second stage electron optics

4.1.2.2.1. General requirements

The second half of the spectrometer is devoted to collecting a certain fraction of those electrons which have been scattered by an angle θ with respect to the incident beam and to determining the current of such electrons which have lost a specified amount of their initial kinetic energy as a result of the scattering process. The electron beam entering the second stage has an energy distribution consisting approximately of a superposition of Gaussian functions (refer to section 4.1.1.4.), each peaked at an energy $E_0 - W_n$, where E_0 is the initial beam kinetic energy and W_n is the excitation energy of a particular molecular transition. The FWHM of these peaks is determined by the monochromator and consequently the second stage energy analyzer (selector) should be chosen to have an intrinsic FWHM approximately equal to that of the monochromator. Further, this beam is usually of very low intensity ($\sim 10^{-14}$ A) compared to the beam leaving the gun ($\sim 10^{-6}$ A). Finally, since we are to determine differential scattering cross sections, the collected beam should have a suitably small angular divergence (approximately the same as that of the incident beam).

4.1.2.2.2. Selector

Space charge effects can be neglected due to the low current densities in the selector. Otherwise, the same considerations that were pertinent to the monochromator are applicable to the selector. The latter was chosen to be identical in construction to the mono-

chromator primarily to simplify the operation and preserve the symmetry of the apparatus.

4.1.2.2.3. Lens systems

The lens system between the scattering chamber and the selector is identical in design concept to that between the monochromator and the scattering chamber (see section 4.1.2.1.3.) with one important exception. The transmission of the entire second stage must have no overall energy-loss dependence, i. e., electrons leaving the scattering chamber with different kinetic energies (corresponding to different energy-loss processes) must be detected with the same efficiency when that particular energy-loss is being transmitted by the selector. This behavior is not quantitatively "built-in" to the present apparatus. Rather, it is to be determined empirically. We have used a three-lens system at the exit of both the scattering chamber and selector. Qualitatively, it should provide a weak lens followed by a strong one so that relatively large changes in electron kinetic energies entering or leaving the lenses do not change the eventual focal point appreciably. The experimental justification for the usefulness of this simple system is given in section 4.4.6. There are more sophisticated approaches to this problem now available⁽¹¹⁰⁾ which may be incorporated into future modifications of this instrument.

4.1.3. External Fields

4.1.3.1. Introduction

Throughout the discussion of electron optics and analyzers (sections 4.1.1., 4.1.2.) the electrons were assumed to travel in field-free regions except for those regions in which electric fields were desired for focusing, etc. In practice, of course, electric and/or magnetic fields from television and radio stations, nearby electronic equipment, or the Earth itself may seriously affect the performance of the spectrometer. In this section, we shall attempt to assess the magnitude of these disturbances and outline methods of reducing them.

The classical force $\underline{F}$ acting on an electron due to electric fields of strength $\underline{E}$ and magnetic fields of induction $\underline{B}$ is given by the Lorentz force equation

$$\underline{F} = e(\underline{E} + \underline{v} \times \underline{B}) \quad (4-60)$$

in which e and $\underline{v}$ are the charge and velocity of the electron, respectively. This force can distort the electron's trajectory as well as cause an actual energy change. Since a trajectory distortion in the analyzer can be related to an apparent kinetic energy change, the kinetic energy resolution can be affected in either case. If ΔE_s is the change in the FWHM of the electron beam energy distribution due to these effects, then the inequality

$$\Delta E_s < \Delta E_{\frac{1}{2}} \quad (4-61)$$

must be satisfied for an allowable field disturbance ($\Delta E_{\frac{1}{2}}$ is the FWHM in the absence of such fields).

4.1.3.2. D.C. magnetic fields

Consider an electron with kinetic energy E , traveling in a direction perpendicular to a uniform magnetic field B , and radial field $\mathcal{E}$. From the radial force equation we obtain

$$\frac{2E}{R} = e(\mathcal{E} \pm \sqrt{\frac{2E}{m}} B) \quad (4-62)$$

in which R is the radius of curvature of the electron's path, $\pm$ refers to the two possible orientations of the electron's velocity vector with respect to the magnetic field direction, and m is the electron mass. Assume that $\mathcal{E}$ is the desired electric field ($\mathcal{E} = -\nabla V(R)$) within one of the hemispherical analyzers while B is an undesired magnetic field. Let $E = E_0$ be the solution of (4-62) with $B = 0$. If B is small (4-62) will be satisfied for another energy $E = E'$ for which

$$E' \approx E_0 \left(1 \pm \frac{eRB}{\sqrt{2mE_0}} \right) \quad (4-63)$$

Then with $\Delta E_s \equiv |E' - E_0|$ and relation (4-61), B must satisfy the inequality

$$B < \left(\frac{\Delta E_{\frac{1}{2}}}{E_0} \right) \frac{\sqrt{2mE_0}}{|e|R} \quad (4-64)$$

(4-64) yields the rather surprising result that for constant resolution ($\Delta E_{\frac{1}{2}}$) and fixed analyzer dimensions (R), a higher

analyzing energy (E_0) requires better magnetic field compensation (i. e., lower B). This is due to the smaller effective aperture sizes (ΔR) required to maintain a constant FWHM at higher E_0 in the analyzer (see section 4.1.2.1.2.). In the present case, $\Delta E_{\frac{1}{2}} \approx .03$ eV, $R_0 = 2.5$ cm, and $E_0 \approx 2$ eV for which relation (4-67) requires $B < 2.8 \times 10^{-2}$ gauss. Since the Earth's magnetic field is more than 10 times this value, some sort of field cancellation is necessary.

This magnetic field compensation can be provided by a set of Helmholtz coils. A pair of thin coaxial coils containing the same number of turns, carrying the same current, having the same radius, and being separated by a distance equal to their radii, will provide a nearly constant magnetic field vector directed along their axis in a small region about their midpoint. One such pair, properly oriented, could be used to partially neutralize the Earth's field in some particular region. However, in the present case, it is more convenient to use three pairs of fixed, mutually perpendicular coils. By independently varying the current in each pair, the resultant magnetic field vector, nearly constant within the desired region, can be made to point in any direction. The useful region of compensation depends on the radii of the coils, their separation, and the homogeneity of the Earth's magnetic field. Note that relay racks, vacuum equipment, etc. may cause severe local field distortions. The actual construction and performance are given in sections 4.2.2. and 4.3.2., respectively.

4.1.3.3. Radio-frequency (RF) fields

Since this apparatus was used in a region of substantial RF activity (within line-of-sight of the TV transmitters on top of Mt. Wilson), it is important to estimate the effect of these oscillatory fields on the electron beam.

An electromagnetic wave carries with it an electric field $\underline{\mathcal{E}}$, and a magnetic field $\underline{B}$, related by

$$\underline{B} = \frac{1}{c} \hat{k} \times \underline{\mathcal{E}} \quad (4-65)$$

in which $\hat{k}$ is a unit vector in the direction of propagation and c is the speed of light. The force exerted on an electron by such an RF field is given by substituting (4-65) into (4-60).

$$\underline{F} = e \left\{ \left[1 - \frac{v}{c} (\hat{k} \cdot \frac{v}{v}) \right] \frac{\underline{\mathcal{E}}}{c} + \frac{v}{c} \left(\frac{v}{v} \cdot \frac{\underline{\mathcal{E}}}{c} \right) \hat{k} \right\}. \quad (4-66)$$

If $v/c \ll 1$ (i. e., low energy electrons), $\underline{F} \approx e \underline{\mathcal{E}}$. Consequently, it is assumed that the electromagnetic wave disturbance is due entirely to an oscillating electric field of strength $\underline{K}$, and frequency ν , of the form

$$\underline{\mathcal{E}}(t) = \underline{K} \cos(\nu t + \delta_\nu) \quad (4-67)$$

in which δ_ν is the phase of the field at time $t = 0$.

As a further approximation to the actual situation, consider the case of an electron of velocity $\underline{v}_0$, and position $\underline{R}_0$, entering a field of the type (4-67) at $t = 0$. The trajectory $\underline{R}(t)$, of the electron is given by the equation

$$\frac{d^2 \tilde{R}(t)}{dt^2} = \frac{e}{m} \tilde{K} \cos(\nu t + \delta \nu) \quad (4-68)$$

in which radiation of the electron due to acceleration has been ignored⁽¹¹¹⁾. Integration of (4-68) and application of the initial conditions yields

$$\begin{aligned} \tilde{R}(t) &= \tilde{R}_0 + \tilde{v}_0 t \\ &+ \frac{e \tilde{K}}{m \nu^2} [\cos \delta \nu - \cos(\nu t + \delta \nu) - \nu t \sin \delta \nu] \end{aligned} \quad (4-69)$$

The energy $\epsilon(\delta \nu, \nu, t)$ transferred to the electron per unit time for an initial phase $\delta \nu$, is equal to the work done on the electron by the field per unit time or

$$\epsilon(\delta \nu, \nu, t) = [e \tilde{K} \cos(\nu t + \delta \nu)] \cdot \left[\frac{d \tilde{R}(t)}{dt} \right] \quad (4-70)$$

The total energy transferred $\Delta E(\delta \nu, \nu, \tau)$, in time τ , is

$$\Delta E(\delta \nu, \nu, \tau) = \int_0^\tau \epsilon(\delta \nu, \nu, t) dt \quad (4-71)$$

If a random distribution of initial phases $\delta \nu$ is assumed, the average energy $\Delta E_s(\nu, \tau)$ transferred in time τ is given by

$$\Delta E_s(\nu, \tau) = \frac{1}{2\pi} \int_0^{2\pi} \Delta E(\delta \nu, \nu, \tau) d\delta \nu \quad (4-72)$$

Thus, with the use of (4-69) through (4-72), we obtain

$$\Delta E_s(\nu, \tau) = 0.88 \times 10^{11} \frac{K^2}{\nu^2} (1 - \cos \nu \tau) \text{ eV} \quad (4-73)$$

for K in volts/meter and ν in radians/sec.

The deviations in the electron trajectory $\underline{D}$, due to the electric field $\underline{E}$, from (4-67) are

$$\underline{D}(\nu, \delta_\nu, t) = \frac{eK}{m\nu^2} [\cos \delta_\nu - \cos(\nu t + \delta_\nu) - \nu t \sin \delta_\nu] \quad (4-74)$$

For random initial phases, $\underline{D} = 0$. However, the square root of the average squared deviation defined by

$$\overline{\Delta D}(\nu, t) = \left[\frac{1}{2\pi} \int_0^{2\pi} \underline{D} \cdot \underline{D} d\delta_\nu \right]^{\frac{1}{2}} \quad (4-75)$$

is in general non-zero. In particular,

$$\overline{\Delta D}(\nu, t) = \frac{|e|K}{m\nu^2} \left[1 - \cos \nu t + \frac{(\nu t)^2}{2} - \nu t \sin \nu t \right]^{\frac{1}{2}} \quad (4-76)$$

The effect of $\overline{\Delta D}$ is to broaden the FWHM of the electron beam in a manner similar to an increase in ΔR of equation (4-29). Therefore the apparent energy change $\overline{\Delta E_s}(\nu, t)$, within the analyzer due to $\overline{\Delta D}$ is

$$\frac{\overline{\Delta E_s}}{E_0} \approx \frac{\overline{\Delta D}}{2R_0} \quad (4-77)$$

Thus,

$$\overline{\Delta E_s}(\nu, t) = 0.88 \times 10^{11} \frac{E_0 K}{R_0 \nu^2} \left[1 - \cos \nu t + \frac{(\nu t)^2}{2} - \nu t \sin \nu t \right]^{\frac{1}{2}} \text{ eV} \quad (4-78)$$

for R_0 in meters and E_0 in eV.

As a specific example, assume $K \sim 1$ V/M (a reasonable value for nearby sources of RF signals⁽¹¹²⁾) and $\nu = 0.5 \times 10^{-6}$ cycles/sec. For $\tau = 10^{-6}$ sec (approximate time for the electron to

pass through the system), (4-73) yields

$$\Delta E_s \approx .03 \text{ eV}$$

For $\tau \approx 10^{-7}$ sec (approximate time for the electron to pass through the sphere) and $E_0 = 2 \text{ eV}$, (4-78) yields

$$\overline{\Delta E_s} \approx .02 \text{ eV} .$$

This type of interference has been eliminated by enclosing the entire apparatus in an RF shielded enclosure (refer to section 4.2.2.).

4.2. Construction

4.2.1. Vacuum System

Since the mean free path of an electron in air at atmospheric pressure is only on the order of 10^{-4} cm, the entire spectrometer must be enclosed within a vacuum chamber. This chamber must provide a background pressure low enough so that the only electron-molecule collisions of importance occur in the scattering chamber. It should be bakeable in order to obtain better vacuum and electron-optical element surface conditions. Finally, the chamber material should have a low magnetic susceptibility to facilitate the elimination of D.C. magnetic fields along the electron path.

A non-magnetic, type 304 stainless steel vessel (refer to figure 4.2-1) was designed by us and fabricated by C. E. Howard

Figure 4.2-1. The stainless steel main vacuum chamber. Side view (left) and front view (right). (FC 1 through FC 6) flange covers ; (T) flexible stainless steel connecting tube (to pumping system, figure 4.2-2); (O) location of "O"-ring groove in flange; (G) location of gold wire gasket (if used) in flange.

Corporation. The flanges are of a unique design in that either gold wire (.040" diameter) gaskets or rubber "O"-rings can be used (see insert of figure 4.2-1). Table 4.2-1 lists the various "O"-ring seals that can be used on the main chamber as well as other data about the flanges. The flange covers (FC 2, FC 3, FC 4, FC 5, FC 6) were sealed to their respective flanges with gold gaskets while a butyl-rubber "O"-ring was normally used to seal FC 1. All of the spectrometer components are mounted on this latter flange cover. The flanges and flange covers were designed to seal the gold gaskets under a pressure of 1000 lbs/linear-inch at a bakeout temperature of 450° C (if necessary).

The main chamber is evacuated through the 8" diameter flexible stainless steel tube (T) by means of a pumping system shown in figure 4.2-2. It consists (in order from the main chamber) of a Vacuum Research Corporation 10" pneumatically operated gate valve (GV); a Ladish Company 8" diameter, 90°, long radius, type 304 stainless steel elbow (E); an Edwards High Vacuum Incorporated model NTM9A, 9" liquid nitrogen cold trap (CT); an Edwards model CB9A, 9" freon cooled chevron baffle (CB 1); an Edwards model 9M3A, 9" mercury diffusion pump (DP); an Edwards, model CB 2, 2" freon cooled chevron baffle (CB 2); and an Edwards model ED500, mechanical pump (MP). The diffusion pump, baffle, and cold trap can be isolated by closing GV and the Carl Herman Associates (CHA), model Kel-122, 1½", stainless steel bellows valve (V 1). In this way, the main chamber can be vented

TABLE 4.2-1

Construction parameters associated with the main vacuum chamber flanges.

Flange	"O"-Ring* Dimen. I. D. × Width (inches)	Gold Gasket Diam. (inches)	Bolt Circle Diam. (inches)	No. of Bolts Reqd.	Bolt Size (inches)
F 1, F 2	13.975 × .275	15.250	16 $\frac{1}{4}$	32	$\frac{5}{8}$ -11NC × 3 $\frac{3}{4}$ LG.
F 3, F 4	20.955 × .275	22.250	23 $\frac{1}{4}$	36	$\frac{5}{8}$ -11NC × 4 LG.
F 5, F 6	8.975 × .275	10.250	11 $\frac{1}{4}$	20	$\frac{5}{8}$ -11NC × 3 $\frac{1}{4}$ LG.

