INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.
FOLTZ, GREG WILLIAM

COLLISIONAL PHENOMENA BETWEEN ELECTRONS AND HIGH RYDBERG ATOMS

Rice University

University Microfilms International

300 N. Zeeb Road, Ann Arbor, MI 48106

18 Bedford Row, London WC1R 4EI, England

PH.D.

1980
RICE UNIVERSITY

COLLISIONAL PHENOMENA BETWEEN ELECTRONS AND HIGH RYDBERG ATOMS

by

GREG WILLIAM FOLTZ

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

THESIS DIRECTOR'S SIGNATURE:

[Signature]

HOUSTON, TEXAS

MAY 1980
ABSTRACT

Collisional Phenomena Between
Electrons and High Rydberg Atoms

by

Greg William Foltz

Highly excited (Rydberg) atoms are produced and can exist for significant periods of time in various plasma environments. It is necessary to know cross sections for the various collision processes involving these atoms if a complete understanding of the physics of these environments is to be attained.

The experimental investigation of collisional phenomena between high Rydberg sodium atoms and electrons is described in this thesis. A fraction of the atoms in a ground state sodium beam is optically excited (using lasers) to well-defined, high Rydberg states (principal quantum numbers chosen around 40). Subsequent to their production the Rydberg atoms are allowed to interact with 25 eV electrons for a specified time interval following which the collision products are detected. The electrons are produced in a beam which is crossed at right angles with the sodium beam. Important collision processes are 1) electron impact ionization of the Rydberg atom, and 2) electron-Rydberg atom interactions in which the quantum state of the atom is
changed (state changing collisions).

Results are presented for an observed state changing process which is identified as angular momentum state changing only (no change in the value of the principal quantum number). Cross sections for this process are measured to be $10^{-10}$ to $10^{-9}$ cm$^2$. Problems encountered during the work which prevented the measurement of electron impact ionization cross sections are discussed. In the course of the work two other topics required study: 1) the process of electric field ionization of Rydberg atoms (used to detect the atoms), and 2) the effects of background (300 K) radiation (from the chamber walls, for example) on Rydberg atoms. Results of these studies are also presented.
ACKNOWLEDGEMENTS

The work described in this thesis is the result of the efforts of several people and organizations in addition to myself and it is with pleasure that I acknowledge them. I am indebted to Prof. Ron Stebbings, my advisor, who has provided constant guidance, advice, and assistance throughout the work. The freedom that he has allowed me in the pursuit of this work and his willingness to continue the work when, at times, it appeared that it might be more profitable to adopt a different course of study, are much appreciated. I am grateful to Prof. Barry Dunning who has been a constant source of ideas, help, and enthusiasm. I would also like to express my gratitude to Dr. Ken Smith whose expertise in all phases of the work has proved valuable.

Dr. Ed Beiting and Tom Jeys, with whom the day-to-day running of the experiment and maintenance of the apparatus were shared, deserve much credit for the success of this work. In particular Ed's management of the laser system and Tom's work on understanding field effects on sodium Rydberg atoms are certainly appreciated.

I would like to acknowledge Prof. Bill Snow, visiting from the University of Missouri at Rolla, Mike McGuire, and Janice Voss for their assistance at various stages of the
work. Discussions with George Hildebrandt and Forrest Kellert were also helpful.

The financial support provided by the National Science Foundation under Grant No. PHY 78-09860 and by the Robert A. Welch Foundation is appreciated.

Finally, I would like to thank Chris Dunning for her assistance in the preparation of the manuscript.
# TABLE OF CONTENTS

Chapter I: Introduction ............................................. 1  
1.1 Motivation for the Work ........................................ 1  
1.2 Recombination Spectra of Gaseous Nebulae ................. 2  

Chapter II: Previous Work ......................................... 9  
2.1 Ionization ......................................................... 10  
2.2 State Changing Processes ...................................... 13  

Chapter III: Experiment - General ............................... 21  
3.1 Objectives and Outline of Experiment ...................... 21  
3.2 Important Considerations in Rydberg Atom Experiments .... 26  
3.3 Signal Analysis Considerations ............................... 32  

Chapter IV: Experiment - Detail ................................. 37  
4.1 Vacuum System .................................................. 37  
4.2 Alkali Beamline ................................................. 40  
4.3 Grid Assembly and Electron Multiplier ...................... 45  
4.4 High Rydberg Atom Production .............................. 47  
4.5 Lasers ............................................................ 55  
4.6 High Rydberg Atom Detection .............................. 62  
4.7 Ion Detection .................................................... 105  
4.8 Electron Beamline ............................................. 106  
4.9 Signal Measurements ......................................... 126  
4.10 Effects of Small Electric Fields on Rydberg Atoms ....... 165  

Chapter V: Results and Discussion ............................... 173  
5.1 General ............................................................ 173  
5.2 Results of State Changing Processes due to Background Radiation ...................................................... 179  
5.3 Results of State Changing Processes due to Electrons .... 185  

Appendix: Problems with the Measurement of Cross Sections for Electron Impact Ionization of Rydberg Atoms .............................. 204  

References .......................................................... 208
CHAPTER I
INTRODUCTION

There has been a dramatic increase in interest in Rydberg atoms and molecules in the last five years or so. While undoubtedly the result of many factors, this surge in interest is primarily due to the relative ease with which Rydberg species may now be produced in the laboratory via photoexcitation using tunable dye lasers. These recent efforts have combined with the previous work to produce a large amount of information on Rydberg systems. However, one area where comparatively little work has yet been done is the experimental study of electron-Rydberg atom collisional phenomena. A program to experimentally study such interactions has been undertaken in this laboratory and the first results of this study are presented in this thesis.

1.1 Motivation for the Work

Together with the intrinsic interest in collisions between Rydberg atoms and electrons, there are several reasons of a more applied nature for studying these interactions. First of all, the importance of such interactions to the radiative-collisional properties of plasmas has been appreciated for some time now. A long standing area of
research in this connection has been the detailed explanation and modeling of the recombination spectra of gaseous nebulae. Secondly, in addition to providing information directly on such processes as electron impact excitation (de-excitation) and ionization of Rydberg atoms, study of electron-Rydberg atom interactions may indirectly shed light on other processes. For example, application of detailed balance arguments to cross sections for electron impact ionization of Rydberg atoms can yield cross sections for the reverse process: 3-body recombination. Finally, a further reason for studying electron-Rydberg atom collisions lies in the usefulness of such investigations in determining the extent to which various classical and semi-classical approximations made in collision theories are valid. In Sec. 1.2 below the role that high Rydberg atoms and their collisions with electrons play in the determination of the spectra observed from gaseous nebulae is briefly examined.