* Available from Parker Seal Co. , catalog numbers 5427-84, 5-087, and 5427-74, respectively.

Figure 4.2-2. The vacuum chamber pumping system. (G 1 and G 2) ionization gages, (T 1 and T 2) thermocouple gages, (V 1) stainless steel valve, (V 2 through V 4) brass valves, (GV) aluminum gate valve, (E) stainless steel elbow, (GT) liquid nitrogen cold trap, (CB 1 and CB 2) chevron baffles, (DP) diffusion pump, (FL) fore line, (MP) mechanical pump, and (EL) exhaust line.

and subsequently pumped out through the CHA, model RA-12-1, $1\frac{1}{2}$ " bellows valve (V 2) while the diffusion pump remains on. Thermocouple gages (Hastings, model DV-3M) are located at T 1 and T 2 while ion gages (General Electric Co., model 22GT103) are placed at G 1 and G 2. They are controlled by a Veeco thermocouple gage control unit and a G. E. ionization gage control unit, respectively. Two bellows valves (CHA, brass, $\frac{1}{2}$ ") are located at V 3 and V 4 for venting and leak checking. All gases pumped by the system are ducted out of the room through the exhaust line (EL).

The vacuum chamber and pumping system within the shielded enclosure are supported independently by two tables. They are constructed of 2" $\times$ 2" aluminum square tubing and have a jack screw and caster at each leg. The table supporting the vacuum chamber is 33" long by 34" wide by 29" high while the one supporting the pumping system is 58" $\times$ 34" $\times$ 35". The two compressors (which cool the baffles CB 1 and CB 2) and the mechanical pump are located outside of the shielded room.

The vacuum system is equipped with both a temperature and pressure interlock protection network. The diffusion pump will be automatically shut off and the gate valve closed if: (1) power to the mechanical pump is interrupted, (2) the diffusion pump jacket becomes too hot, or (3) the fore line pressure falls below 0.5 torr. The gate valve will also close if power to the diffusion pump is interrupted.

4.2.2. Shielding of External Fields

4.2.2.1. Shielding of D. C. magnetic fields

In order to neutralize the Earth's magnetic field along the electron path, three pairs of Helmholtz coils were constructed and placed around the main vacuum chamber as shown in figure 4.2-3. The coils are wound on plexiglass frames designed for this purpose. Table 4.2-2 gives the construction parameters associated with these coils. Current to the windings was supplied by an Electronic Measurements, model TR 212 AMB, D. C. regulated power supply. Section 4.3.2. summarizes the performance of this system.

4.2.2.2. Shielding of RF fields

In order to shield the spectrometer from interference due to RF sources in the vicinity, most of the apparatus (including the vacuum chamber, part of the pumping system, and the electrical relay racks) was enclosed within a Topatron Incorporated, model 7322, shielded enclosure. The enclosure was originally 12' long $\times$ 8' wide $\times$ 8' high. Since these experiments were performed, it has been expanded to 12' $\times$ 12' $\times$ 8'. All feedthroughs into the enclosure (air conditioning, vacuum, water, compressed air, and electrical power) are supplied by the manufacturer and are designed not to transmit RF signals. The room has a 100 db attenuation for frequencies from 10,000 Hz to 100,000 M Hz. Thus, a K value (section 4.1.3.3.) of 1 volt/meter outside the shielded room will be reduced to approximately 10^{-5} V/m within the enclosure. Since the apparatus has never been operated outside this room, it has been

Figure 4.2-3. Orientation of the Helmholtz coils around the vacuum chamber. X, Y, and Z are the coil-pair designations. The power supply (PS) provides a constant voltage so that the current through a particular coil-pair can be varied by changing the adjustable series resistance.

TABLE 4.2-2

Construction parameters of the three pairs of Helmholtz coils.

Coil* Pair	Coil Radius cm	Coil Separation cm	Number [†] of Turns
X	49	54	720
Y	52	84	697
Z	55	58	662

* The coil-pair designation refers to figure 4.2-3.

† Belden magnet wire, 28 gauge, HNC Nyclad No. 8080.

impossible to empirically verify its usefulness.

4.2.3. Carriage

In order to facilitate the insertion and removal of the flange cover FC 1 (figure 4.2-1), a carriage was constructed as shown in figure 4.2-4. This carriage is a necessity since FC 1 and the spectrometer together weigh about 100 lbs. FC 1 can be bolted to the carriage, which in turn rides on two $2'' \times 2\frac{1}{2}'' \times 72''$ angle-iron rails that are clamped to the table supporting the vacuum chamber. The rails extend a sufficient length beyond the end of the table so that the spectrometer can be "wheeled" completely out of the vacuum chamber for easy access. The Helmholtz coils do not need to be removed, and the carriage with its supporting rails is easily removed from the shielded room after use. (Since the material from which it is made is highly magnetic, it must be removed when the spectrometer is to be operated.)

4.2.4. Spectrometer Components

4.2.4.1. General description

Figure 4.2-5 is a block-schematic representation of the spectrometer components. The electron beam path through the apparatus begins at the electron gun and describes an "S" shaped curve in the plane of the figure, eventually reaching the electron multiplier. This particular geometrical arrangement is chosen to reduce structural interference and to help average out the effects of constant residual fields, i. e., the electron would be deflected

Figure 4.2-4. Carriage assembly mounted to the vacuum chamber support table (side view).

Figure 4.2-5. Block-schematic diagram of the spectrometer components.

The arrows point in the direction of the electron beam.

in one direction through the first half of the "S" but would be deflected the opposite way through the second half.

The construction details of the various elements of the instrument are given in the following sections.

4.2.4.2. Electron gun

A cross-sectional view of the cylindrically symmetric electron gun is given in figure 4.2-6. The cathode housing and grid are of type 304 stainless steel, the apertures are of molybdenum, boron nitride is used for electrical insulation as indicated, and all other elements are of oxygen-free high-purity copper (OFHC). A Picker-Nuclear, No. 80-3236, .005" diameter tungsten hairpin filament is used as the electron source (cathode). The cathode, grid, and aperture A1 of the anode structure comprise the 3 element Soa gun discussed in section 4.1. Aperture A2 is included to block off much of the unwanted beam and to keep the deflectors, which aid in guiding the beam, from drawing an appreciable current. Aperture A3 defines the object of the lens system composed of elements LVL 1 and Herzog 1. (LVL stands for low-voltage-lens which is so named because under usual operating conditions its potential is within a few volts of the anode.) The image of these lenses is the entrance of the monochromator. When LVL 1 is operating at the same potential as the anode structure (note that A1, A2, and A3 are electrically connected to the anode structure while LVL 1 is not), this system operates as the simple double-aperture lens

Figure 4.2-6. Cross-sectional view of the electron gun. The filament holder is of boron nitride, the cathode housing and grid are of stainless steel (type 304), and the other components are of copper (OFHC). The abbreviations are defined in the text.

discussed in section 4.1. However, the potential of LVL 1 can be varied independently to provide another degree of freedom in focusing the electron beam.

The entire gun structure is approximately 3.2" long and .985" in diameter. It is constructed of interlocking elements separated by short gaps to decrease the number of electrons which can be emitted radially while providing a reasonably open structure that can be easily outgassed. Table 4.2-3 summarizes the more important element dimensions and spacings.

4.2.4.3. Monochromator and selector

The hemispherical electrostatic energy analyzer used in this research is relatively easy to construct. It consists of an inner and outer hemisphere as shown in figure 4.2-7. The construction materials are indicated in the figure.

The analyzer is assembled as follows:

(1) the inner sphere is mounted rigidly to the inner-sphere-support bracket using the three sapphire balls ($.1250'' \pm .0001''$ diameter) and a machine screw;

(2) with the inner-sphere-support bracket clamped to the outer sphere, the space between the inner and outer sphere is filled with $.2500'' \pm .0001''$ ball bearings;

(3) the inner-sphere-support bracket is positioned and clamped such that there is uniform contact between the inner sphere-ball bearings-outer sphere surfaces. In addition, the faces

TABLE 4.2-3

(a) Gun element dimensions

Element	Dimension (inches)	
	Bore	Thickness
Grid	.040	.040
A1	.040	.005
A2	.080	.005
A3	.030	.005
LVL 1	.125	-
Herzog 1	.125	-

(b) Gun element separations as measured between the nearest faces of the elements along the electron beam path.

Elements	Separation (inches)
Cathode - Grid	.018
Grid - A1	.080
A1 - A2	.180
A2 - A3	.700
P	.555
LVL 1 - Herzog 1	.125
Q	.555

Figure 4.2-7. Front view (right) and cross-sectional side view (left) of the electrostatic energy analyzer (monochromator and selector). Dimensions are in inches. The inner hemisphere support bracket (IHSB) is of stainless steel (type 304). The hemispheres are of copper (OFHC).

of the inner and outer sphere are constrained to lie in the same plane;

(4) the bracket is drilled and screwed permanently in place. The inner sphere can be removed from the bracket and replaced to within $\pm .0005''$ of its initial position since it is accurately located by the sapphire balls.

4.2.4.4. Lens system 1

The function of this lens system is to decelerate and focus a portion of the energy-dispersed electron beam leaving the monochromator onto the entrance aperture (A4) of the scattering chamber. This lens system is shown in figure 4.2-8 and consists of three basic elements--Herzog 2, LVL 2, and the scattering chamber aperture (A4)--as well as two perpendicular pairs of deflector plates for beam alignment. If LVL 2 is held at the scattering chamber potential (ground), the lens system is equivalent to the double-aperture lenses discussed in section 4.1, which image the monochromator exit on A4. The potential of LVL 2 can be varied independently to provide greater flexibility in focusing the beam as was done in the electron gun. Likewise, this lens system has an open but interlocking structure. The lens assembly is bolted to the scattering chamber support bracket. Table 4.2-4 lists the more important lens element dimensions and spacings.

Figure 4.2-8. Cross-sectional view of lens system 1. (ME) exit of the monochromator, (SE) entrance to the scattering chamber. The other abbreviations are defined in the text.

TABLE 4.2-4

(a) Lens system 1 element dimensions.

Element	Dimension (inches)	
	Bore	Thickness
Herzog 1	.125	-
LVL 2	.125	-
A4	.020	.005

(b) Lens system 1 element separations as measured between the nearest faces of elements along the electron beam path.

Elements	Separation (inches)
Herzog 2 - LVL 2	.125
P	.555
Q	.555

4.2.4.5. Scattering chamber

The scattering chamber is designed to contain the target gas at a significantly higher pressure than that in the main vacuum chamber (10^{-2} torr compared to 10^{-7} torr, respectively). For this reason, it is completely sealed except for a sample inlet tube and the apertures through which the incident and scattered beams pass. Further, the scattering chamber is flexible so that the angle between the incident electron beam (beam leaving the monochromator) and that portion of the scattered beam we wish to detect (beam entering the selector) can be varied. This angle is defined as the scattering angle.

The complete scattering chamber assembly (figure 4.2-9) is composed of four basic units--the scattering-chamber-support bracket at the end nearest the monochromator (SCSBM), the actual bellows assembly with its three end flanges (BAF 1, BAF 2, BAF 3), the scattering-chamber-support bracket nearest the selector (SCSBS), and a remotely actuated current measuring electrode or "faraday cup" (FC).

Figure 4.2-9 gives a cross-sectional view of the scattering chamber in a plane perpendicular to the axis of rotation for a scattering angle of 30° .

Note that lens system 2 actually fits inside the SCSBS in order to bring this lens and the selector nearer to the scattering center.

Figure 4.2-9. Cross-sectional view of the scattering chamber assembly (L 2) location of lens system 2; (BCD 1) bolt-circle for the attachment of flange BAF 1 to the SCSBM; (BCD 2) bolt-circle for the attachment of BAF 2 to the SCSBS; (BCD 3) bolt-circle for the attachment of BAF 3 to the SCSBS; (FC) current measuring electrode (faraday cup, shown in the retracted position). The rotation axis (+) is perpendicular to the plane of the figure.

The SCSBM is made of type 304 stainless steel. The deflector plates and aperture A4 of lens system 1 are assembled within it. A4 is directly shorted to it while the deflector plates are electrically insulated by boron nitride spacers.

Because of space limitations (the distance between the monochromator and selector should be as short as practical), the bellows assembly flanges were not made thick enough to ensure a reliably vacuum tight seal using gold gaskets, which require about 1000 lbs./linear-inch. Thus, hollow tubular metallic "O"-rings made of inconel plated with silver and supplied by United Aircraft Products, Inc. were used to provide the vacuum seals between BAF 1, BAF 2, and BAF 3 and both the SCSBM and the SCSBS. These "O"-rings require less than 200 lbs./linear-inch for effective sealing since they have a cross-sectional diameter of only $1/32$ " and a .005" thick wall. .020" thick stainless steel spacers were used between the bellows assembly flanges and their respective support brackets to position these "O"-rings and insure that the proper amount of deformation occurred when the flanges and brackets were bolted together.

The bellows assembly, which consists of two concentric, welded bellows and flanges, was fabricated of type 345 stainless steel by Metal Bellows Corp. Each bellows consists of about 700 "S" shaped convolutions individually welded together. This results in an extremely flexible structure with the additional advantage that electrons striking the walls are effectively trapped. In a linear

bellows configuration (as in figure 4.2-9), the inner bellows has a minimum inner diameter of 1.12" and a maximum outer diameter of 1.37" while the outer bellows has a minimum inner diameter of 1.67" and a maximum outer diameter of 2.10". The scattering chamber is mounted so that the rotation axis is 1.50" from aperture A4 and .75" from aperture A5 (lens system 2). Thus, the electron path length through the target gas is approximately $2\frac{1}{4}$ ". One end of the bellows can be rotated by $\pm 60^\circ$ with respect to the other about the rotation axis. However, by having the incident electron beam enter the bellows at an angle of 30° with respect to a normal to BAF 1, scattering angles from -30° to $+90^\circ$ can be obtained. For example, a scattering angle of 0° (the angle at which a line through A4 and A5 intersects the rotation axis) is obtained when the bellows assembly is "bent" by -30° while for a scattering angle of $+30^\circ$ the bellows assembly is linear. This configuration was suggested by Simpson⁽²⁵⁾.

Temperature control of the target gas contained within the inner bellows could be obtained by circulating a suitable fluid through the space between the inner and outer bellows. However, no use of this feature has been made in the present study. All data were taken at ambient (room) temperature since the substances studied so far are "permanent" gases.

The inner and outer bellows are welded to two separate concentric flanges (BAF 2, BAF 3) on the end nearest the selector. These flanges are bolted to the SCSBS.

A pneumatically operated actuator constructed of type 347 stainless steel by Metal Bellows Corporation was attached to the SCSBM. Its function is to push the copper faraday cup into the path of the incident electron beam (in order to measure its intensity) and retract the faraday cup until it is electrically shorted to BAF 1 (when scattering measurements are to be taken). The actuator is shown in figure 4.2-10. It has an overall stroke (the maximum extension under 35 lbs./sq. in. air pressure in bellows 1 minus the minimum extension with bellows 1 evacuated) of 1.00 inch. The ceramic-insulator vacuum feedthrough was supplied by Photocon Research Products. The same type of metallic tubular "O"-rings as were used above provide the required vacuum seals.