1.2 Recombination Spectra of Gaseous Nebulae

The spectra of gaseous nebulae consist of both line and continuum radiation spread over a broad range of frequencies from the visible to the radio region of the spectrum. Ultraviolet radiation from a local hot star

---

1 For a more comprehensive discussion of this subject see Seaton (1968,1972) and Dupree and Goldberg (1970).
photoionizes the gas in the cloud creating a plasma.

\[ H + h\nu \rightarrow H^+ + e \]  \hspace{1cm} (1-1)

The free electrons rapidly thermalize and can be described by a Maxwellian distribution characterized by an electron temperature, \( T_e \). Radiative recombination

\[ H^+ + e \rightarrow H(n) + h\nu \]  \hspace{1cm} (1-2)

and free-free transitions

\[ H^+ + e \rightarrow H^+ + e + h\nu \]  \hspace{1cm} (1-3)

contribute to the continuum portion of the spectra. Here \( n \) denotes all of the important quantum numbers of the state. The recombination processes, which may also include radiationless 3-body recombination

\[ H^+ + e + e \rightarrow H(n) + e \]  \hspace{1cm} (1-4)

in addition to (1-2), can result in atoms in any state of excitation and radiative cascade transitions between these excited states

\[ H(n) \rightarrow H(n') + h\nu \]  \hspace{1cm} (1-5)

give rise to line emissions. It is the radiation that is emitted as a result of the recombination events which forms
the recombination spectra. In particular, transitions between states having large principal quantum numbers, i.e. high Rydberg states, produce radio frequency radiation lines called radio recombination lines. Letting \( R \) denote the Rydberg constant in units of energy, the frequency of a line produced by a transition between initial and final states having principal quantum numbers \( m \) and \( n \) respectively is given by

\[
\nu = \frac{R}{h} \left( \frac{1}{n^2} - \frac{1}{m^2} \right) .
\]  (1-6)

For \( m,n \gg 1 \) and \( (m-n) \ll m,n \), this reduces to

\[
\nu \approx \frac{2R}{h} \frac{(m-n)}{n^3} .
\]  (1-7)

This frequency lies in the radio frequency part of the spectrum. The designation \( \alpha, \beta, \gamma \), etc. is applied to the transitions where \( (m-n) = 1,2,3 \), etc. respectively.

The study of gaseous nebulae, aside from understanding them in their own right, constitutes one method of obtaining information on the interstellar medium in general. The emitted spectrum of a nebula is observed with the objective being to determine the physical state of the cloud, e.g. electron density and temperature, and chemical composition. Experimentally, observations can be divided according to whether they are done at optical or radio frequencies and
to whether they deal with line or continuum emission. Since the topic of this thesis concerns Rydberg atoms, only line emissions will be considered further.

In order to determine the properties of a nebula from observations of the recombination line spectrum it is necessary to have an accurate theory of line formation and line intensities. This theory requires a knowledge of the population of atoms in any given excited state. Such level populations, $N(n)$, are governed by the variety of radiative and collisional processes occurring in the plasma and are obtained by solving an equilibrium rate equation for $N(n)$ in which the rates for populating level $n$ are set equal to the rates for depopulating that level. The rates depend on the cross sections for the processes and the electron density and temperature. With a knowledge of the cross sections obtained from experiment and/or theory, the electron density and temperature are adjusted until the line intensities determined from the calculated level populations agree with observations. In practice this comparison of theory with observation is traditionally made via the $b_n$ coefficients which express the difference between the actual values of the level populations and those given by the Saha equation (i.e. for thermodynamic equilibrium).
Thus\(^1\)

\[ N(n) = b N_+ N_e \left( \frac{\hbar^2}{2\pi mkT_e} \right)^{3/2} \frac{g_n}{2g_+} e^{\frac{h\nu_n}{kT_e}} \]  

(1-8)

where \( N_+ \) and \( N_e \) are the number densities of ions and electrons respectively, \( g_n \) and \( g_+ \) are the statistical weights of the level \( n \) and the ion respectively, and \( \nu_n \) is the frequency required for ionization of the level \( n \) at threshold.

In the early work\(^1\) only radiative processes in hydrogen were considered and the first calculations were done under the assumption that the angular momentum states of a given value of the principal quantum number, \( n \), (from now on \( n \) will mean only the principal quantum number) are statistically populated. These calculations agree fairly well with observations. When the work was extended to allow for non-statistically populated \( \ell \) levels the agreement worsened. Therefore the process of collisional angular momentum state changing in Rydberg atoms by charged particles were examined to see if they could be effective in maintaining a statistical population among the \( \ell \) states.\(^2\) Due to the large cross

\(^1\) See, for example, Seaton (1968)

\(^2\) It has been the study of the recombination spectra of gaseous nebulae which has prompted much of the theoretical work done on charged particle-Rydberg atom collision processes (see Seaton (1968) and Chapter II of this thesis).
sections found for $\Delta l = \pm 1$ processes in hydrogen at high $n$, it was determined that such collisions would, for $n \gtrsim 15$, result in statistical distributions among the $\ell$ states. Seaton (1968) points out that line intensities for transitions between low energy states are influenced by these $\ell$-changing processes occurring at high $n$.

Angular momentum changing is not the only collisional process involving Rydberg atoms which is possible. Since collisions between free electrons are assumed to establish a Maxwellian velocity distribution for these electrons, it is expected that collisions between free electrons and hydrogen Rydberg atoms will also change the energy of the Rydberg electron. This results in changes in $n$ in the Rydberg atoms or in ionization of the atoms. Based on calculations for the cross sections for $\Delta n = \pm 1$ transitions, it is felt that these processes are effective at values of $n \gtrsim 40$. Goldberg (1966) has underscored the necessity of understanding the state populations at the Rydberg level of excitation. In thermal equilibrium the population of a Rydberg state is a slowly changing function of $n$ and consequently neighboring states have nearly equal populations. Differences from thermal equilibrium can result in population inversions among the states allowing the occurrence of stimulated emission and therefore
enhancement of the observed line intensities.
CHAPTER II
PREVIOUS WORK

The purpose of this chapter is to discuss several aspects of the previous work which has dealt with collisions between electrons and Rydberg atoms. Theoretical work in the area of electron-Rydberg atom collisions has been undertaken by numerous investigators due to the importance of these collisions in plasmas. Since, as will be seen, the present work deals with high energy collisions, the emphasis in this discussion will be placed on such collisions.\(^1\)

On the other hand, as mentioned in the last chapter, the experimental work on electron-Rydberg atom collisions has been somewhat limited to date and therefore all experiments dealing with these collisions will be discussed.

The nature of the Rydberg atom makes completely quantal calculations very difficult and only the Born and Bethe approximations and first order perturbation methods have had extensive application. On the other hand the high values of quantum numbers in Rydberg atoms allow the atoms to be viewed somewhat classically and consequently semi-classical calculations have been made. Furthermore the degree of

\(^1\) For a complete review of the theoretical work on charged particle-Rydberg atom collisions up to 1975, see Percival and Richards (1975).
success of classical calculations for collision problems in general coupled with their simplicity compared with quantal calculations, has lead to a new interest in classical and semi-classical collision theory.

Classical calculations for collisions between charged particles and atoms can be classified into three groups (see Percival and Richards (1975)): 1) binary encounter approximations, also called the classical impulse approximation, used at high energies and for large energy transfers, 2) classical perturbation calculations used for small energy transfers, and 3) Monte Carlo calculations used at intermediate energies. The binary encounter method is the easiest to apply and consists of viewing the collision as occurring only between the incident charged particle and one of the atomic electrons. The Coulomb interaction is described via the Rutherford scattering formula. In fact, the success of the classical collision theory results from the fact that the Rutherford expression is in exact agreement with the quantum mechanical calculation for scattering in a Coulomb field.

2.1 Ionization

The ionization of an atom by electron impact was first considered theoretically by Thomson (1912). This calculation used the binary encounter method in which the motion
of the atomic electron was ignored and only those events were considered in which the energy transferred from the incoming electron to the bound electron exceeded the binding energy of the atomic electron. In present day notation the result is

\[ \sigma_I(n,E) = \left( \frac{1}{E^2} \right) \left( \frac{E}{U_n} - 1 \right) \] (2-1)

where \( E \) is the energy of the incident electron in atomic units, \( U_n = 1/2n^2 \) is the atomic electron's binding energy in atomic units, and \( \sigma_I(n,E) \) is given in units of \( a_0^2 \). In the high energy limit this becomes

\[ \sigma_I(n,E) = \frac{1}{E U_n} \] (2-2)

The motion of the atomic electron was considered by several people in the late 1920's and again by Gryzinski (1959) whose work stimulated new interest in classical theory. The results of Gryzinski's work, again a binary encounter type of calculation, are for ionization

\[ \sigma_I(n) = \begin{cases} \frac{1}{U_n E} \left( \frac{E}{U_n + E} \right)^{3/2} \left( \frac{5}{3} - \frac{2U_n}{E} \right) & \text{when } 2U_n \leq E \\ \frac{1}{U_n E} \left( \frac{E-U_n}{E+U_n} \right)^{3/2} & \text{when } 2U_n > E \end{cases} \] (2-3)

where the same notation has been used as that above and

1 As given by Kingston (1964a).
again $\sigma_I$ has units of $\pi a_0^2$. In the high energy limit this reduces to

$$\sigma_I(n) = \frac{5}{3} \frac{1}{E U_n}$$  \hspace{1cm} (2-4)

Improvements in this calculation have been made more recently. Monte Carlo calculations for electron impact ionization of highly excited hydrogen atoms have been carried out by Abrines et al. (1966) for impact energies relatively close to the ionization limit. The results of these calculations also exhibit the $1/E$ high energy dependence. Percival and Richards (1975) have empirically adjusted the binary encounter formula so as to obtain better agreement with the Monte Carlo results. This semi-empirical electron impact ionization formula is

$$\sigma_I(n,E) = \frac{4U_n(5E + 2U_n)(E - U_n)}{3E^2(E + 3U_n)} \pi a_0^2$$  \hspace{1cm} (2-5)

where $E$ is the energy of the incident electron and $U_n$ is the atomic electron's binding energy.

Concerning quantum mechanical calculations, Johnson (1972) has developed a semi-empirical expression for electron impact ionization of excited hydrogen atoms. He has modified the high energy formula

$$\sigma_I(n,E) = \frac{2U_H}{E} \left( A_n \ln \frac{E}{2U_H} + B_n \right) \pi a_0^2$$  \hspace{1cm} (2-6)
where $E$ has its usual meaning, $U_H$ is the ionization energy of a ground state hydrogen atom, and $A_n$ and $B_n$ are dimensionless (Bethe) coefficients, so as to obtain more accurate results at the lower energies where (2-6) is not valid. Matsuzawa (1974a) has calculated form factors for bound-free transitions out of excited states of hydrogen. These form factors or generalized oscillator strengths are encountered in a variety of theoretical methods.

It should be noticed that the results quoted above fall off as $1/E$ at high energy. It is this $1/E$ dependence of the cross section which poses the greatest difficulty in the classical method. Quantum mechanical Born calculations for the ground state and low lying excited states of hydrogen yield a $(\log E)/E$ dependence which is verified by experiment. The reason for the incorrect high energy behavior of the classical results stems from the violation of the uncertainty principle at large impact parameters.

2.2 State Changing Processes

The state of a Rydberg atom may be changed in a variety of ways. The general cases are $\ell$-changing collisions in which $n$ remains constant and $n\ell$-changing collisions in which both $n$ and $\ell$ are changed. Since the theory has most often been applied to hydrogen, results for $n\ell$-changing processes are sometimes given averaged over all values of $\ell$. 
in both the initial and final n states (resulting in cross sections for \( n \to n' \) transitions). For \( \ell \)-changing collisions the dipole selection rule \((\ell \to \ell + 1)\) is often used. This selection rule is applied in \( n \ell \)-changing collisions as well, i.e. \( n\ell \to n'(\ell + 1)\). There is evidence, however (Kocher and Smith (1977) and Schiavone et al. (1977, 1979) experimentally and Flannery and McCann (1979 and to be published) theoretically) that the dipole rule may not apply even at the higher energies as is usually thought.

The Gryzinski binary encounter formula for \( n \to n' \) transitions is\(^1\)

\[
\sigma_{n \to n'}(E) = \frac{1}{(n')^3 E(U_n - U_{n'})^2} \left( \frac{E}{E + U_n} \right)^{3/2} \left\{ \begin{array}{ll}
\frac{1}{3} \left( \frac{7U_n - 3U_{n'}}{U_n - U_{n'}} \right) - \frac{U_n}{E} & \text{when } 2U_n - U_{n'} \leq E \\
\frac{1}{3} \left( \frac{2U_n - U_{n'}}{U_n} \right)^{1/2} \left[ \frac{(5U_n - U_{n'})}{(U_n - U_{n'})} + \frac{(U_n - 2U_{n'})}{E} \right] \left( 1 - \frac{(U_n - U_{n'})}{E} \right)^{1/2} & \text{when } 2U_n - U_{n'} \geq E
\end{array} \right.
\]

(2-7)

where \( E \) is the energy of the incident electron in atomic units, \( U_n \) and \( U_{n'} \) are the binding energies of the atomic electron in states \( n \) and \( n' \) respectively, and the cross

\(^1\) As given in Kingston (1964a)
section is in units of \( \pi a_0^2 \). In the high energy limit

\[
\sigma_{n-n'}(E) = \frac{1}{3} \frac{(7U_n - 3U_{n'})}{(n')^3 (U_n - U_{n'})^3} \frac{1}{E}
\]  

(2-8)

which again exhibits the \( 1/E \) dependence.