4.2.4.6. Lens system 2

The function of lens system 2 is to: (1) define the geometry (diameter and angular divergence) of the scattered beam which is to be energy analyzed by the selector, and to (2) focus this beam at the entrance of the selector in a manner that is relatively insensitive to the electron energy-loss being detected.

Lens system 2 is shown in figure 4.2-11 and consists of three basic elements--aperture A5, LVL 3, and Herzog 3. A5 is shorted directly to SCSBS while LVL 3 and Herzog 3 are electrically insulated. Table 4.2-5 lists the important lens element dimensions and spacings.

Figure 4.2-10. Cut-away view of the actuator assembly to extend and retract the faraday cup. The extreme right and left ends of the assembly are fixed relative to each other. 35 lbs/sq. inch air pressure in bellows 1 will cause it to expand and bellows 2 to contract, extending the faraday cup into the scattering chamber (figure 4.2-9).

Figure 4.2-11. Cross-sectional view of lens system 2 installed in the SCSBS. The arrow points in the direction of the collected electron beam.

TABLE 4.2-5

(a) Lens system 2 element dimensions.

Element	Dimension Inches	
	Bore	Thickness
A5	.030	.005
Sleeve	.250	-
LVL 3	.125	-
Herzog 3	.125	-

(b) Lens system 2 element separations as measured between planes of minimum bore along the electron beam path.

Elements	Separation (inches)
A5 - LVL 3	.94
LVL 3 - Herzog 3	.125
Herzog 3 - Selector	.555

The boron nitride insulator-spacer elements are not quite cylindrically symmetric but are cut away along much of one side to allow for better outgassing of the lens elements.

The conical half-angle defined by this lens system is approximately .05 rad. which implies a solid angle acceptance of about 1.6×10^{-2} steradians. The realization of function (2) above depends upon the voltages applied to the lens elements and will be discussed in section 4.4.

4.2.4.7. Lens system 3

The function of lens system 3 is to focus the electron beam leaving the selector onto the first dynode of the electron multiplier. As in the other lens systems, it consists of three basic elements (as shown in figure 4.2-12)--Herzog4 and two tube lenses (TL 1, TL 2). TL 1 contains aperture A6 which, along with lens system 2, helps determine the energy resolution of the scattered beam (section 4.1.). TL 2 contains two perpendicular pairs of deflector plates to aid in aligning the beam. Table 4.2-6 summarizes the important lens element dimensions and separations. This lens system is rather long (selector to first dynode of multiplier is $\sim 7''$) because the electron multiplier is too large to be moved closer to the selector.

4.2.4.8. Electron multiplier

The electron multiplier is used to detect the energy-analyzed scattered electron beam. It is a Nuclide Corporation,

Figure 4.2-12. Cross-sectional view of lens system 3. (SX) selector exit, (MH) multiplier housing. The other abbreviations are defined in the text.

TABLE 4.2-6

(a) Lens system 3 element dimensions.

Element	Minimum Bore (inches)
Herzog 4	.125
TL 1	.125
TL 2	.30
A6	.030

(b) Lens system 3 element separations as measured between the planes of minimum bore along the electron beam path.

Elements	Separation (inches)
Selector - Herzog 4	.555
Herzog 4 - TL 1	.125
Herzog 4 - A6	.555
A6 - TL 2	1.12

model EM-2, electron multiplier, consisting of twenty copper-beryllium dynode stages in a "pie" configuration as shown in figure 4.2-13. The dynodes are assembled on inconel discs separated by ceramic washers. Bakeable 0.38 M Ω resistors (International Resistance Company, No. 00736) are used between each disc. The base of the multiplier assembly contains leads from the anode and last dynode. Leads from the first dynode and the three lens plates (in front of the first dynode) were brought out through the rear of the stainless steel enclosure around the multiplier. The enclosure interlocks with lens system 3 as shown in the figure and is wrapped with aluminum foil in addition. This was necessary to reduce the number of electrons being detected which had not passed through lens system 3. The base of the multiplier contains two $\frac{1}{4}$ " diameter holes through which the multiplier (and lens system 3) is outgassed.

4.2.5. Support Structure

The spectrometer components are held in the required relative orientation to each other (refer to figure 4.2-5) in the following way, depicted in figure 4.2-14. The electron gun (EG), monochromator (M), and the SCSBM are mounted on a Pic Design Corp., model Q7-29SP, type 304 stainless steel gear wheel (GW) while the SCSBS, selector (S), lens system 3 (L 3), and the multiplier (EM) are mounted to a support frame which is rigidly attached to flange cover FC 1. The gear wheel shaft (GWS) is mounted by means of two bearings contained in the bearing

Figure 4.2-13. Cross-sectional view of the electron multiplier and its shield.

(R) $0.38\text{ M}\Omega$ bakeable resistors; (G) glass insulator; the discs supporting the dynodes are not shown to scale. The arrows indicate the direction of the incident electron and the resulting cascade.

Figure 4.2-14. Side view of the spectrometer components mounted on the support frame. The scale is approximately correct but many details have been omitted. (SF) shelf welded to FC 1, (AST) actuator support table (bolted to gear wheel), (BP) support frame base plate, (M) monochromator, (BH) bearing housing, (GWS) gear wheel shaft, (EG) electron gun, (GW) gear wheel, (S) selector, (SCB) scattering chamber bellows, (L 3) lens system 3 (mounted between sides of support frame), (EM) electron multiplier (mounted between sides of support frame), (A) faraday cup actuator, (F) support frame side plate. The other abbreviations are defined in the text.

housing (BH) to this same support frame. Thus, by rotating the gear wheel, the first half of the spectrometer, which produces the incident electron beam, can be rotated with respect to the second fixed half, which defines and detects a portion of the scattered beam.

The support frame is constructed from two approximately rectangular $\frac{1}{4}$ " plates (F) which are welded to a $\frac{1}{4}$ " thick base plate (BP) forming a rigid, box-like structure (type 304 stainless steel, electropolished). The various spectrometer components are mounted within this structure, either to the gear wheel or to the support itself. The entire unit is then bolted to a shelf (SF) that is welded to the inside of FC 1.

The actuator assembly (A) has one end rigidly attached to the SCSBM (figure 4.2-10) while its opposite end is attached to a plate (AST) extending radially from the gear wheel and bolted to it.

The electron multiplier (EM) fits between the sides of the support frame and is bolted to it. However, the multiplier shield is electrically insulated from the frame. In fact, the scattering chamber is the only spectrometer component which is internally grounded.

Figure 4.2-15 shows the monochromator and selector support brackets in more detail. The bracket for the monochromator is bolted to the gear wheel while that for the selector is bolted to the frame.

Figure 4.2-15. Front view (left) and side view (right) of the energy analyzer (selector or monochromator) support bracket. (A) stainless steel plate, (B) Boron nitride insulators which support and position the analyzer.

The electron gun and lens system 3 are mounted to the gear wheel and the support frame, respectively, by "electron-optical" benches shown in figure 4.2-16. They are identical in concept to those employed by Simpson⁽²⁴⁾.

4.2.6. Bakeout Heaters

A furnace which could enclose the main vacuum chamber was constructed for us by Kenneth C. Holloway, Inc. Its specifications are listed below:

Dimensions: $47\frac{1}{2}$ " long $\times$ $39\frac{1}{2}$ " wide $\times$ 44" high.

Material: Type 304 stainless steel, glass wool insulation.

Electrical: Heaters of 19 gauge, chromel-A wire; current supplied by two 220V 3-phase, 20 amp Variacs wired in a Y circuit. Total power output available is ~ 8.8 KW.

Construction: Six separate pieces including top, bottom, and four sides. Each piece is $1\frac{1}{2}$ " thick, double-walled, containing the insulation.

To install the furnace, the Helmholtz coils are removed and the top, bottom, and sides of the furnace are bolted together around the chamber. The furnace is supported by the same table which supports the vacuum chamber. The gate valve and about half of the length of the tube connecting it to the main chamber (as well as the rest of the pumping system) lie outside the furnace and are kept cool (less than 80°C) during bakeout. The vacuum chamber and the components within it can be heated to more than 450°C in about

Figure 4.2-16. Side view (upper) and end view (lower) of the "electron-optical" bench support structure used to mount the electron gun and lens system 3. (A) element to be supported by bench, (B) alumina rods ($.2500'' \pm .0001''$ diameter), (C) stainless steel hold-down strap which is screwed into element (A) with a No. 2-56 stainless steel machine screw (D), (E) stainless steel support for the alumina rods.

8 hours. It was found, however, that such severe overall bakeout was not necessary for acceptable apparatus performance. Instead, a small resistance heater was installed directly on some of the internal (inside the vacuum chamber) components of the spectrometer. It consists of about five feet of .020 inch diameter tungsten wire covered with thin walled ceramic tubes for electrical insulation. Several loops of this wire are clamped to the monochromator, selector, SCSBM, and SCSBS. A 20 amp. 120 V Variac is used to supply the required heating power (about 600 Watts). Iron-constantan thermocouples are mounted at several places on the spectrometer to monitor the temperature.

4.2.7. Rotary Motion

Figure 4.2-17 shows the rotary motion drive train. The gear wheel (GW), on which the electron source is normally mounted, is rotated by a Pic Design Incorporated, model Q8-2, stainless steel worm gear (WG). The worm is driven from outside the vacuum chamber by means of a CHA, model D-909, bakeable, bellows sealed rotary feedthrough (RFT). The rotary feedthrough is supplied with a Varian conflat flange, model 954-5072 for attaching it to FC 1.

The worm gear bearing housing (WGBH) contains four (two on each side of the worm) Miniature Precision Bearings, Inc., type N614, copper-beryllium, ball bearings. Two flexible connectors (FXC) are used in the drive shaft to allow for any misalignment between the rotary feedthrough and the worm gear shaft.

Figure 4.2-17. Top view of the rotary motion drive train. For clarity, none of the spectrometer components are shown. The rotation axis (RA) is perpendicular to the plane of the figure. (TC) Durrant, model 4-Y-40591-412-L-CL, turn counter, (RFT) rotary feedthrough, (GW) gear wheel, (WGBH) worm gear bearing housing, (WG) worm gear, (FXC) flexible couplings.

4.2.8. Vacuum Feedthroughs

All of the feedthroughs required for the operation of the spectrometer within the vacuum chamber are installed on FC 1. The feedthrough arrangement is shown in figure 4.2-18 and table 4.2-7 gives their use and specifications. FC 1 has 8 Varian conflat flanges, model 954-5072, which seal with copper-gaskets (Varian, model 953-5014) and 6 "home-made" flanges which seal with .040" diameter gold wire. The Varian flanges are extended about 1" away from the face of FC 1 while the other flanges are staggered and extend either $1\frac{1}{2}$ " or $4\frac{1}{2}$ ". 11-conductor, glass-wool insulated cable supplied by Sante Fe Textiles is used for wiring the components inside the chamber. All internal air and sample lines are of stainless steel supplied by U. S. Flexible Metallic Tubing, Inc. Cajon type 316 stainless steel vacuum couplings with copper gaskets are used throughout for connecting these lines in place.

4.2.9. Electrical Components

The power supplies, batteries, counting equipment, and their associated circuitry are assembled in three electrical relay racks external to the vacuum chamber but within the shielded room. Figure 4.2-19 is a block-schematic diagram showing the overall interrelation of the various electrical components. A circuit diagram for each of the components is given below (figures 4.2-20 through 4.2-26). Table 4.2-8 lists the resistors, batteries, and power supplies indicated in these figures. In addition, the potential

Figure 4.2-18. Front (external to vacuum chamber) view of the flange cover FC 1. Flanges 1-6 are "home-made" while 7-14 are supplied by Varian. Refer to table 4.2-7 for a list of their uses and specifications.

TABLE 4.2-7

The uses and specifications of the feedthroughs on FC 1.

Feedthrough Number (Fig. 4.1-18)	Use	Specification
1,2,3,4,6	Voltages (<100V) to spectro- meter components	RCA, model J1946, 11-pin
5		Blank
7	Leads to dynodes 1 and 20 of multiplier	Cermaseal, Inc.
8	Internal bakeout heaters, thermocouples, lenses in multiplier	Varian, model 954-5013, 20- pin.
9	Leads to outer sphere of selector and faraday cup	Cermaseal, Inc.
10	Sample inlet line and air to gage port actuator	Varian conflat blank with $\frac{1}{4}$ " O.D. stainless steel tubes through and welded.
11		Varian conflat blank
12	Lead to anode of multiplier	Cermaseal, Inc.
13	Rotary motion	CHA, model D-909, bellows sealed rotary feedthrough
14	Gas lines for temperature control of scattering chamber and air line to faraday cup actuator	(Same as 10)

Figure 4.2-19. Block-schematic diagram of the electrical controls for the spectrometer. The dotted lines represent the vacuum wall. The arrows indicate the direction of control. The number within each box is the figure number of the circuit diagram for that control.

Figure 4.2-20. Circuit diagram of the electron gun control system. (RVS) reference voltage supply. The other abbreviations used for figures 4.2-20 through 4.2-26 are listed in table 4.2-8.

Figure 4.2-21. Circuit diagram of the energy analyzer (monochromator and selector) control unit (see table 4.2-8). R3 is adjusted to 7.9 K Ω to give the proper voltage balance with respect to CVM (CVS for the selector). See section 4.1.1.2, figure 4.1-1. (RVS) reference voltage supply. Kepco 1 is used for the monochromator system while Kepco 3 is used for the selector.

Figure 4.2-22. Circuit diagram of the control unit for lens system 1. (See table 4.2-8.)

(a)

(b)

Figure 4.2-23. Block schematic diagrams of the sweep control when the function generator (FG) is used (a), and when the Nuclear Data system (ND) is used (b). The connector labelled OUT goes to the control units indicated by figure 4.2-19. (See table 4.2-8)

Figure 4.2-24. Circuit diagram of the lens system 2 control unit. (See table 4.2-8.)

Figure 4.2-25. Circuit diagram of the lens system 3 control unit. (See table 4.2-8.)

Figure 4.2-26. Block schematic of the detector electronics.

(See table 4.2-8.)

TABLE 4. 2-8

Parts list for circuit diagrams 4. 2-19 through 4. 2-26. The first column gives the part designation as it appears in the figures. The second column gives its specification and/or manufacturer.