There have been numerous applications of the Born and Bethe approximations to the calculation of state changing collision cross sections in the high energy limit. These cross section formulae can be reduced to the usual expressions

\[
\sigma_{n-l-n'-l'}(E) = \frac{1}{E} \left( A_{n,l,n',l'} \log E + B_{n,l,n',l'} \right)
\]  

(2-9)

\[
\sigma_{n-n'}(E) = \frac{1}{E} \left( A_{n,n} \log E + B_{n,n'} \right)
\]  

(2-10)

for n-changing collisions.\(^1\)

Using the Born approximation McCoyd and Milford (1963) have evaluated the A coefficient in (2-9) while Kingston and Lauer (1966a, b) have determined both coefficients in (2-9) for \( n \leq 10, \Delta n = \pm 1, \pm 2 \) and \( \Delta l = \pm 1 \). These results may be summed over \( l \) and \( l' \) to yield the coefficients of (2-10). Furthermore Kingston and Lauer give extrapolation expressions from which it is possible to obtain values of \( A_{n,n} \) and \( B_{n,n'} \) at larger

\(^1\) The high energy formulae (2-6), (2-9) and (2-10) can be written in a variety of different forms for a given process and the values and dimensions of the Bethe coefficients will depend on the form that is chosen.
values of n. Matsuzawa (1974a) has calculated generalized oscillator strengths for bound-bound transitions in hydrogen from which the coefficients in (2-10) may be obtained. Podlubnyi and Sergeev (1969), employing the Born approximation, have obtained an expression for \( n \rightarrow n + 1 \) transitions which reduces to (2-10) at high energies. Also Beigman et al. (1970) have derived a formula for \( n \rightarrow n' \) state changing collisions by use of a Green's function technique. In the high energy limit their expression becomes (2-10). Gee et al. (1976) give a semi-empirical expression for the cross section for the general n-changing process, \( n \rightarrow n' \).

Two theoretical investigations are of special importance to the present work: Percival and Richards (1977) and Herrick (1978). While all the calculations discussed so far have been done for hydrogen Rydberg atoms, these two studies allow for non-degeneracy among angular momentum states having the same value of n (i.e. non-hydrogenic systems). This is important because, as will be seen, sodium is the atomic system used in the present work. In fact Percival and Richards apply their results specifically to sodium while Herrick considers the case of helium, the atom used in other experimental work to be discussed below. Percival and Richards, using perturbation theory and taking
into account the possibility of loss to adjacent states from the initial and/or final states of the collision induced transition, have derived expressions for cross sections, valid at high energies, for dipole-allowed \( n\ell \rightarrow n'(\ell \pm 1) \). For the case of loss to adjacent states from only one of the states involved in the transition (single resonance):

\[
\sigma_{n\ell-n'n',\ell'}(E) = \frac{2D}{3} \frac{R}{E} \ln \left( \frac{0.7 \frac{n^2 E}{(\omega/\omega_n)^2}}{2R} \right) \pi a_0^2 n^4
\]

while for the case of loss from both states of the transition (double resonance):

\[
\sigma_{n\ell-n'n',\ell'} = \frac{2D}{3} \left( \frac{n'}{n} \right)^2 \frac{R}{E} \ln \left( \frac{0.25 \frac{nn'}{\sqrt{EE'}}}{\omega^2 / (\omega_n \omega_n') R} \right) \pi a_0^2 n^4
\]

In these equations \( E \) and \( E' \) are the energies of the incident electron before and after the collision respectively, \( R \) is the Rydberg unit of energy, \( \omega \) is the angular frequency corresponding to the energy between the states of the transition and is given by

\[
\omega = \frac{\Delta E_{n\ell,n'n',\ell'}}{2R_{n\ell,n'n',\ell'}}
\]

\( \omega_n \) and \( \omega_n' \) are the angular frequencies corresponding to the energies between adjacent states of hydrogen at the level of the principal quantum numbers \( n \) and \( n' \) respectively and are given by
\[ \kappa_{n} = \frac{\hbar v_0}{n^3 a_0^3} \quad \text{and} \quad \kappa_{n'} = \frac{\hbar v_0}{(n')^3 a_0^3} \quad (2-14) \]

where \( v_0 \) is the atomic unit of velocity, and finally, \( D \) is a dimensionless quantity which is proportional to the square of the dipole radial matrix element of the transition, \( (R_{n\ell}^n')^2 \), and is given by

\[ \frac{D n^4 a_0^2}{2} = \frac{\max (\ell, \ell')}{2\ell + 1}(R_{n\ell}^n')^2. \quad (2-15) \]

It should be noted that (2-11) and (2-12) may be used for \( \ell \)-changing collisions in which case \( n = n' \).

Herrick (1978), using the impact parameter approximation, has derived a cross section formula, valid at high energies, for dipole-allowed \( \ell \)-changing collisions: \( n\ell \rightarrow n(\ell \pm 1) \). For the incident electron energy, \( E \), in eV

\[ \sigma_{n\ell \rightarrow n\ell'} = 3.59 \times 10^{-15} \left[ \frac{\ell (n^2 - \ell^2)n^2 \ln(\gamma E n^2)}{(2\ell + 1)E} \right] \, \text{cm}^2. \quad (2-16) \]

In this expression \( \ell > = \max (\ell, \ell') \) and

\[ \gamma = \frac{1}{27.21(\delta_{n\ell} - \delta_{n\ell'})^2} \quad (2-17) \]

where \( \delta_{n\ell} \) and \( \delta_{n\ell'} \) are the quantum defects of the two states involved in the collision induced transition. In this derivation Herrick has approximated the dipole radial matrix element for the transition for the matrix element for
hydrogen.

Finally, it should be noted that (2-11), (2-12), and (2-16) exhibit the \((\ln E)/E\) quantal energy dependence.

Only a few experimental investigations of electron-Rydberg atom state changing collisions have been conducted. In experiments in which ground state helium atoms were excited to an ensemble of Rydberg states by electron impact at energies from 30 to 300 eV, Schiavone et al. (1977) have detected excited atoms in high \(\lambda\) states. The production of these atoms is interpreted as resulting not from the initial excitation process, which is expected to favor the production of low \(\lambda\) states at these energies (Fano (1974)), but rather from subsequent \(\lambda\)-changing collisions between the Rydberg atoms and electrons. An empirical cross section formula, based on the quantal \((\ln E)/E\) formula, was determined for these \(\lambda\)-changing collisions to be

\[
\sigma_{\Delta \lambda} \cong 5 \times 10^{-15+0.3} \ln(100E_n^2)n^4/E
\]  

(2-18)

where \(\sigma_{\Delta \lambda}\) is in \(\text{cm}^2\) and \(E\), the incident electron energy, is in eV. Schiavone et al. (1979) have recently extended this work to include the study of other rare gas atoms and results similar to helium were obtained for neon and argon. This \(\lambda\)-changing process has also been observed by Kocher and Smith (1977) in experiments in which ground state lithium
atoms were excited to Rydberg states by electron impact at energies several times threshold. A question yet to be answered in each of these experiments concerns the exact collisional mechanism by which the high \( \ell \) states are created. It is uncertain whether these states are accessed directly in single collision events (i.e. \( \Delta \ell > 1 \)) or are populated via a succession of electron-Rydberg atom collisions in which only small changes in \( \ell \) occur (i.e. \( \Delta \ell = 1 \)).