Part	Specification
Reference voltage supply (RVS)	Princeton Applied Research Corp., model TC 100. 2BR voltage reference source. Accuracy $\pm .01\%$, stability $\pm .001\%$, resolution $100 \text{ m}\mu\text{V}$.
Recorder	Moseley, model 7001 AMR, X-Y recorder.
Kepco 1 (and 3)	Kepco, model HB2A(M), power supply. Load regulation $.01\%$, stability $.01\%$.
Kepco 2	Kepco, model KS36-5M, power supply (used in current regulation mode). Load regulation $\pm .02\%$.
PAR	Princeton Applied Research Corp., model TC-100. 2R voltage reference supply. Accuracy $\pm .01\%$, stability $\pm .001\%$, resolution 1 mV .
FG	Exact Electronics Incorporated, type 251 function generator. $10,000$ to $.0001$ cycles/sec.
HV	Dynamic Associates, PDI, Inc., model 1545 D. C. high voltage source. Regulation $\pm .001\%$, stability $\pm .02\%$ day, resolution $.01 \text{ V}$.
CRM	Nuclear Chicago Corp., RIDL, model 35-7B, log-linear count-rate- meter.
NPA	RIDL, model 31-1B, nuvistor pre- amplifier
DDL AMP	RIDL, model 30-23, double delay line amplifier

TABLE 4. 2-8 (continued)

Part	Specification
SCPHA	RIDL, model 33-10B, single channel pulse height analyzer.
ND	Nuclear Data Corp. , specially modified 1024 channel counting system.
ND AMP	Nuclear Data, model 180-014 control unit.
ND DAC	Raytheon,digital to analog converter (part of Nuclear Data system).
ND TB	Nuclear Data, model 180ITB time base generator.
ND M	Nuclear Data, model 181M, 1024 channel memory unit.
B1	Burgess, type U-15 dry cell, 22.5 V.
B2	Mallory, size D, 1.35 V mercury cell.
B3	Burgess, 300 V. B-battery.
R1	Welwyn, 1%, 10K Ω resistor.
R2	Welwyn, 1%, 90K Ω resistor.
R3	Ohmite, type U-linear, 10K Ω potentiometer.
R4	Ohmite, type U-linear, .5M Ω potentiometer.
P1	Beckman Inst. , Helipot, model 7216, 10K Ω , 10 turn potentiometer.
P2	Helipot, model 5611, single turn 5K Ω potentiometer.
P3	Helipot, model 7216, 1K Ω , 10 turn potentiometer.
P4	Ohmite, type U-linear, 500K Ω potentiometer.

between any two elements could be measured with a Fairchild, model 7000, digital voltmeter. The current drawn by the elements could be measured with either a Keithley, model 600A, or a Cary, model 31, vibrating reed electrometer.

4.2.10. Sample Inlet System

The sample inlet system used in this research is shown schematically in figure 4.2-27. It is pumped by means of an Edwards, model 1SC150B mechanical pump (MP) located outside of the shielded enclosure. It can be isolated from the system by closing the Vacuum Accessories Corp., model FV-100, 1" stainless steel bellows valve (V1). V2, V3, and V4 are Nupro, model SS-6BG-SW, bakeable, $\frac{3}{8}$ ", stainless steel valves. A Granville Phillips, model 203001-02-011, variable leak (VL) is used to regulate the flow of sample gas to maintain the desired pressure in the scattering chamber.

A gage-port assembly (GPA) is mounted to the support frame (figure 4.2-14) inside the vacuum chamber. It contains a G.E. miniature ionization gage (IG) and an RCA, model 1946, thermocouple gage (TC) for monitoring the scattering chamber pressure. A pneumatically operated stainless steel bellows valve (BV) can be used to open one end of the gage-port assembly to the main vacuum. All fittings and tubulation are of stainless steel. The inlet system is bakeable (to about 350°C) from V1 to the main vacuum chamber.

Figure 4.2-27. Schematic diagram of the sample inlet system.

(TSC) tubulation to scattering chamber; (IG) ionization gage;
(TC) thermocouple (bakeable) gage; (GPA) gage port assembly;
(BV) pneumatic bellows valve; (VCW) vacuum chamber wall;
(V2 through V4) bakeable $\frac{3}{8}$ " valves; (V1) 1" bellows valve; (VL)
variable leak; (CT) liquid nitrogen cold trap; (MP) mechanical
pump; (S/E) shielded enclosure wall; (EL) exhaust line.

180

4.3. Procedure

4.3.1. Pump-Down and Bake-Out

Before operating the spectrometer, the vacuum chamber must be evacuated and the internal components baked-out. A great deal of experience with this apparatus has shown that a bake-out after each exposure to air is absolutely necessary for acceptable spectrometer performance, although it has little effect on the ultimate vacuum chamber pressure.

To initiate the pump-down, valves V3 and V4 are closed (refer to figure 4.2-2), valves V1, V2, and GV are open, and the mechanical pump (MP) is started. When thermocouple (T2) indicates that the fore line pressure is below .020 torr (this usually requires 10 minutes), the two freon compressors to chill baffles CB1 and CB2 are started. After 15 minutes, GV is closed and the diffusion pump is started. By this time both T1 and T2 should indicate a pressure of 10^{-2} torr or less. 25 minutes later, the liquid nitrogen cold trap (CT) is filled. When G2 indicates a pressure of 1×10^{-6} torr (about 10 more minutes), valve V2 is closed and GV is opened. The chamber pressure usually drops to about 5×10^{-6} torr in a few seconds. After about 1 hour a background pressure of 1×10^{-6} torr is usually obtained.

At this point the internal bake-out heater is turned on at low power (200 watts) until the monochromator and selector reach about 120°C (one-half hour). The power is then increased in increments of about 100 watts every 5 minutes until 600 watts is

reached. After about 4 hours, the selector, monochromator, and scattering chamber are at approximately 250°C. The pressure, which usually rises to about 10^{-5} torr during the initial phase of the bake-out, falls back to about 10^{-6} torr. The bake-out is terminated at this point. The apparatus will return to room temperature in about ten hours with a residual pressure of about 5×10^{-8} torr. Even if the components were not baked, this value of the pressure would be obtained after about 48 hours.

4.3.2. Magnetic Field Compensation

The construction and placement of the Helmholtz coils has been discussed in section 4.2.2.1. With all spectrometer components in place (especially relay racks and power supplies), a Bell, model 120, gaussmeter and a Hall effect probe (maximum sensitivity is 1 m gauss full scale) were used to measure the residual magnetic field. By suitable adjustment of the current through the coil-pairs, the residual field was reduced to ± 5 m gauss over the entire region of the electron beam path. Table 4.3-1 gives some specific values of the field after compensation.

4.3.3. Sample Introduction

The sample inlet system has been described in section 4.2.10 and shown in figure 4.2-27. During the pump-down and bake-out (section 4.3.1) of the main chamber, valves BV, V5, V2, and V4 are kept open while valves V1 and V3 are closed. The mechanical pump is used to evacuate that part of the line below

TABLE 4.3-1

Helmholtz coil operation. I is the current through the coil-pair, $|B|$ is the residual magnetic field component in the direction of the coil-pair axis measured at the element indicated, and Δ is the rate of change of the residual magnetic field component with the current through the coil-pair.

Coil Pair	Current (mA)	$ B $ /m gauss		Δ (m gauss/mA)	
		Monochromator	Selector	Monochromator	Selector
X	3.3	0.5	3.5	11.1	10.8
Y	8.5	3.0	0.1	8.3	7.8
Z	10.1	3.2	5.5	12.5	9.3

V1, and the cold trap is immersed in liquid nitrogen. The inlet system is flushed several times with the gas to be studied by closing valve BV, admitting the sample through V3 until TC1 indicates about 0.5 torr, and then pumping the target gas away through V1. To obtain the desired sample pressure in the system, valves BV, V1, and V4 are closed. Valves V5, V2, and V3 are open and the gas-flow through the variable leak (VL) is adjusted to give the desired constant pressure (.001 to .010 torr) in the gage port assembly. This constant pressure is the result of a dynamic balance between the sample leaking in through VL and out through apertures A4 (fig. 4.2-8) and A5 (fig. 4.2-11).

Since the pressure monitoring gages (IG, TC1) are separated from the actual scattering region (the inside of the inner scattering chamber bellows, fig. 4.2-9) by a 0.375" I.D. $\times$ 2 $\frac{1}{2}$ " long stainless steel tube (TSC of figure 4.2-27), the scattering chamber pressure will be somewhat lower than that indicated by the gages. An estimation of this pressure difference can be obtained from the equations and tables of Pirani and Yarwood⁽¹¹³⁾.

The total conductance U_A of apertures A4 and A5 is approximately .075 liter/sec for air at 20°C if one assumes that molecular effusion conditions⁽¹¹³⁾ prevail. The conductance U_T of the tube connecting the gage port assembly (at pressure P_{GPA}) and the scattering chamber (at pressure P_S) is about 2 liter/sec (see fig. 1.3 of reference 113). The throughput Q is constant throughout the system for a steady state (pressure) condition and is given by

$$Q = U(P_1 - P_2) \quad (4-79)$$

in which P_1 and P_2 are the pressures in any two regions and U is the conductance of the orifices (or tubes) separating them. In particular,

$$U_A(P_S - P_{MC}) = U_T(P_{GPA} - P_S) \quad (4-80)$$

where P_{MC} is the pressure in the main vacuum chamber ($\sim 10^{-7}$ torr) which is negligible compared to P_S ($\sim 10^{-3}$ torr). Thus, solving for P_S yields,

$$P_S \cong \frac{U_T}{U_A + U_T} P_{GPA} \quad (4-81)$$

With the values of U_T and U_A as given above, one finds that P_S is about 4% lower than P_{GPA} . Since no attempt has been made to calibrate the pressure gage used to measure P_{GPA} , this additional uncertainty is of little consequence.

4.3.4. Spectrometer Operation

4.3.4.1. Tuning

The overall objective in tuning the apparatus is to obtain the maximum electron beam intensity compatible with a given resolution (FWHM of the energy-analyzed electron beam). As yet, we have not been able to devise a step-by-step procedure which will guarantee the realization of this objective. However, by trial and error, a procedure has been developed which usually results in acceptable performance. This procedure is discussed below. Refer to figure 4.3-1 for the designations of the voltages to the various elements and to table 4.3-2 for the definitions of the abbreviations used.

Figure 4.3-1. Schematic diagram of the spectrometer components and voltage supplies. Table 4.3-2 contains the definitions of the abbreviations. The arrows indicate the direction of the electron beam.

TABLE 4.3-2

Abbreviations used for the electron-optical elements, voltages, and currents. The voltage and/or current to each element is labelled in the text by V_{SUB} and/or I_{SUB} , respectively, where SUB is the element abbreviation.

<u>Abbreviation</u>	<u>Designation</u>
C	Cathode (heating current supplied by Kepco 2, voltage supplied by reference voltage supply (RVS)).
AD	Anode. Refer to circuit diagram, fig. 4.2-20.
LVL 1 } LVL 2 } LVL 3 }	Low voltage lenses 1, 2, 3. Refer to circuit diagrams, figs. 4.2-20, 4.2-22, and 4.2-24, respectively.
H 1 } H 2 } H 3 } H 4 }	Herzogs (field matching elements) 1, 2, 3, 4. Refer to circuit diagrams, figs. 4.2-20, 4.2-22, 4.2-24, and 4.2-25, respectively.
OSM	Outer sphere of the monochromator. Refer to circuit diagram, fig. 4.2-21.
OSS	Outer sphere of the selector. Refer to circuit diagram, fig. 4.2-21.
G	Grid. Refer to circuit diagram, fig. 4.2-20.
CVM } CVS }	Center tap on monochromator (CVM) and selector (CVS). Refer to circuit diagram, fig. 4.2-21.
DPA	Deflector plates in anode structure. Refer to circuit diagram, fig. 4.2-20.
DP1	Deflector plates in lens system 1. Refer to circuit diagram, fig. 4.2-22.
DP3	Deflector plates in lens system 3. Refer to circuit diagram, fig. 4.2-25.
FC	Faraday cup collector in scattering chamber (pneumatically operated, see section 4.2.4.5).

TABLE 4.3-2 (Continued)

<u>Abbreviation</u>	<u>Designation</u>
ΔV_M } ΔV_S }	Voltage applied across hemispheres of monochromator (ΔV_M) and selector (ΔV_S). Refer to circuit diagram, fig. 4.2-21.
FD	First dynode of electron multiplier.
V_{SWP}	Voltage applied by sweep circuit. (Voltage between points labelled "OUT" and "RVS" of fig. 4.2-23)
TL 1 } TL 2 }	Tube lenses of lens system 3, fig. 4.2-25.

The apparatus is tuned in essentially four stages:

(1) V_C is set by the reference voltage supply to yield the desired impact energy in the scattering chamber (section 4.3.4.2); AD and LVL 1 are grounded; V_{H1} is set to the desired analyzing voltage (related to E_0 of equation 4-29); the filament power supply (Kepco 2) is turned on (usually 2.3A); and I_{OSM} is maximized by adjusting V_G and V_{DPA} .

(2) Then V_{H2} and V_{CVM} are set equal to V_{H1} ; LVL 2 and DP1 are grounded; and I_{FC} is maximized by adjusting ΔV_M . Next, V_{DP1} then V_{LVL1} , V_{LVL2} , and finally V_{H1} , V_{H2} , V_{AD} , V_G , V_{DP1} , V_{DPA} , and ΔV_M are adjusted for maximum I_{FC} . The optimization of this procedure is complicated by the fact that I_{FC} , as a function of the applied voltages, defines a mathematical hyper-surface with many local maxima. As a result, determining the highest of these is practically impossible.

(3) To tune the second half of the spectrometer, the FC is withdrawn; $V_{SWP} = 0$; LVL 3 and H3 are grounded; and the gear wheel is rotated until the beam current to the outer sphere of the selector is maximized. Then V_{H3} is set equal to V_{CVM} . First V_{LVL3} and then all of the variable stage (1) and (2) controls are adjusted for maximum current.

(4) Next, V_{CVS} and V_{H4} are set equal to V_{CVM} ; TL 1, TL 2, and the deflectors of lens system 3 (DP 3) are grounded; and the current to the first dynode (I_{FD}) of the multiplier is maximized by adjusting first ΔV_S and then all controls in this stage (except

V_{CVM} and V_{SWP}) and stages (1), (2), and (3). A typical set of operating voltages and currents are given in table 4.3-3.

4.3.4.2. Method of sweep

The energy distribution of the beam which has just been maximized in the previous section is obtained by measuring the current (I_{FD}) collected at the multiplier (detector) as a function of the sweep voltage (V_{SWP}). This can be understood as outlined below.

Let the potential of the cathode be V_C volts with respect to ground and the potentials applied to the CVS by the selector control and to the selector control by the sweep control be $+V_{CVS}$ and 0, respectively, with respect to the cathode. Thus, the kinetic energy (K. E.) distribution of the electron beam in the grounded scattering chamber will be peaked at an energy $E_C = |e|V_C$ (in the absence of "contact potentials"). Likewise, electrons of K. E. $E_{CVS} = |e|V_{CVS}$ are transmitted with the highest efficiency by the selector (E_{CVS} corresponds to E_0 of equation 4-29). Since we have adjusted the selector to pass the maximum current, the electrons of K. E. E_{CVS} in the selector are the ones which had a kinetic energy E_C in the scattering chamber. Now, suppose that the sweep voltage is changed from 0 to V_{SWP} volts while all other controls are left unchanged. Electrons of K. E. E_{CVS} in the selector are still detected with the highest efficiency (recall that the electron's orbit through the analyzer depends only on its K. E. if the potential across the hemispheres remains constant), but the electrons which

TABLE 4.3-3

A typical set of voltage and current conditions.

<u>Element</u>	<u>Voltage (Current)</u>	<u>With Respect To</u>
V_{CAT}	-35.00	Ground
V_G	1.00	V_{CAT}
V_A	0	Ground
$V_{LVL\ 1}$	- 5.26	Ground
V_{H1}	2.02	V_{CAT}
V_{CVM}	1.82	V_{CAT}
ΔV_M	1.03	
I_{OSM}	1.3×10^{-6} A	
V_{H2}	1.82	V_{CAT}
$V_{LVL\ 2}$	- 6.24	Ground
I_{FC}	4×10^{-8} A	
$V_{LVL\ 3}$	28.25	V_{SWP}
V_{H3}	5.25	V_{SWP}
V_{CVS}	1.63	V_{SWP}
ΔV_M	.92	
V_{H4}	1.63	V_{SWP}
V_{TL1}	35.00	V_{SWP}
V_{TL2}	265	Ground
V_{FD}	265	Ground

had K. E. E_C in the scattering chamber now have K. E. $E'_{CVS} = E_{CVS} + |e|V_{SWP}$ in the selector. However, electrons of K. E. $E'_C = E_C - |e|V_{SWP}$ in the scattering chamber will have the proper K. E. (E_{CVS}) to be detected with greatest efficiency. As a result, the current measured at the detector for a given value of the sweep voltage V_{SWP} is due to electrons of K. E. $E'_C \pm \delta E$ in the scattering chamber where δE depends on the resolution of the selector. Electrons losing a portion W of their K. E. through inelastic collisions with the target molecules will be detected with peak efficiency when $|e|V_{SWP} = W$. Thus, a plot of current reaching the detector versus sweep voltage will yield an energy-loss spectrum in which the elastic processes appear as a peak at 0 volts and each inelastic process appears as a peak at $V_{SWP} = W/|e|$ volts. Since we are in effect measuring directly the difference between the incident and scattered electron K. E. (and not the actual magnitude), the contact potentials which render the value of E_C uncertain to within 1 or 2 eV cancel out.

4.3.4.3. Method of detection

If the direct or low-angle elastically scattered beam is to be measured, the signal level is usually high enough for the first dynode of the multiplier to be used as a faraday cup collector in conjunction with a Cary, model 31, vibrating reed electrometer. Otherwise, the energy-analyzed scattered beam is detected by using the electron multiplier with suitable pulse counting equipment, as shown in figure 4.2-26.

With approximately 4.5 K. V. across the multiplier resistor string, an electron with a K. E. of about 200 eV striking the 1st dynode produces several secondary electrons which are accelerated to the second dynode, etc., producing a relatively narrow (in time) pulse at the 20th dynode containing 10^7 to 10^8 electrons. This "charge" pulse is transmitted by the 100 $\mu\mu\text{f}$ blocking capacitor, converted to a voltage pulse by the nuvistor preamplifier, amplified by the double delay line amplifier, and routed into the single channel pulse height analyzer (SCPHA). The latter has variable threshold and window controls for an adjustable pulse height discrimination. If the input pulse has an amplitude greater than the threshold voltage setting and less than the threshold plus window voltage, a standard output pulse (50 η sec rise time, 10 V peak, 0.5 μ sec duration) is generated. If the input pulse does not satisfy both of the above criteria, no output pulse is generated. In this way, low-level (amplifier noise, pick-up, stray electrons) and high-level (cosmic ray) pulses can be eliminated. The output pulses from the SCPHA (typically one output pulse for each electron striking the first dynode of the multiplier) can then be counted by the count-rate-meter (CRM) or the Nuclear Data 1024 channel scalar (MCS).

The CRM converts these pulses into a D. C. current proportional to the average count-rate. If the measured count-rate (number of counts/sec) is N , then from the statistical nature of the counting process the uncertainty in N (one standard deviation) is $\sqrt{N/\tau}$ where τ is the time constant (variable from 0.5 to 50 sec)

of the CRM. Thus, for low signal levels (low count-rates) τ must be made relatively large for a reasonable "statistical" accuracy.

The CRM generates an output D. C. voltage that is directly proportional to the input count-rate (current) which can be used to drive the Y axis of an X-Y recorder.

The MCS, on the other hand, adds all of the pulses reaching it within a certain time interval into a designated channel of its memory. If the number of counts stored in this channel is M , the statistical uncertainty is simply $\sqrt{M}$. For lower count-rates, one must use a longer counting time in each channel to increase the relative precision of the measurement. The number of counts stored in each channel of the memory can be displayed on an oscilloscope, X-Y recorder, or punched paper tape.

4.3.4.4. Sweep-signal correlation

It has already been noted in section 4.3.4.2. that the value of the sweep voltage determines the energy-loss being detected. The variation of this sweep voltage can be obtained in two quite different ways (refer to fig. 4.2-23).

If the CRM is being used, the sweep is provided by the ramp-function output of an Exact, type 251, function generator (with an additional $10\mu\text{f}$ capacitor to reduce the lowest standard sweep-rate by a factor of 10). The PAR is used to set the voltage at which the sweep is to start. The total sweep voltage (PAR + FG) is applied simultaneously to the X axis of the recorder and to the spectrometer (as indicated in fig. 4.2-19). Since the Y axis of

the recorder is driven by the CRM output, a plot of the count-rate versus the energy-loss will be obtained directly. The relation of this count-rate to the differential scattering cross-section is discussed in section 4.4.

However, if the MCS mode of operation is used, the sweep voltage is provided by the MCS itself and is correlated to the signal as outlined below (refer to fig. 4.2-23(b)).

The output of the SCPHA is connected to the memory (ND-M) unit of the Nuclear Data system, and the pulses are counted into one of the 1024 channels. The digital-to-analog converter (ND-DAC) samples the channel number into which counts are being stored, and converts it to an analog voltage which is directly proportional to the channel number. This voltage is amplified by the ND-AMP and applied to the spectrometer as indicated in fig. 4.2-19. The time base generator (ND-TB) advances the channel number into which counts are stored by one after a preset time interval (dwell time). The ND-DAC and ND-AMP, in turn, apply a higher voltage (corresponding to the higher channel number) to the spectrometer. In this way, each channel of the memory stores counts which are correlated with a specific value of the sweep voltage (and energy-loss). Since the dwell time in each channel is the same, a plot of the number of counts in each channel versus that channel number corresponds to the count-rate versus energy-loss at a set of 1024 points.

The MCS mode of operation has one very significant advantage over the CRM mode when low count-rates are to be recorded. As noted previously (section 4.3.4.3), for the detection of low level signals by the CRM, τ must be relatively long, and, hence, the sweep rate must be very slow. Since the collection of the last part of the spectrum will occur so long after that of the first, a relatively slow drift in the beam intensity, sample pressure, or collection efficiency can cause an appreciable distortion in the energy-loss spectrum.

On the other hand, the MCS mode can be used to sweep through the entire energy-loss spectrum repetitively and quickly compared to "instrumental" drift (collecting very few counts in each channel, of course). In this way, the relative peak heights within the energy-loss spectra will not be distorted by instrumental changes, and the "statistical" accuracy can be improved by adding the counts from many sweeps. Appendix II gives a more detailed list of the MCS specifications and operation.

4.3.5. Obtaining a Spectrum

(1) The spectrometer is tuned and the gas sample is introduced into the scattering chamber as discussed in sections 4.3.4.1 and 4.3.3., respectively.

(2) The scattering angle is changed to $\sim 40^\circ$, the multiplier high voltage and detector electronics are turned on, and the spectrometer is retuned on the elastic peak.

(3) The instrument is allowed to stabilize for about 2-8 hours, depending on the measured elastic peak drift.

(4) The desired scattering angle is set, the PAR (fig. 4.2-23) is set to the desired initial energy-loss, the voltage sweep is initiated, and the energy-loss spectrum is registered on the X-Y recorder or in the MCS memory.

4.4. Performance

4.4.1. Vacuum Characteristics

The mercury diffusion pump (section 4.2.1) is rated at a pumping speed of 1500 litre/sec (for air). However, due to the baffle, cold trap, and tubing between it and the main vacuum chamber, the pumping speed at the chamber is significantly reduced. It was calculated in the usual way⁽¹¹³⁾ to be 400 ± 50 litre/sec. in the vicinity of the spectrometer. The effective pumping speed can also be determined experimentally by measuring the pressure differential between the scattering chamber and main chamber.

From the definitions and equation (4-79) of section 4.3.3,

$$S_{MC}P_{MC} = U_A(P_S - P_{MC}), \quad (4-82)$$

in which S_{MC} is the effective pumping speed at the main vacuum chamber. Since $P_{MC} \ll P_S$;

$$S_{MC} \approx U_A P_S / P_{MC} . \quad (4-83)$$

U_A is known (approximately) and P_{MC} was measured for various values of P_S . From the average value of P_S/P_{MC} and U_A ,

$$S_{MC} \approx 375 \text{ litre/sec} .$$

The pressure in the main chamber must be less than 2×10^{-6} torr for satisfactory operation of the spectrometer. This means that the maximum allowable sample pressure in the scattering chamber (with the present aperture dimensions and pumping speed) is about .010 torr.

4.4.2. D.C. Collector Efficiency

There are basically four elements of the spectrometer which are used routinely for D.C. current collection to assess the instrument performance--the outer spheres of the monochromator and selector, the first dynode of the multiplier, and the faraday cup in the scattering chamber. The first two of these were found to have a collection efficiency for electrons of K. E. 20 eV or higher of over 90% when the current to them was measured to ground (that is, the electrometer was connected directly between the element and ground). The efficiencies of the last two, however, exhibited pronounced dependencies on a bias voltage applied between the electrometer and ground. A typical result is shown in figure 4.4-1 for the collection of electrons with a K. E. of 35 eV by the faraday cup. This result is dependent on the beam kinetic energy and varied from 33% to 85% at 0 bias. The behavior of the first dynode was quite similar. Thus, these collectors were operated at a holding voltage sufficient

Figure 4.4-1. Collection efficiency of the scattering chamber faraday cup as a function of bias voltage. The incident beam energy and current were 35 eV and 1.2×10^{-9} A, respectively. 100% current collection was assumed at a 60 volt bias.

to collect more than 95% of the incident current.

4.4.3. Electron Beam Characteristics

4.4.3.1. Energy distribution from the gun

As a preliminary test of the operation of the gun and monochromator, the electron kinetic energy distribution leaving the gun was measured. The experimental procedure was as follows:

(1) A simple sweep circuit consisting of a battery and voltage divider (10 turn Helipot) was inserted between CVM and P1 (refer to figure 4.2-21). Herzogs number 1 and 2 were connected directly to CVM.

(2) The gun and monochromator were tuned for maximum current to the scattering chamber faraday cup (FC) with this sweep voltage equal to 0. The anode and deflectors DPA and DP 1 (fig. 4.3-1) were grounded.

(3) The current to FC (Y-axis) was measured as a function of the sweep voltage (X-axis) on an X-Y recorder with all other controls unchanged. In effect, the electron energy distribution entering the monochromator was measured with a constant resolution which was determined by observing the selector output.

If $f(E)$ is the "true" electron energy distribution, i. e., the current per unit energy carried by electrons of kinetic energy E and $g(E)$ is the intrinsic line shape of the monochromator (assumed to be Gaussian, refer to section 4.1), then the measured current distribution at FC will be

$$I(E) = \int_{-\infty}^{\infty} g(E - x) f(x) dx \quad (4-84)$$

in which E is numerically equal to the sweep circuit voltage plus an unknown constant (due to contact potentials).

If we make the usual assumptions inherent in the "free-electron" theory of metals (see reference (94b) and (114), for example), the rate at which electrons within the metal with momenta between $\underline{p}$ and $\underline{p} + d\underline{p}$ strike a unit area of the surface is

$$dR = \frac{2}{mh^3} \frac{p_z dp_x dp_y dp_z}{\exp\left\{\frac{W - E_f}{kT} + 1\right\}} \quad (4-85)$$

The metal surface defines the xy plane of the coordinate system. W is the electron kinetic energy in the metal ($W = p^2/2m$) and E_f is the Fermi energy. In the absence of an external electric field, only those electrons which possess a momentum in the z direction such that

$$p_z^2/2m > W_f + E_f = W_a, \quad (4-86)$$

where W_f is the work function of the metal, can escape. Since W_f/kT is generally $\gg 1$, the emission current density dJ_z normal to the surface is given approximately by:

$$dJ_z = \frac{2ep_z^3}{mh^3} e^{-(W-E_f)/kT} dp_x dp_y dp_z \quad (4-87)$$

when (4-86) is satisfied and dJ_z equals 0 otherwise.

Nottingham⁽¹¹⁵⁾ found that a "reflection coefficient", presumably at the metal surface, of the form

$$r(p_z) = e^{-[(p_z^2/2m - W_a)/w]} \quad (4-88)$$

(in which w is an experimental parameter equal to 0.191 eV) was required to best represent his careful retarding-potential measurements on tungsten and thoriated tungsten. Also, Hutson⁽¹¹⁶⁾ found this reflection coefficient with the same value of w to be adequate in fitting his direct measurements of the electron kinetic energy distributions from single crystals of tungsten.

It should be noted that such a reflection function is not compatible with our present understanding of the image-force potential model of the potential barrier at the metallic surface. For example, a typical result of Belford, et al.⁽¹¹⁷⁾ obtained by numerical integration of the Schrödinger equation for various image-force potentials is shown in figure 4.4-2 along with the experimentally derived result. The discrepancy between Nottingham's curve (N) and Belford's curve (B) may be due to a number of things, such as surface contamination and irregularities, and crystal lattice effects. The experimental situation is further complicated by the possibility of potential drops across the filament (cathode) and anomalous energy spreading⁽¹¹⁸⁾.

Leaving the resolution of these problems to future investigators, let us proceed by incorporating a transmission function

Figure 4.4-2. Schematic representation of the image-force-potential (IFP) at the metal surface and the fraction transmitted (F) according to reference (117) (B) and reference (115) (N). W_f and E_f are 4 eV and 6 eV, respectively. The potential energy scale $V(z)$ is simply $p_z^2/2m - 10$ eV. The dashed line continuation of the IFP line is the "bend over" which arises from draw-out electric fields. The resulting barrier is presumably responsible for quantum mechanical reflection. z measures the distance from the metal surface (S).

$$F = 1 - \text{Ar}(p_z) \quad (4-89)$$

in equation (4-87). If $A = 0$, F is a good approximation to the image-force-potential transmission function, while if $A = 1$, F is equivalent to the transmission function employed by Nottingham and Hutson.

The multiplication of (4-87) by (4-89) and conversion of the result to a distribution in laboratory kinetic energy E yields

$$dJ = \frac{8\pi me}{h^3} e^{-(E + W_f)/kT} (E + W_a) H(E) dE \quad (4-90)$$

after integration over φ and θ (noting relation (4-86)). In (4-90), $E = W - W_a$ and

$$\begin{aligned} H(E) &= \frac{1}{2} \int_{W_a/W}^1 [1 - A e^{-(Wx^2/w - W_a/w)}] dx \\ &= \frac{1}{2} \left(\frac{E}{E + W_a} \right) \left[1 - \frac{Aw}{E} (1 - e^{-E/w}) \right] \end{aligned}$$

Consequently, $f(E)$ of equation (4-84) is

$$f(E) = C E^{-E/kT} \left[1 - \frac{Aw}{E} (1 - e^{-E/w}) \right] \quad (4-91)$$

where C is a constant depending on the work function and temperature but not on E or w . If $g(x)$ of equation (4-84) is assumed to be of the form e^{-x^2/a^2} , then performing the integration indicated by (4-84) yields

$$\begin{aligned} I(E) &= D e^{-E/kT} \left\{ (aB_1 - w)(1 + \text{erf } B_1) + \frac{a}{\sqrt{\pi}} e^{-B_1^2} \right. \\ &\quad \left. + Aw(1 + \text{erf } B_2) \exp(-E/w + a^2/4w^2 + a^2/2wkT) \right\} \end{aligned} \quad (4-92)$$

where $B_1 = E/a - a/2kT$

$$B_2 = B_1 - a/2w$$

and D is a suitable normalization constant. Notice that for values of E large compared to kT , a , and w ,

$$I(E) \sim 2DE e^{-E/kT} \quad (4-93)$$

The effects of reflection (w, A) and finite resolving power (a) will become negligibly small. Further, a plot of $\ln I(E)$ versus E in the region where (4-93) is valid should be nearly a straight line of slope $-1/kT$.