Investigations of electron induced \( n \)-changing collisions have been carried out by Delpech et al. (1977) and Devos et al. (1979). In these experiments metastable helium \( 2^3S \) atoms in a helium afterglow were laser excited to single well-defined \( n^3P \) Rydberg states (\( 8 \leq n \leq 17 \)). Following excitation, these atoms collided with electrons characterized by a Maxwellian distribution whose temperature was selected from the range 300 K to about 3000 K. While the conditions in the afterglow prevented detailed examination of the \( \ell \)-changing process (this process was saturated in a time short compared to the temporal resolution of the experiment), collisions resulting in a change of \( n \) were observed and studied in detail. Rate constants as large as \( 10^{-4} \) cm\(^3\)/sec were reported for the \( n \)-changing process and it was found that \( \Delta n > 1 \) transitions were important.
CHAPTER III

EXPERIMENT - GENERAL

In this chapter the basic experimental procedure is outlined. Attention is given to the types of measurements which need to be made in order to examine the processes involved and to determine the desired cross sections.

3.1 Objectives and Outline of Experiment

It was mentioned in Chapter I that the first results of a program to study collisional phenomena between electrons and high Rydberg atoms are reported in this thesis. It is normal in the initial phases of such a study to concentrate on the processes which are most likely to occur under reasonably attainable experimental conditions. In the present case emphasis has been placed on the process of electron impact ionization of Rydberg atoms and on electron-Rydberg atom interactions which result in a change of state of the Rydberg atoms. While the ionization process is well defined, the state-changing process can be quite complex depending on both the actual interactions and on the definition of the initial and final Rydberg state.

In order to facilitate the interpretation of the experimental results and obtain detailed information on the
collision processes, it was decided that Rydberg atoms prepared in selected, well-defined states and reasonably monoenergetic (within ~10%) electrons would be employed in the present experiment. The production of atoms in selected, well-defined Rydberg states is accomplished using optical excitation which provides the ability to access such states through wavelength and selection rule considerations. The use of tunable, dye lasers in this connection can make this production method quite efficient.

It is, in general, desirable to make the initial measurements of a process on systems having the greatest simplicity. In the present case atomic hydrogen would be the obvious choice to meet such a criterion. However, due to the nature of the energy level structure and the high ionization potential of the hydrogen atom and the fact that hydrogen normally occurs in molecular form, high Rydberg atoms of hydrogen are hard to produce at all, let alone in the quantity necessary for a collision experiment. On the other hand, sodium atoms can be efficiently laser excited to well-defined high Rydberg states. Furthermore, while not hydrogen, sodium nonetheless has a relatively simple structure. The single valence electron outside a closed shell of inner electrons results in angular momentum terms identical to hydrogen and field-free energy levels
which are simply related to those of hydrogen through their quantum defects. For these reasons sodium was chosen as the atom in which to excite high Rydberg states in the present experiment.

The experiment is performed using a crossed-beams experimental arrangement shown schematically in Fig. 3-1. A beam of ground state sodium atoms is intersected at right angles by the pulsed output of two simultaneously pumped, tunable dye lasers. During the laser pulse a fraction of the atoms in the sodium beam is excited via a two-step process to a selected high Rydberg state. The high Rydberg atoms so produced are detected by ionizing them in a strong electric field and measuring the resulting ion or electron signal with an electron multiplier.

Collisional phenomena between the Rydberg atoms and electrons are studied by directing an electron beam across the portion of the sodium beam in which the Rydberg atoms are excited. This beam is collinear with, but oppositely directed to, the laser beam. Techniques are used which are capable of detecting the products of state-changing collisions and ionizing collisions. Following a laser pulse the laser excited Rydberg atoms are allowed to interact with the electrons for a specified time interval. At the end of this interval either Rydberg atoms resulting
Fig. 3-1 Schematic diagram of crossed-beams arrangement.
from state-changing collisions may be detected and identified using state-selective field ionization or ions resulting from ionizing collisions may be detected by sweeping them to the electron multiplier with a small electric field. Here small means a field less than that required to ionize any Rydberg atom of importance. From the results of these measurements, the nature of the state-changing process as well as cross sections for the state changing and ionizing collisions may be determined.

The signal levels observed depend on the electron energy and beam current, on the number of Rydberg atoms excited, and on the type of Rydberg states excited. Technical considerations, primarily, dictated both the choice of electron energy and principal quantum numbers of the Rydberg states used in the present work. It would, of course, be desirable to examine the collision processes from threshold to high energies. At low energies threshold behavior can be ascertained and since the theoretical difficulties encountered at these energies are often greater than at higher energies, a more critical test of theory can be applied. As the electron impact energy is increased different types of interaction processes become possible. However, for collisions with Rydberg atoms threshold energy means milli-electron volts for the ionizing events and even
smaller energies for state-changing. Experimental work at these energies using beam techniques is very difficult and is probably not warranted for initial measurements if the study can be conducted at higher energies. In the present work an electron energy of 25 eV is employed. The decision to use this energy represents the desire to work at low energies where the cross sections for the collision processes are larger while still maintaining a well-defined electron beam. Concerning the level to which the sodium atoms are excited, Rydberg states are produced where the value of the principal quantum number, n, is selected from the range $25 \lesssim n \lesssim 40$.\footnote{States of larger n have been produced, however it is likely that more than one state is excited at such values of n (see Chapters IV and V).} This choice of the degree of excitation results from a compromise between 1) working at low enough values of n so that the laser linewidth is sufficient by itself to determine that a single state be excited, and 2) working at high values of n where the cross sections for the processes are larger.

3.2 Important Considerations in Rydberg Atom Experiments

As with all experiments of this nature, there are a variety of competing processes with which the experimenter must contend. In the present experiment, in addition to

\footnote{States of larger n have been produced, however it is likely that more than one state is excited at such values of n (see Chapters IV and V).}
the more conventional sources of noise (e.g. electron impact ionization of the background gas in the chamber and of sodium in the beam, laser beam interactions with surfaces, etc.), there exist several uncommon (and perhaps surprising at first) features which result from the unusual nature of high Rydberg atoms. These supplementary considerations include 1) the radiative lifetimes of the Rydberg atoms, 2) the effects of extraneous electric and magnetic fields on Rydberg atoms, and 3) the interactions between Rydberg atoms and the background gas in the chamber, the background electromagnetic radiation, and other Rydberg atoms. Of course these processes are interesting in their own right and their study constitutes part of the current research interest in high Rydberg atoms. Such current study means that these interactions are not completely understood and this lack of knowledge has caused some problems in the present work. The more conventional sources of noise can be dealt with in the next chapter while a brief discussion of each of the above mentioned considerations involving the Rydberg atoms is given below.