The experimental energy distribution obtained from the tungsten hairpin cathode used in the present research is given in figure 4.4-3. The FWHM of the distribution is .63₅ eV. If (a) and (A) were 0, this half-width would imply a cathode temperature of 2900°K. The high energy tail is nearly a straight line (as expected) but its slope gives a cathode temperature of only 2560°K. This indicates that the shape in the low energy region of the curve has been distorted--possibly due either to the "reflection function" or anomalous energy broadening⁽¹¹⁸⁾.

With the latter value of the temperature, $A = 1$, and a resolution of .07 eV, equation (4-92) was used to calculate the expected current distribution for $w = .19$ eV (solid line of figure 4.4-3). w can be changed by $\pm .02$ eV before significant deviations from the experimental points are evident. The curve with $A = 0$ is shown for comparison (dashed line of fig. 4.4-3). The calculated

Figure 4.4-3. Electron kinetic energy distribution from the gun.

The circles are experimental points for a primary beam energy of 35 eV and an analyzing energy of 5.0 eV. The FWHM of the monochromator output (as measured by the selector) was .07 eV. The solid curve is the calculated distribution assuming the reflection function of references (115, 116) with $w = 0.19$ eV. The dashed curve is the calculated distribution assuming no reflection. The cathode temperature, as determined from the slope of the high energy ($E > 1.25$ eV) tail is 2560°K .

distribution is normalized to the experimental one by assuming that the experimental points on the high energy side coincide with the calculated curve and the origin of E is determined as the point on the low energy side of the distribution where the slope is characteristic of the analyzer. Note that the position of the dashed curve is fixed with respect to that of the solid one.

The good agreement of this result with those of Nottingham and Hutson seems to preclude the importance of surface effects in view of the quite different surface preparation in the present case (none). Also, it is doubtful that the energy broadening associated with dense beams⁽¹¹⁸⁾ is important since beam currents leaving the gun are only about 2 μ A.

In summary, we can only conclude that the situation with regard to an "expected" energy distribution is indeed confusing and requires further study.

4.4.3.2. Angular divergence

Since the angular resolution of the exit end of the scattering chamber has been designed to be comparable to that of the incident beam, it is not possible to measure them separately. However, an effective overall angular resolution for the system can be determined simply by measuring the current reaching the first dynode of the multiplier as a function of the rotation angle of the gear wheel, with the scattering chamber evacuated. This has been done under many conditions. Two such profiles obtained under different beam conditions (but the same aperture geometry) are shown in figure 4.4-4.

Figure 4.4-4. Effective angular profiles of the electron beam at the scattering chamber. The current is measured at the 1st dynode of the multiplier as a function of the mechanical rotation angle of the gear wheel.

	Curve A	Curve B
Incident beam energy	50 eV	30 eV
Peak current (1st dynode)	1.2×10^{-9} A	1.7×10^{-9} A
FWHM (energy distribution)	0.10 eV	0.10 eV
FWHM (angular distribution)	1.6°	2.0°
Base width (angular distribution)	5°	6°
Apertures used	Discussed in section 4.2 (same for both)	

Note that the shapes are nearly Gaussian but that the peaks occur at angles significantly different from mechanical 0° . (Mechanical 0° is the angle for which a direct "line-of-sight" was obtained through the scattering chamber and the apertures of lens systems 1 and 2. It is not possible to "see" through the chamber at a mechanical rotation angle greater than $\pm 1\frac{1}{2}^\circ$.)

The effect of magnetic fields on the mechanical rotation angle of the direct beam was tested by using the Helmholtz coils to vary the residual field in both magnitude (from near $\lesssim 5$ m gauss to 100 m gauss) and direction (maximum field component along the X, Y, or Z coil-pair axis as well as several positions in between). Although the peak angle could be changed by $\sim 5^\circ$, the peak symmetry was destroyed. Also, the resolution and beam current were drastically affected (unfavorably). When the residual magnetic field was ~ 5 m gauss or less, I_{FC} was found to be independent of rotation angle (as expected) from $0^\circ - 85^\circ$. However, if the residual field was varied by enough (~ 20 m gauss) to change the beam angle by as much as 1° , I_{FC} was observed to change by 15% or more over the same angular range.

This effect (direct beam angle different from mechanical 0°) seems to be an electron-optical one. The angle of entrance into the scattering chamber is defined in part by aperture A4 but also by the position of the beam leaving the monochromator and the deflector plate voltages (fig. 4.2-8). Indeed, the angle for maximum beam current through the scattering chamber was found to depend strongly ($\pm 5^\circ$) on these controls.

As a result, all scattering measurements were made at mechanical rotation angles below 0° as well as above. The 0° scattering angle was then defined as the angle about which the particular process was symmetric.

It is also of interest to assess what effect the angular resolution will have on the measurement of differential scattering cross sections (DCS). Suppose the instrument is set at a scattering angle θ_0 . The true DCS can be expanded in a Taylor series about this angle as

$$\begin{aligned} \sigma(\theta) = & \sigma(\theta_0) + \left(\frac{\partial \sigma}{\partial \theta}\right)_{\theta_0} (\theta - \theta_0) + \frac{1}{2} \left(\frac{\partial^2 \sigma}{\partial \theta^2}\right)_{\theta_0} (\theta - \theta_0)^2 \\ & + \frac{1}{6} \left(\frac{\partial^3 \sigma}{\partial \theta^3}\right)_{\theta_0} (\theta - \theta_0)^3 + \text{order } (\theta - \theta_0)^4 \end{aligned} \quad (4-94)$$

If a Gaussian angular acceptance function of FWHM = $\Delta\theta_{\frac{1}{2}}$ is assumed, the measured cross section at θ_0 will be

$$\sigma_{\text{EXP}}(\theta_0) = \frac{1}{\sqrt{\pi} A} \int_{-\infty}^{\infty} e^{-(\theta - \theta_0)^2 / A^2} \sigma(\theta) d\theta \quad (4-95)$$

where

$$A^2 = \frac{\Delta\theta_{\frac{1}{2}}^2}{4 \ln 2}$$

Substitution of (4-94) into (4-95) and integration yields

$$\begin{aligned} \sigma_{\text{EXP}}(\theta_0) = & \sigma(\theta_0) + \frac{1}{4} A^2 \left(\frac{\partial^2 \sigma}{\partial \theta^2}\right)_{\theta_0} \\ & + \text{order } A^4 \left(\frac{\partial^4 \sigma}{\partial \theta^4}\right)_{\theta_0} \end{aligned} \quad (4-96)$$

As one would expect, if the curvature of the DCS $(\frac{d^2\sigma}{d\theta^2})$ is small compared to the FWHM of the beam profile (in angle), the shape of the experimental cross section will agree with that of the true one.

Let us consider a specific example. Simpson, et al.⁽³¹⁾ have measured the relative DCS for the $1^1S \rightarrow 2^1P$ excitation in helium with an angular resolution of less than 1° and a beam energy of 56.5 eV. This cross section varies about as rapidly with angle as the steepest ones measured in this research. The maximum curvature occurs at about $\theta_0 \approx 22^\circ$ and, in terms of the value of the cross section at that angle,

$$\left(\frac{\partial^2 \sigma}{\partial \theta^2}\right) \approx .024 \sigma(22^\circ) \text{ per (degree)}^2.$$

Thus, with $\Delta\theta_{\frac{1}{2}} = 2^\circ$, equation (4-96) implies that

$$\sigma_{\text{EXP}}(22^\circ) \approx 1.009 \sigma_s(22^\circ)$$

where $\sigma_s(22^\circ)$ is the value for the relative cross section obtained by Simpson⁽³¹⁾. This is a negligible distortion.

4.4.3.3. Line shape

The expected line shape from the monochromator (that is, the energy distribution of the electron beam after one energy analysis) has been previously discussed in section 4.1. Equation (4-39) has been used to calculate the line shape for several different values of the parameters involved. The resulting line shapes were then

compared with Gaussians of the same FWHM. Such a comparison is shown in figure 4.4-5 in which the solid line is the Gaussian and the circles are the calculated (equation (4-39)) values. As expected, the agreement is quite good. However, this line shape cannot be compared directly with experimental energy distributions as measured at the first dynode since a second analyzer (selector) with the same intrinsic line shape is used to measure them. Consequently the convolution of the line shape with itself should be used for the comparison. Since this is a rather tedious problem in numerical integration and since a simple Gaussian function seems adequate, the convolution of two Gaussians (which is Gaussian itself, as shown in appendix I) can be compared with experiment. Figure 4.4-6 shows such a comparison in which the solid line is a Gaussian of the same FWHM as the experimental data (circles). Again, the agreement is reasonably good.

4.4.3.4. Current versus resolution

Since the electron energy distribution from the gun (section 4.4.3.1) and the line shape of the monochromator (section 4.4.3.3) have already been determined, it is possible to estimate the current I_s one should expect at the scattering chamber. If, for mathematical simplicity, it is assumed that the monochromator passes a "slice" (of $\text{FWHM} = \Delta E_{\frac{1}{2}}$) of the current distribution of equation (4-91) centered at the peak position of that distribution, then

Figure 4.4-5. Comparison of the line shape calculated according to equation (4-39) (circles) and a simple Gaussian of the same FWHM (solid line). The parameters used in equation (4-39) were $E_0 = 10$ eV, $a = b = .012''$, $R_0 = 1''$.

Figure 4.4-6. Comparison of the electron beam energy distribution as measured on the first dynode of the multiplier with a Gaussian of the same FWHM. 35 eV incident beam energy, 1.3×10^{-9} A peak current. The peak position is defined as 0 energy-loss.

$$I_S(\Delta E_{\frac{1}{2}}, kT) \approx \frac{I_0}{(kT)^2} \left(1 + \frac{w}{kT}\right) \int_{E_0 - \frac{\Delta E_{\frac{1}{2}}}{2}}^{E_0 + \frac{\Delta E_{\frac{1}{2}}}{2}} E e^{-E/kT} \left[1 - \frac{w}{E} (1 - e^{-E/w})\right] dE \quad (4-97)$$

in which T is the cathode temperature in $^{\circ}\text{K}$, I_0 is the total current entering the monochromator, w is the reflection parameter and E_0 is the peak of distribution (4-91). Since the cathode was ordinarily operated under the same conditions as those represented in figure 4.4-3, it will be assumed that the parameters associated with this figure may be used in (4-97), i. e., $E_0 \approx 0.40$ eV, $kT \approx 0.22$ eV, and $w \approx 0.19$ eV. Integration of (4-97) yields

$$\begin{aligned} \frac{I_S}{I_0} = & 2\left(1 + \frac{w}{kT}\right) e^{-E_0/kT} \left[\left(1 + \frac{E_0 - w}{kT}\right) \sinh\left(\frac{\Delta E_{\frac{1}{2}}}{2kT}\right) \right. \\ & + \frac{w^2}{(kT)^2} \frac{e^{-E_0/w}}{\left(1 + \frac{w}{kT}\right)} \sinh\left[\frac{\Delta E_{\frac{1}{2}}}{2} \left(\frac{1}{kT} + \frac{1}{w}\right)\right] \\ & \left. - \frac{\Delta E_{\frac{1}{2}}}{2kT} \cosh\left(\frac{\Delta E_{\frac{1}{2}}}{2kT}\right) \right] \end{aligned} \quad (4-98)$$

Figure 4.4-7 shows the behavior of (4-98) for the parameter values indicated above. Some typical values actually obtained for this ratio are also plotted in the figure for comparison. Table 4.4-1 gives the experimental conditions under which these data were taken. The measured fraction is considerably below the expected one. This same kind of behavior has been observed by Simpson⁽²⁴⁾. Also, the current obtained at the scattering chamber is a steep function of

Figure 4.4-7. Fraction of the current entering the monochromator which gets into the scattering chamber. $\Delta E_{\frac{1}{2}}$ is the FWHM associated with the monochromator (FWHM as measured by the selector times 0.7). The solid curve was calculated according to equation (4-98). The circles are experimentally determined by measuring the ratio of current to the faraday cup to that leaving the gun (refer to table 4.4-1 for the operating conditions). (0.001) refers to the ordinate of the indicated point.

TABLE 4.4-1

Operating conditions for the data presented in figure 4.4-7. The spectrometer construction details are in section 4.2. The electron-optical element voltage abbreviations have been defined in table 4.3-2.

V_{RVS} (volts)	-25	-35	-35	-65
Current into monochromator (μA)	1.0	1.3	1.5	2.2
V_{CVM} (volts)	1.5	3.0	3.0	4.5
$\Delta E_{\frac{1}{2}}$ monochromator (m eV)	.03	.07	.14	.21
Current into scattering chamber (μA)	.001	.033	.27	.51

$\Delta E_{\frac{1}{2}}$. Figure 4.4-8 shows this current (curve T) for the same type of conditions under which the experimental ratios of figure 4.4-7 were determined. Curve M represents the maximum values yet observed. Maximum values reported by Kuyatt and Simpson⁽²⁵⁾ and Meyer, et al.⁽²¹⁾ are shown for comparison. Both of these investigators used double-hemispherical analyzers but with different dimensions and different energies of operation. The former authors used analyzers of 1" mean radii and analyzing energies of ~ 5 eV while the latter ones used analyzers of 5" mean radii and ~ 200 eV analyzing energies. The maximum values we obtain compare favorably with these investigators. Also, the overall second stage collection efficiency ($\sim .10$) defined as I_{FD}/I_{FC} , compares well with that reported by Kuyatt⁽²⁵⁾ ($\sim .08$).

4.4.3.5. Contact potential

The electron beam kinetic energy E in the scattering chamber differs from eV_c by an "effective contact potential energy" $e\bar{V}_c$, on the order of 1 or 2 eV⁽²⁴⁾. Since the contact potential between the monochromator and scattering chamber is negligible⁽¹¹⁹⁾ (tens of mV) on this scale, the full effect of $\bar{V}_c$ will be apparent in the monochromator. $\bar{V}_c$ includes the offset between the peak of the electron energy distribution and the zero of energy at the center tap of the cathode ($\sim .4$ eV), IR drops in the cathode circuit, and the true "contact potential between the monochromator and the hot tungsten filament"⁽²⁴⁾.

Figure 4.4-8. The variation of beam current into the scattering chamber with the resolution of the monochromator. The solid curve (T) was obtained under the conditions of fig. 4.4-7, the solid curve (M) represents values we obtained, the ($\diamond$) values are reported in reference (25); and the ($\square$) values are the maximum ones reported in reference (21). $\Delta E_{\frac{1}{2}}$ is the FWHM of the monochromator (FWHM as measured by the selector times 0.7).