Radiative lifetimes. Perhaps the most obvious consideration for experiments involving Rydberg atoms is their finite radiative lifetimes. For the range of Rydberg states laser excited in the present work these lifetimes are tens
of micro-seconds. In hydrogen the radiative lifetime scales as $n^3$ for a given value of the orbital angular momentum quantum number, $\ell$. For fixed $n$ the lifetime also increases with $\ell$. This radiative decay will compete with all collision processes in depopulating any Rydberg state. It is important to note that for Rydberg atoms in zero-field (see below) the largest branching ratios in the radiative decay process occur for transitions to low lying energy states well below the Rydberg manifold of excited states. This is important because as a result there need be no concern about a Rydberg atom radiatively decaying from one Rydberg state to a neighboring Rydberg state of slightly less energy. Instead the process results in the complete loss of an atom from the entire Rydberg regime of states and not in populating another Rydberg state.

**Electric fields.** High Rydberg atoms exhibit large electric polarizabilities and hence are easily perturbed by small electric fields. This is manifested in the Stark effect. This interaction with an electric field, $F$, causes the field-free energy levels to be shifted as $F$ is increased. In the case of sodium this shift is initially quadratic in the value of $F$ since the states are non-degenerate. In principle this results in a change of the energy resonance conditions for the second step of the excitation process.
However, before this shift becomes important on the practical scale (i.e. comparable to the laser linewidth), level mixing occurs. This mixing becomes significant when the energies of the states which are mixed become degenerate due to their Stark shifts. Level mixing results in Stark states whose character can be expressed as a superposition of the field-free wavefunctions so that the field-free wavefunctions can no longer be associated with a single state. For the level of Rydberg atom excitation used in this experiment, a field of only several volts per centimeter is required to mix a given nd state with all the higher lying states of the same value of n. As a consequence of this mixing, the existence of small electric fields can substantially alter the type of Rydberg atoms produced. In addition, collisions occurring in the presence of small electric fields may, in reality, involve Rydberg atoms in Stark states even if the initial Rydberg atoms were originally produced in zero field. Furthermore, state changing collisions occurring in the presence of fields so small that the Rydberg atoms initially involved in the collisions are not perturbed by the field may result in more highly excited Rydberg atoms which are affected by the field and are therefore in Stark states. Finally the radiative lifetimes of Stark states are different than those of field-free
states and if the field is large enough or the Rydberg state high enough, the lifetime against field ionization becomes important.

**Magnetic fields.** Magnetic fields will produce effects on Rydberg atoms similar to those produced by electric fields, however the size of the effect in the magnetic field case will be smaller than that for the corresponding electric field case.

**Background gas.** Collisions between high Rydberg atoms and neutral atoms and molecules have been studied at thermal energies in some detail theoretically and experimentally. Both state-changing collisions and collisional ionization of the Rydberg atom are possible depending on the nature of the neutral species. Such collisions are of interest in the present work due to the presence of background gas in the vacuum chamber. Collisions between Rydberg atoms and low-energy electron attaching molecules have been examined and found to exhibit cross sections of $\sim 10^{-12}\text{cm}^2$ for collisional ionization and probably similar cross sections.

---

1 This is evident from the fact that the field-free states composing a Stark state each have a different lifetime.

2 Such collisions in electric fields may be important in gaseous nebulae where the electric field is created by neighboring ions of the plasma.

3 See Hotop and Niehaus (1967), Matsuzawa (1972, 1975), Stockdale et al. (1974), Foltz et al. (1977), and Hildebrandt et al. (1978)
sections for state-changing processes. Collisions involving polar molecules yield cross sections which can be as large as $10^{-11} - 10^{-12}$ cm$^2$ for ionization and state-changing.\footnote{See Hotop and Niehaus (1967), Matsuzawa (1971, 1974b), Latimer (1977), Gallagher \textit{et al.} (1977a), and Smith \textit{et al.} (1978)} A number of studies have been undertaken involving Rydberg atom-neutral collisions which result in a change in the orbital angular momentum of the Rydberg atom.\footnote{See Smirnov (1974), Gallagher \textit{et al.} (1975a), Gounand \textit{et al.} (1976), Gersten (1976), Olson (1977), Deeck \textit{et al.} (1977), Gallagher \textit{et al.} (1977b), Gounand \textit{et al.} (1977), Gallagher \textit{et al.} (1977a), Omont (1977), Gallagher \textit{et al.} (1978), Hickman (1978), Derouard and Lombardi (1978), Prunelé and Pascale (1979), and Hugon \textit{et al.} (1979)} These studies have primarily centered on rare gas atoms as the collision partners. In the specific case of sodium nd states, cross sections of $10^{-12} - 10^{-13}$ cm$^2$ have been obtained for this state-changing process.\footnote{Flannery (1970, 1973) has theoretically investigated n-changing and ionizing collisions between hydrogen Rydberg atoms and 1) ground state hydrogen and helium atoms, and 2) hydrogen molecules. For n=30 cross sections for all of these processes are smaller than those given above.}

\textbf{Background electromagnetic radiation.} The interaction of high Rydberg atoms with the ambient thermal (300 K) radiation emitted by surrounding objects has recently received attention (Gallagher and Cooke (1979a) and Beiting \textit{et al.} (1979)). This radiation, often characterized by a black-body spectrum which maximizes at $\sim 10$ $\mu$m
at 300 °K, is capable of both photoionizing Rydberg atoms and inducing transitions between the Rydberg states (absorption and stimulated emission). This interaction has lead Gallagher and Cooke (1979b) and Ducas et al. (1979) to suggest that Rydberg atoms be used as detectors of far infrared radiation.

**Rydberg atom-Rydberg atom interactions.** This topic is relatively new in Rydberg atom research. The author is aware of only one study - the theoretical one of Olson (1979) - which is applicable to the conditions of the present experiment. Olson's investigation shows that collisions at low relative velocity between the two atoms tend to result in the ionization of one atom with the concurrent de-excitation of the other atom. Cross sections about ten times the geometric cross section are deduced for low velocity collisions.