From equation (4-19), the voltage across the spheres ΔV and the kinetic energy E_0 of an electron which will describe a circular orbit of radius R_0 are related by $E_0 = q\Delta V \left(\frac{R_2}{R_1} - \frac{R_1}{R_2} \right) = 1.91 q\Delta V$ (in this case $R_1 = .875''$, $R_2 = 1.125''$). The true electron K.E. in the monochromator will be $qV_{CVM} + q\bar{V}_C$. Thus,

$$\bar{V}_C = 1.91 \Delta V - V_{CVM} \quad (4-99)$$

Since ΔV and V_{CVM} are known applied voltages, $\bar{V}_C$ is determined. (Note that for a given V_{CVM} , ΔV is the voltage needed to maximize the current to the scattering chamber.) Values of $\bar{V}_C$ from .02 V to 2.3 V have been observed (usually they are ~ 1 V as determined by (4-99)).

4.4.3.6. Resolution versus analyzing energy

From equation (4-29) the resolution of the monochromator should vary as

$$\Delta E_{\frac{1}{2}} \approx .01 E_0 \quad (4-100)$$

if the angular terms are negligible and the apertures are imaged properly by the lens systems. Figure 4.4-9 shows a comparison between the calculated resolution according to (4-100) (solid line) and the measured resolution (circles) of the monochromator. The effective contact potential has been incorporated into E_0 . For this measurement $V_{H1} = V_{H2} = V_{CVM}$ and $V_{LVL1} = V_{LVL2} = 0$ with respect to ground. In this way the lenses which image the beam into the monochromator and scattering chamber should perform as

Figure 4.4-9. Variation of the resolution with the electron kinetic energy in the analyzer. $\Delta E_{1/2}$ is the FWHM associated with the monochromator. E_0 includes the "effective contact potential" discussed in section(4.4.3.5). The solid line is calculated according to (4-100) and the circles are experimentally determined under the conditions described in the text.

initially intended. Also, the voltage ratio V_{RVS}/V_{CVM} was kept constant at about 10. The agreement is reasonably good. However, it should be noted that the beam currents into the scattering chamber obtained under these conditions were about a factor of 5 below those labelled typical in figure 4.4-8. The independent variation of V_{H1} , V_{H2} , V_{LVL1} , and V_{LVL2} evidently changes the effective image sizes which determine the monochromator resolution. It was found (see table 4.4-1) that, for a given resolution, a higher V_{RVS}/V_{CVM} ratio (~ 15) coupled with changes in the voltages above produced more intense beams than V_{RVS}/V_{CVM} ratios of about 10 with or without offsetting V_{H1} , V_{H2} , V_{LVL1} , and V_{LVL2} .

4.4.4. Relation of the Differential Scattering Cross Section to the Scattered Signal

4.4.4.1. Calculation

As previously stated, it is one of the aims of these experiments to obtain differential scattering cross sections for various molecular excitations. Thus, it is essential to relate the final signal (at the multiplier) to the cross section.

Consider the configuration depicted in figure 4.4-10. In order for an electron to get through S (and have any chance of being detected) after a single scattering event, it must scatter while in volume $V(\theta)$ at an appropriate angle χ near θ . If I_0 is the total beam intensity entering the scattering chamber containing the target gas at a density ρ , the unscattered beam I_u reaching the scattering volume is given by

Figure 4.4-10. Schematic diagram of the incident and scattered beam configuration at a scattering angle of θ ($\sim 45^\circ$). L_1 and L_2 are the distances from the scattering center to A4 and A5, respectively. $V(\theta)$ is the volume in which single scattering events must occur if they are to be detected.

$$I_u \cong I_o e^{-\bar{Q}(E_o)\rho L_1} \quad (4-101)$$

in which $\bar{Q}(E_o)$ is the average total scattering cross section for electrons in the beam and L_1 is the distance from aperture A4 to the scattering center.

$$\bar{Q}(E_o) \equiv \int_{-\infty}^{\infty} f(E_o - E) Q(E) dE \quad (4-102)$$

where $Q(E)$ is the total cross section for all scattering processes for electrons of kinetic energy E and $f(E_o - E)$ is the incident beam energy distribution, normalized to unity and peaked at E_o .

Equation (4-101) is only approximately correct since different parts of the electron beam have different electron densities and travel different distances. Nevertheless, it is probably a very good approximation in this case.

The current $i_{SC}dE$ per unit solid angle and energy-loss due to electrons with incident energies E to $E + dE$, which scatter in this volume at an angle χ after losing an energy W is

$$i_{SC}dE \cong I_u \frac{V(\theta)}{A} \sigma(E, W, \chi) \rho f(E_o - E) dE \quad (4-103)$$

where $\sigma(E, W, \chi)$ is the DCS per unit solid angle and energy-loss for the particular process, and A is the cross-sectional area of the beam at the scattering center.

Since the scattered beam is attenuated approximately by a factor $e^{-\rho \bar{Q}(E_o - W)L_2}$ before reaching A5, the current $I_{SC}dE$ per unit energy-loss leaving the scattering chamber through aperture S

is then

$$I_{SC} dE \cong e^{-\rho \bar{Q}(E_0 - W)L_2} dE \int_{\Omega} i_{SC} d\Omega, \quad (4-104)$$

in which the Ω integration is over the range of angles accepted by the exit aperture system.

Assume that the selector is tuned to pass electrons that have lost an energy W with an efficiency $\epsilon_S(W)$. The current actually detected is then

$$I_D \cong \int_E \int_W \epsilon_1 \epsilon_S \epsilon_2 \epsilon_3 I_{SC} dE dW, \quad (4-105)$$

in which ϵ_1 is the fraction of electrons leaving S which reach the selector, ϵ_2 is the fraction of electrons through A6 (refer to fig. 4.2-12) which reach the first dynode of the multiplier, and ϵ_3 is the fraction of electrons hitting the first dynode which are actually counted. The integration is over all E and W (the distributions $f(E_0 - E)$ and $\epsilon_S(W)$ are sharply peaked, thus limiting the effective range of this integration). Notice that the sweep voltage V_{SWP} is assumed constant. $\epsilon_S(W)$ can be written more explicitly as

$$\epsilon_S(W) = \epsilon_S^0(E_{SWP}) e^{-(E_{SWP} - W)^2 / \Delta^2}$$

where Δ is related to the selector resolution, $E_{SWP} = |e|V_{SWP}$, and $\epsilon_S^0(E_{SWP})$ is the fraction of electrons entering the analyzer after suffering the energy-loss $W = E_{SWP}$ which actually pass through A6.

Combining equations (4-101) through (4-105) we obtain:

$$\begin{aligned}
 I_D \cong I_o \frac{V(\theta)}{A} p e^{-\rho \bar{Q}(E_o) L_1} \int_W \int_E \int_{\Omega} \\
 \times [\epsilon_1 \epsilon_2 \epsilon_3 \epsilon_S(W) f(E_o - E) \sigma(E, W, \chi)] \\
 \times [e^{-\rho \bar{Q}(E_o - W) L_2} d\Omega dE dW] \quad (4-106)
 \end{aligned}$$

$f(E_o - E)$ is a narrow enough distribution (FWHM $\approx .07$ eV) so that variations in electron-optical properties (ϵ_1 , ϵ_2 , ϵ_3 , and ϵ_S^0) and the variations in $\sigma(E, W, \chi)$ over the range of E for which f is appreciable are negligible in the absence of resonances⁽¹²⁰⁾.

The range of acceptance angles (Ω) is small enough in most cases (section 4.4.3.2) so that $\sigma(E, W, \chi)$ can be removed from the Ω integral as well as the E one and be replaced by $\sigma(E_o, W, \theta)$.

$\bar{Q}(E_o - W)$ and the various electron-optical effects vary slowly enough with W that they may be assumed constant over the range of $\epsilon_S(W)$ (about .07 eV also).

The application of the approximations discussed above and the ideal gas law to convert ρ to a sample pressure P reduce equation (106) to

$$I_D(E_{SWP}, \theta) \cong \frac{I_o V(\theta)}{A k T} \Delta \Omega P e^{-P/P_o} \epsilon(E_{SWP}) \bar{S}(E_o, E_{SWP}, \theta) \quad (4-107)$$

with

$$\Delta \Omega \equiv \int_{\Omega} d\Omega \text{ (the acceptance solid angle defined by A5)}$$

and S),

$$\bar{S}(E_0, E_{SWP}, \theta) \\ \equiv \frac{1}{\sqrt{\pi} \Delta} \int_W \sigma(E_0, W, \theta) e^{-[E_{SWP} - W]^2 / \Delta^2} dW ,$$

$$\epsilon(E_{SWP}) \equiv \epsilon_1 \epsilon_2 \epsilon_3 \epsilon_S^0 \sqrt{\pi} \Delta$$

$$P_0 \equiv kT / (\bar{Q}(E_0) L_1 + \bar{Q}(E_0 - E_{SWP}) L_2) ,$$

k is Boltzmann's constant ($\approx 1.03 \times 10^{-19}$ torr - cc/ $^{\circ}$ K), and T is the sample temperature in $^{\circ}$ K.

In the following sections we shall discuss some aspects of the application of (4-107) to obtain the DCS (σ) from a measurement of I_D .

4.4.4.2. Pressure dependence

It has been pointed out⁽¹²¹⁾ that double scattering events may cause serious errors in the measurement of differential scattering cross sections. This problem seems most severe for inelastic processes measured at large scattering angles and high incident energies. However, the demonstration that the pressure dependence indicated by equation (4-107) holds at every angle, for all incident energies, and for every process investigated is sufficient to insure that only single scattering events are contributing to the measured signal. Although such a complete study is indeed

sufficient, it may not be necessary. It seems more "economical" to determine the particular experimental conditions we might use for which double scattering would have the highest probability and then demonstrate that (4-107) holds in this case (i. e., that under our experimental conditions, we do not detect double scattering events).

The principal contribution to double scattering usually comes from large-angle elastic scattering in or near the scattering volume V preceded, or followed, by small-angle inelastic scattering along the view cone⁽¹²¹⁾. In particular, the current (I_2) due to electrons which have scattered twice compared to that (I_1) due to electrons which have scattered once varies approximately as

$$\frac{I_2(\theta)}{I_1(\theta)} \approx \frac{\rho \ell_{\text{eff}} \langle \sigma(E_0, 0, \theta') \sigma(E_0, W, \theta - \theta') \rangle_{\theta}}{\sigma(E_0, W, \theta)} \quad (4-108)$$

where $\sigma(E_0, W, \theta)$ is the differential cross section for the particular inelastic process being considered, $\sigma(E_0, 0, \theta)$ is that for the elastic one, and ℓ_{eff} is an "average" scattering path length on the order of $L_1 + L_2$. $\langle \sigma(E_0, 0, \theta') \sigma(E_0, W, \theta - \theta') \rangle_{\theta}$ is the DCS product averaged over all possible combinations of scattering angles for the two events which would be detected as if from a single scattering event occurring within V at an angle θ .

At incident energies high enough for the Born approximation to be valid, $\sigma(E_0, W, \theta)$ is much more sharply peaked forward than is $\sigma(E_0, 0, \theta)$ ⁽¹²²⁾. The principal contribution to the average in (4-108)

will come from terms in which $\theta - \theta' \approx 0$. Thus,

$$\frac{I_2(\theta)}{I_1(\theta)} \sim \rho \ell_{\text{eff}} \frac{\sigma(E_0, 0, \theta) \sigma(E_0, W, 0)}{\sigma(E_0, W, \theta)} \quad (4-109)$$

under these conditions and double scattering becomes increasingly more important at higher scattering angles⁽¹²¹⁾.

In the lower energy range in which we operate, the situation is not so clear. Inelastic processes, though certainly less intense, do not seem to decrease much more rapidly with angle than the elastic one. For example, the ratio of elastic to inelastic ($\tilde{X}^1\Sigma_g^+ \rightarrow \tilde{C}^1\Pi_u$) scattering in acetylene was found to be constant from $40^\circ \rightarrow 80^\circ$ at an impact energy of 35 eV. In addition, spin-exchange inelastic processes are often nearly isotropic, and hence the ratio of inelastic to elastic scattering is actually smallest at small angles.

For cases in which the elastic/inelastic ratio is nearly constant with angle, the value of the cross section product in (4-108) will be the same at both high and low θ' . If it is assumed that the principal contribution to the product is for $\theta' \approx 0$,

$$\frac{I_2(\theta)}{I_1(\theta)} \sim \rho \ell_{\text{eff}} \sigma(E_0, 0, 0) \quad (4-110)$$

(4-110) implies, as expected, that double scattering will be least important in those instances for which the forward elastic DCS is lowest, regardless of the magnitude of the inelastic DCS. It also indicates that the effect is independent of angle.

Finally, there is the case of spin-exchange excitations in which $\sigma(E_0, W, \theta)$ can be assumed to be independent of angle but $\sigma(E_0, 0, \theta)$ is still forward peaked. The result (4-110) is also obtained under these conditions.

In conclusion, it seems that the relative effect of double scattering will not be highly angular dependent for low (< 50 eV) incident energies. Thus, checking relation (4-107) as a function of pressure at one high and one low angle for the most sharply forward peaked cross section should be sufficient. Parenthetically, Doering^(36c) did not observe double scattering effects at 90° scattering angles and .05 torr sample pressures for low incident energies (of the order of 10-30 eV).

Finally, let us consider a specific example. The natural logarithm of (4-107) can be written as

$$\ln \left(\frac{I_D}{I_0 P} \right) = C(E_{SWP}, \theta) - P/P_0 \quad (4-111)$$

in which $C(E_{SWP}, \theta) \equiv \ln \left\{ \frac{V(\theta) \Delta \Omega}{A kT} \epsilon(E_{SWP}) \bar{S}(E_0, E_{SWP}, \theta) \right\}$.

It is clear from (4-111) that a plot of $\ln \left(\frac{I_D}{I_0 P} \right)$ versus P should be a straight line of slope $-P_0^{-1}$ for single scattering. Figure 4.4-11 shows the results of such a plot for two transitions in helium ($1^1S - 2^3P$, nearly isotropic $\sigma(E_0, W, \theta)$; $1^1S - 2^1P$, forward peaked one) at two scattering angles (20° and 70°). The dashed line has a slope of -25 torr^{-1} . The ordinate has been shifted by an arbitrary constant for each of the four sets of data points at each angle.

Figure 4.4-11. Demonstration of single scattering in helium. The pressure P is the reading of an uncalibrated ion-gage multiplied by 7 (to correct for the ionization efficiency difference between N_2 and He). The $\ln(I_D/I_0 P)$ was computed in arbitrary units for each of the four sets of data points: (○) $2^1 P, \theta = 20^\circ$; (□) $2^3 P, \theta = 20^\circ$; (●) $2^1 P, \theta = 70^\circ$; (■) $2^3 P, \theta = 70^\circ$. The constant C was determined by normalizing the four data sets to the dashed line at the highest pressure side (where the signal was largest).

An attenuation in the direct beam of about $10 \pm 3\%$ was observed at 5×10^{-3} torr which indicates that $P_0 \approx .05 \pm .02$ torr. P_0 can also be estimated if values are assumed for the cross sections and path lengths involved. Choosing $\bar{Q}(45 \text{ eV}) = 1.5 \text{ \AA}^{(6e)}$, $\bar{Q}(24 \text{ eV}) = 2.3 \text{ \AA}^{(6e)}$, $L_1 = 3.8 \text{ cm}$, and $L_2 = 1.9 \text{ cm}$, implies that $P_0 \approx .03$ torr (P_0 was defined in equation (4-107)). Phenomenologically, P_0 is the pressure (for a given apparatus, incident energy, and scattering sample) for which the mean free path of an electron in the scattering chamber is equal to the length of that chamber.

4.4.4.3. Energy-loss efficiency

Equation (4-107) was derived assuming that $\epsilon(E_{\text{SWP}})$ was a slowly varying function of E_{SWP} over a range of $\sim .07 \text{ eV}$. At this point, we shall endeavor to show that ϵ is essentially independent of E_{SWP} over a range of $\sim 10\text{-}20 \text{ eV}$. The importance of this energy-loss independence is evident from equation (4-107). At a fixed scattering angle θ and incident energy E_0 , an energy-loss spectrum is obtained (refer to section 4.3.4.2) by varying V_{SWP} (and consequently E_{SWP}). In order to relate the scattered intensities (I_D) observed at different values of E_{SWP} to the effective differential cross sections $\bar{S}(E_0, E_{\text{SWP}}, \theta)$ for these values of the energy-loss, it is essential that $\frac{d\epsilon}{dE_{\text{SWP}}}$ be zero or a known function of E_{SWP} . Due to the extreme difficulty in actually measuring such a dependence, the former alternative is a practical necessity.

Consider a scattered electron beam composed of an elastically scattered (K. E. of E_0) and an inelastically scattered (K. E. of $E_0 - W$) component. Assume that V_{LVL3} , V_{H3} , V_{CVS} ($=V_{H4}$), ΔV_S , V_{TL1} , V_{TL2} , and V_{DP3} have been adjusted for a maximum transmission of the elastically scattered component (case (1), $V_{SWP} = 0$) for a given resolution. Then change $|e|V_{SWP}$ to W (all other voltages unchanged) to transmit the inelastically scattered component (case (2)) and consider the changes, if any, in the electron-optical properties of the lenses and selector.

In case (1) the electrons are decelerated from a K. E. of E_0 in the scattering chamber to $|e|V_{LVL3}$ in LVL3 while in case (2) they are decelerated from $E_0 - W$ in the scattering chamber to the same value $|e|V_{LVL3}$ in LVL3. Since the voltages of all elements from LVL3 to TL1 with respect to one another are not affected by a change in V_{SWP} , the electron-optical properties of these elements are the same for both beam components. However, the lens formed by the scattering chamber exit aperture (A5, at ground potential) and LVL3 will have different focal properties in the two cases. Likewise the lens formed by TL1 and TL2 will have a slightly different effective voltage ratio in each case. This latter effect is probably negligible since for typical cases ($V_{TL2} = 250$ V with respect to ground, $E_0 = 35$ eV, $W \approx 15$ eV, and $V_{TL1} = 35$ V with respect to cathode) the ratio of the K. E. in TL1 to the K. E. in TL2 would be .123 and .130 for cases (1) and (2), respectively.

The K. E. ratio between the electrons at A5 and those at LVL3 is usually near 1 (see table 4.3.2) for the elastic component of the beam (case (1)). For the same conditions as above, this ratio is $\approx .6$ for the inelastic component (case (2)). Both ratios are typical of weak lenses. Since the LVL-H3 pair is a relatively strong lens, (ratio ≈ 5.5) it should be much more effective in determining the image at the selector. As a result, one might expect the overall transmission to be relatively insensitive to W over a range of 10 or 20 eV. That this is indeed the case has been tested as outlined below.

The instrument is tuned for a maximum transmission of the elastically scattered current with helium in the scattering chamber. It was found that there were essentially two "modes" in which this maximum could be obtained--mode (1), in which $\frac{E_o}{|e|} \sim V_{LVL3} > V_{H3} > V_{CVS}$ as indicated in table 4.3.2, and mode (2), in which $\frac{E_o}{|e|} \sim V_{H3} > V_{LVL3} > V_{CVS}$. When the maximum elastic current was obtained, V_{SWP} was changed to 21.21 V to collect the current $I_{2^1P^0}$ scattered after causing the $1^1S \rightarrow 2^1P$ ($W = 21.21$ eV) transition. Then, V_{LVL3} , V_{H3} , V_{TL1} , and V_{DP3} were changed in an attempt to obtain a larger inelastically scattered current $I_{2^1P}^{max}$. It was assumed that the change in current would be indicative of the sensitivity of $\epsilon(E_{SWP})$ to E_{SWP} over a rather extreme range of 21.2 eV. In other words, the smaller the percentage current change, the less ϵ varies over this range. Figure 4.4-12 shows this

Figure 4.4-12. Percent change in efficiency for the detection of the elastic peak and the 2^1P peak (21.21 eV energy-loss) as a function of incident energy. The percent efficiency is defined as $\{(I_{2^1P}^0 - I_{2^1P}^{\max})/I_{2^1P}^0\} \times 100$. ($\circ$) mode (1) and ($\square$) mode (2) as described in the text.

percentage change, $\{(I_{2^1P}^{\max} - I_{2^1P}^0)/I_{2^1P}^0\} \times 100$, at several incident energies for both "mode (1)" and "mode (2)" operation. Mode (2) is clearly unacceptable (as expected, since A5 - LVL3 from a strong lens in this case). Mode (1) gives acceptable performance until $(E_0 - W)$ becomes less than about 7 eV. In general it was found that the instrument could be tuned such that the percentage current change as defined above was less than 3% over any 10 eV energy-loss region, provided $(E_0 - W) \gtrsim 10$ eV.

4.4.4.4. Volume correction

It is apparent from figure 4.4-10 that the scattering volume is a function of the scattering angle, and further that the solid angle of acceptance $\Delta\Omega$ (defined by A5 and S) is not constant over the length of the collision volume (it is a maximum at the volume center and drops to 0 at the ends⁽¹²³⁾). Thus, one should average the solid angle over the collision volume at each scattering angle. This would result in an effective value of scattering volume times solid angle, $(V\Delta\Omega)_{\text{eff}}$. Several calculations for experimental arrangements similar to that of figure 4.4-10 have been performed in which apertures A5 and S were assumed to be slit-slit⁽¹²⁴⁾, slit-hole⁽¹²⁵⁾, and hole-hole⁽¹²⁶⁾ combinations. For any particular case, the result may be expressed as

$$(V\Delta\Omega)_{\text{eff}} = \frac{B(1 + C(\theta))}{\sin \theta} \quad (4-111)$$

where θ is the scattering angle defined by the axes of the aperture systems (θ of fig. 4.4-10), B is a constant which depends on the

geometrical arrangement, and $C(\theta)$ is a correction term which is negligible for θ large compared to the beam and view cone angles.

Since the beam and view cone angles in the present case are of the order of 4° , the quantity $(V\Delta\Omega)_{\text{eff}}$ was calculated⁽¹²⁷⁾ as a function of assumed beam geometries. The electron beam was considered to have a Gaussian intensity distribution of the form $e^{-\varphi^2/\alpha^2}$ where φ is the angle between a particular ray originating at A4 and the beam axis while α is the angle at which the density drops to e^{-1} of its value along the axis. For computational convenience, the intensity distribution was truncated at $\varphi = 2\alpha$. Since B (of equation (4-111)) is not important for our purposes, the values of $(V\Delta\Omega)_{\text{eff}}$ were normalized to the value obtained at $\theta = 90^\circ$ (where $C(\theta)$ is negligible). In particular, the quantity $(V(\theta)/V(90^\circ))_{\text{eff}}$ was determined where

$$\left[\frac{V(\theta)}{V(90^\circ)} \right]_{\text{eff}} = \frac{(1 + C(\theta))}{\sin\theta(1 + C(90^\circ))} \cong \frac{1 + C(\theta)}{\sin\theta}. \quad (4-113)$$

Figure 4.4-13 shows a plot of $C(\theta)$ for two sets of assumed conditions. In either case, the error in assuming $C(\theta) = 0$ is less than 10% above $\theta = 20^\circ$. The difficulty with this entire approach is that the effective beam and view cone angles are not well defined. Thus, the choice of the "correct" $C(\theta)$ is somewhat arbitrary. It has been assumed that the lower curve in figure 4.4-13 corresponds to the present situation and all differential cross sections quoted have been corrected by the factor $\frac{\sin\theta}{1 + C(\theta)}$. Notice that the relative behavior of

Figure 4.4-13. Plot of $-C(\theta)$ (refer to equation (4-113)) as a function of scattering angle θ for a beam cone of 4° and a view cone of 4.5° --curve (1); and a beam cone of 5° and a view cone of 3.5° --curve (2).

two differential cross sections with angle is independent of this volume correction since from (4-107) (and the arguments of section 4.4.4.3)

$$\frac{I_D(\theta, E_{SWP})}{I_D(\theta, E'_{SWP})} \cong \frac{\bar{S}(E_O, E_{SWP}, \theta)}{\bar{S}(E_O, E'_{SWP}, \theta)} \quad (4-114)$$

Where E_{SWP} and E'_{SWP} are the two energy-losses in question.

4.4.5. Detector and Background Characteristics

The detector arrangement has already been presented in fig. 4.2-26 and its operation was discussed in section 4.3.4.3. Some of the specific parameters associated with its operation will be described in this section.

Usually, 4.5 KV is applied between the anode and first dynode of the multiplier (fig. 4.2-13) with R4 (fig. 4.2-26) adjusted to 0.4 MΩ. This implies a total load resistance for the high voltage of 8 MΩ, a current through the resistor string of about .56 mA, a first-dynode-to-ground voltage of ~220 V, and a stage-to-stage voltage of ~210 V. The gain of the multiplier under these conditions can be estimated as follows. The voltage pulse out of the DDL AMP will have an amplitude V_{OUT} where

$$V_{OUT} = G_M G_{PA} G_{AMP} \quad (4-115)$$

in which G_M is the multiplier gain in coulombs/ incident electron, G_{PA} is the NPA gain in volts/coulomb, and G_{AMP} is the DDL AMP

voltage gain (dimensionless). For $G_{AMP} \approx 125$ and $G_{PA} \approx 10^{10}$ V/coulomb, V_{OUT} is usually about 2 to 5 V. Solving (4-115) for G_M implies that $G_M \approx 2$ to 4×10^{-12} coulomb/incident electron or approximately 1 to 2×10^7 electrons out per incident electron. The count-rate can be made nearly independent of the multiplier gain over about a factor of 10 change by proper adjustment of the SCPHA. The maximum count rates which can be handled by the NPA, DDL AMP, SCPHA, CRM, and ND MCS are 10^5 , 3×10^5 , $\sim 10^6$, 2×10^4 , and $\sim 10^6$ counts/sec, respectively.

The background "noise" in the system can arise from three principal sources:

(1) At low scattering angles the intense direct beam can enter the selector. Even if E_{SWP} is quite different from 0 eV, a significant number of electrons can "bounce" through the selector and reach the multiplier. As expected this type of background is angle dependent, becoming completely negligible (less than 1 count/min) at angles greater than about 10° .

(2) For E_{SWP} near 0 eV, the tail of the elastic peak may contribute to the scattered signal. Since we have operated at E_{SWP} always > 3 eV, this type of background has not been observed.

(3) It was found that electrons could strike the multiplier without having passed through the scattering chamber. With all voltage controls off except V_C and the filament supply (Kepco 2), electrons could be detected. As expected, this effect was dependent on the total filament emission. With $V_C = 0$, this type of noise disappears (less than 1 count/min).

As a specific example, the total background count-rate at $\theta = 45^\circ$ with $E_{\text{SWP}} = 15$ eV for helium (the lowest lying excited state is the 2^3S state at 19.8 eV) at a pressure of .050 torr in the scattering chamber was ~ 1.5 counts/sec, due primarily to source (3).

Under usual operating conditions, electrical noise (power supplies, amplifiers, etc.) was not detected since the SCPHA threshold was set high enough to discriminate against it (usually about 0.5 V). For example, with all spectrometer controls off except 4.5 KV to the multiplier, only 1 count was obtained in five minutes of counting.

In conclusion, it is of interest to estimate the actual numerical relation between the measured signal and the differential scattering cross section (recall equation (4-107)). If one assumes that $(\Delta\Omega)_{\text{AVG}} \approx 10^{-2}$ steradians (from lens system 2 geometry, section 4.2.4.6); $\frac{V(45^\circ)}{A} \approx 0.5$ cm, $\epsilon \approx 0.1$ (section 4.4.3.4), a sample pressure of 10^{-2} torr (with $P/P_0 \ll 1$), and a typical incident beam current of 3×10^{-8} A, then

$$I_D(E_{\text{SWP}}, 45^\circ) \sim 3 \times 10^6 \bar{S}(E_0, E_{\text{SWP}}, 45^\circ) \quad (4-116)$$

where I_D is in counts/sec when $\bar{S}$ is in units of $\text{\AA}^2/\text{steradian}$. Note that (4-116) can be incorrect by an order of magnitude due to the uncertainty in the instrument parameters. If we assume the minimum detectable signal (with the CRM) to be on the order of the background (1.5 cts/sec), then the minimum detectable cross section is

approximately

$$\bar{S}(E_O, E_{SWP}, 45^\circ) \sim .5 \times 10^{-6} \text{Å}^2/\text{steradian}.$$

This detection limit can be decreased by the use of the ND MCS system to repetitively scan the feature for a long period of time. By way of comparison table 4.4-2 below lists some measured⁽³²⁾ DCS for an optically allowed ($1^1S \rightarrow 2^1P$), symmetry-forbidden ($1^1S \rightarrow 2^1S$), and spin-and symmetry-forbidden ($1^1S \rightarrow 2^3S$) transition in helium.

TABLE 4.4-2
DCS for three transitions in helium⁽³²⁾

Incident Energy (eV)	Scattering Angle (degrees)	DCS (Å ² /steradian)		
		$1^1S \rightarrow 2^1P$	$1^1S \rightarrow 2^1S$	$1^1S \rightarrow 2^3S$
100	20	$.49 \times 10^{-1}$	$.82 \times 10^{-2}$	$.50 \times 10^{-3}$
225	15	$.32 \times 10^{-1}$	$.93 \times 10^{-2}$	$.73 \times 10^{-4}$

4.4.6. Energy-Loss Determination

One very important aim of this research is to obtain the positions of atomic and molecular energy levels through a measurement of the energy-losses of the scattered electrons. We have already indicated in section 4.3.4.2 that the value of the applied sweep-voltage V_{SWP} is related to the electron energy-loss being detected (W) by

$$|e|V_{\text{SWP}} = W$$

without any arbitrary constants or "contact potential" corrections. This means that the value of V_{SWP} in volts (measured by the digital voltmeter or the X-axis potentiometer of the X-Y recorder) corresponding to a particular peak in the measured energy-loss spectrum is numerically equal to the excitation energy (of the target) W in eV giving rise to that peak. The accuracy with which we can locate the energy of a specific molecular energy level depends only on the instrumental resolution (how well the peak can be separated from neighboring features) and the accuracy of our voltage measuring devices (approximately $\pm .001$ eV for the digital voltmeter). At present, the latter limitation is negligible compared to the former in most cases.

The energy-loss spectrum of helium provides a good test for these as yet unsupported statements. (Simpson⁽²⁴⁾ suggested the method of energy-loss sweep which we use and has, of course, verified its utility for his instrument.) A comparison of the well-known

excitation energies of helium with those determined simply by measuring V_{SWP} is presented in section 5.2.3. The agreement is excellent and limited only by the resolution. These same considerations are valid as well for the molecules we studied.