3.3 Signal Analysis Considerations

Although the Rydberg atoms and electrons are produced in a crossed-beams arrangement, the actual experimental technique involved is somewhat like a beam-cell method. This is because the Rydberg atoms are excited completely within the electron beam which has been made uniform in number density and large enough so that, in the time interval allowed for interactions between the electrons
and the Rydberg atoms, the Rydberg atoms always remain in
the electron beam. Therefore in the absence of any other
processes producing the same type of signal, the rate of
signal production, $\frac{dS}{dt}$, for a given electron-Rydberg atom
process at time, $t$, after the laser pulse is given by

$$\frac{dS}{dt} = N_L(t)n_e \sigma v_r \approx N_L(t)n_e \sigma v_e$$

(3-1)

where $N_L(t)$ is the number of laser excited Rydberg atoms at
time $t$, $n_e$ is the number density of electrons, $\sigma$ is the
cross section for the particular process, and $v_r$ is the
relative velocity between the electrons and the Rydberg
atoms and is closely equal to the electron velocity,
$v_e$, under the present conditions. If no other processes
besides the one under investigation influence the time
dependence of $N_L$, then the above expression can be
integrated to give the conventional formula

$$S = N_L(0) (1 - e^{-n_e \sigma v_e t})$$

(3-2)

where $N_L(0)$ is the number of Rydberg atoms produced by the
laser at $t = 0$ and $t$ is the interaction time interval.\footnote{This analysis assumes that the laser pulse is short compared to the other characteristic times of the system such as the collision times and the interaction time interval. When this is the case the laser simply produces some number of Rydberg atoms, $N_L(0)$, at time $t=0$. If the laser pulse is long, then $t=0$ occurs at the start of the pulse and the time dependence of the excitation of the Rydberg atoms must be included in $N_L(t)$ in (3-1).} \footnote{Although it is evident that the beam-cell technique is applicable under the above stated conditions, this fact may be derived from the conventional crossed-beams analysis involving the beam overlap integral.}

In reality, as discussed in Sec. 3.2, other processes involving the Rydberg atoms are occurring in addition to the electron-Rydberg atom process of interest. $N_L(t)$ and $S$ are dependent on all these processes. It is apparent that any measured signal (e.g. non-laser excited Rydberg atoms, sodium ions, etc.) will be composed of contributions from several processes. Perhaps less apparent is the fact that the processes which exert large influences on the time development of $N_L$ are coupled together as a result of this influence. This means that simple subtraction of signals obtained for the various processes from each other in order to obtain the signal for the desired process is incorrect. Such coupled processes must be
analyzed simultaneously.¹

Finally, it should be noted that the objective of the present experiment is to study collisions between electrons and Rydberg atoms which are in well-defined states, i.e. the initial state of the Rydberg atoms should be known. It is important, therefore, to insure that single collision conditions hold in the present work, i.e. there will be no contribution to a signal due to a collision involving the product of an earlier collision. For example, in the case of the ionization signal, under single collision conditions no component of that signal will result from the collisional ionization of a Rydberg atom whose state has already been changed by an earlier collision from the initial laser excited state. Under such conditions the signal analysis need only be carried

¹ Strictly speaking, this situation of coupled processes arises in most all collision experiments since there are always background processes occurring. However, the effect is negligible under the thin target conditions that most beam experiments employ. In these cases subtraction of background signals from the total signal is quite accurate. In the present experiment, however, thin target conditions do not necessarily apply, especially when the definition is broadened to include the process of radiative decay.
to first order, i.e. only single event processes are included.¹

¹ When invoking single collision conditions, it is important to guard against situations in which the second collision event can proceed with a very high probability. For instance, if the state of a laser excited Rydberg atom is changed by some process to a very high lying energy state, it may be very easily ionized in a subsequent collision and thus contribute to the ionization signal.
CHAPTER IV

EXPERIMENT-DETAIL

The details of the apparatus and measurements outlined in the last chapter are discussed in this chapter. The sources of error are identified and their magnitudes evaluated. The basic vacuum system and the alkali beamline have been described at length elsewhere (Cook, 1977) and, except for modifications made during the present work, will therefore be treated only briefly here. The remaining parts of the apparatus and the measurement methods will be described in detail.

4.1 Vacuum system

The vacuum system, see Fig. 4-1, consists of two cylindrical chambers - the interaction or main chamber and the alkali beam source chamber - coupled together at right angles. Oil diffusion pumps are used to achieve a vacuum in the two chambers. In addition to the water-baffled, 4" pump used previously on the interaction chamber, a 4" liquid nitrogen trap (Leybold-Heraeus Vacuum Products, Inc.)\textsuperscript{1} has been installed between the baffle and the chamber.

\textsuperscript{1} The names of manufacturers are given in parentheses for all permanent equipment modifications made to the apparatus during the present work and for all other important equipment and material used in the experiment.
Fig. 4-1 Diagram of apparatus. Scale drawing.
This trap provides extra cryopumping and more efficient pump oil trapping. The liquid nitrogen cold finger attached to the interaction chamber has been retained and its surface area increased by about a factor of three by clamping a strip of brass shim stock to it. A 2" diffusion pump is employed on the source chamber. The homemade water baffle used with this pump has been replaced with a commercial baffle (Varian Vacuum Division). Both diffusion pumps exhaust into a single mechanical pump through a backing manifold and line. A cut-off valve\(^1\) (Leybold-Heraeus Vacuum Products, Inc.) has been added to the backing line at the intake port of the mechanical pump to protect the system in the event of a power failure. The pressure in the backing manifold is monitored by a thermocouple gauge while the pressures in the two chambers are measured using separate ionization gauges. During normal operation the base pressure in the interaction chamber with only the 4" liquid nitrogen trap filled (cold finger dry) is about \(7 \times 10^{-8}\) torr while a pressure of about \(2 \times 10^{-8}\) torr can be achieved with both trap and finger filled. Liquid nitrogen is always maintained in the 4" trap while the cold finger is only filled when a measurement is being made. The

\(^1\)When power fails this valve automatically closes isolating the vacuum system from the mechanical pump and then venting the mechanical pump to atmospheric pressure.
base pressure in the source chamber is about $1 \times 10^{-7}$ torr. The backing manifold pressure is about 5 microns. The water plumbing for the water baffles and diffusion pump cooling coils has been remodeled several times; the present arrangement uses de-ionized water in a closed-loop circuit.

A novel design feature of the system consists of the manner in which the equipment inside the chambers is mounted. In the interaction chamber the entire electron beamline, grid plate assembly, and electron multiplier, are mounted on a platform extending from the 12" diameter flange which forms the end of the chamber. In the source chamber the alkali oven, collimating apertures, and final beam defining aperture are mounted off the 12" diameter flange which forms the end of that chamber. Finally, the alkali beam profiling device and catcher are mounted on an 8" flange attached to the interaction chamber opposite to the source chamber. Such equipment mounting schemes allow entire assemblies to be removed intact from the apparatus for examination and, most importantly, alignment.

4.2 Alkali Beamline

The alkali beamline is, for the most part, unchanged from the one described by Cook (1977). The alkali beam source is a conventional effusive oven source. The oven is
resistively heated and contains two connected chambers - a larger one (in the oven "body") in which, for the present experiment, a 1 gm vial of 99.95% pure sodium (Callery Chemical Co.) is placed, and a smaller chamber (in the oven "nose") at the end of which is located a 0.043" diameter hole through which the alkali vapor effuses. The resulting effusive flow is apertured twice before reaching the final square beam defining aperture. This defining aperture, previously located in the interaction chamber, has been moved back to a position near the vacuum wall which separates the source and interaction chambers. The aperture is attached to the rest of the beam aperture assembly. The size of the aperture has been decreased so that the cross sectional dimension of the beam at the interaction region (point of intersection of sodium, laser, and electron beams) is the same as when the defining aperture was at the old location. Although there are some inherent disadvantages in placing the defining aperture closer to the oven (e.g., plugging the smaller aperture with sodium - negligible with the present beam fluxes used; increasing the effects which cause a penumbra around the beam), they are outweighed by the advantages gained by getting better beam aperture alignment and by keeping all excess sodium confined to the source chamber. This latter consideration can be important
since an accumulation of sodium can degrade insulators and reduce the work functions of the various surfaces. Therefore it is desirable to keep the amount of sodium present in the interaction chamber to a minimum. No problems that can be associated with the relocation of the beam defining aperture have been identified in the present work.

Following final definition, the beam crosses the interaction chamber and is deposited on a cooled copper surface. Hot wire ionization is used to detect the presence of the beam. This is accomplished by means of a movable, hot wire ionizing device located immediately in front of the beam collecting surface. When employed to its fullest capability, this device may be used to obtain a cross-sectional profile of the beam. Such a profile contains information on beam position, size, and uniformity (see Cook (1977) for details of such a measurement\(^1\)).\(^2\) The

---

\(^1\) The efficiency of hot wire ionization of sodium on clean tungsten wire is only about 5% (Datz and Taylor (1956)). However, it is possible to increase this efficiency to what is taken to be unity by treating the wire with oxygen (see Datz and Taylor).

\(^2\) Placement of the beam catcher and profiling device in the interaction chamber (as opposed to a separate beam "dump" chamber) does not pose a problem as far as sodium contamination of the main chamber is concerned since the profiler only intercepts the beam when a profile measurement is being made and the surface of the catcher is maintained at reduced temperature. For the beam fluxes used, the catcher appears to trap the beam adequately.
important dimensions of the sodium beamline as shown in Fig. 4-2.

The sodium beam used in the present work is quite tenuous by conventional standards. Under normal operating conditions the oven body is maintained at 190 °C while the oven nose runs at 200 °C. The differential temperature helps to prevent clogging of the hole through which the sodium effuses. When running at equilibrium at these temperatures, the oven draws about 30 watts of power. Using the standard effusion analysis (see for example Lew (1967)) along with the thermodynamic tables of Stull and Sinke (1956) and the beam geometry given in Fig. 4-2, an atom flux on the beam axis of approximately $5 \times 10^{11}$ atoms/cm$^2$-sec is obtained for these operating conditions. This corresponds to a beam density at the interaction region of about $7 \times 10^6$ atoms/cm$^3$ and a total atom current in the beam of about $2.5 \times 10^{11}$ atoms/sec. It should be noted that this density is less than that of the surrounding background gas. A potential problem in experiments using alkali vapor is the dimer content of the vapor. Again using the tables of Stull and Sinke, it is found that, for the present oven operating conditions, the ratio of dimer density to atom density in the beam is approximately $3 \times 10^{-3}$. 
Fig. 4-2 Geometry of alkali beamline.
4.3 Grid Assembly and Electron Multiplier

The intersection of the alkali beam, laser beams, and electron beam defines the interaction region where high Rydberg atoms are produced, detected, and allowed to interact with various targets (electrons, background radiation, and background gas). A grid assembly surrounds this region and provides the capability to apply electric fields across the region to 1) collect charged reaction products, and 2) field ionize the Rydberg atoms and collect the resulting charged particles. The charged particles are driven by the action of the field toward an electron multiplier (Johnston Laboratories, Inc., MM-1) where they are detected. A side view of the grid assembly and multiplier is shown in Fig. 4-3. Each grid consists of a square frame 3 1/2" on a side with a hole in the center across which the grid wires are stretched. The grids are mounted parallel to the plane, containing the beams on four insulated thread stock posts and, with the exception of Grids 2 and 3 which straddle the interaction region, are separated and electrically isolated from each other by Delrin spacers. While small Delrin spacers are used to insure the electrical isolation between Grids 2 and 3, the majority of the 1.0" spacing is maintained with metal spacers so as to minimize the amount of insulator exposed to charged particles and therefore
**Fig. 4-3** Side view of grid assembly and electron multiplier. Scale drawing; dimensions in inches. Dashed square is sodium beam (perpendicular to page); dashed arrow pointing left is blue laser beam; dashed arrow pointing right is electron beam. Diameter of hole in Grids 1, 4, 5, and 6 equals 1.375"; diameter of hole in Grid 2 equals 2.0"; rectangular hole in Grid 3 is 1.0" x 0.4" with long dimension parallel to sodium beam axis.
decrease the possibility of charging up the insulators. Grids 1, 4, 5, and 6 each consist of a stainless steel frame with a 1 3/8" diameter hole in the center across which tungsten wire, 0.001" in diameter, is mounted with a 0.1" pitch. The design of Grids 2 and 3 has been dictated by the nature and results of the measurements and therefore will be discussed in Sec. 4.6 and 4.8.

The electron multiplier, located beneath the grid assembly, is a focused-mesh structure consisting of twenty copper-beryllium dynodes. It has a circular sensitive area 1.3" in diameter and is capable of gains up to about $10^8$ with very little dark current when a voltage of 3500 V is applied across it.

The voltages at which the multiplier and various grids are operated will be discussed in Sec. 4.6 and Sec. 4.7.

4.4 High Rydberg Atom Production

The first step in the production of high Rydberg sodium atoms is the formation of a beam of ground state sodium atoms. This is done by conventional means as discussed in Sec. 4.2. Concerning the actual excitation scheme, a number of possibilities exist. However, one technique — two-step optical excitation — overshadows the rest. This method (depicted in Fig. 4-4), when applied under field-free conditions, consists of first exciting
Fig. 4-4 Two-step Rydberg atom excitation scheme.
either the $3s^{2}S_{1/2} \rightarrow 3p^{2}P_{1/2}$ transition with $5896 \, \AA$ light or the $3s^{2}S_{1/2} \rightarrow 3p^{2}P_{3/2}$ transition with $5890 \, \AA$ light (these are the well-known sodium D resonance lines) and then exciting the Rydberg level via 1) the $3p^{2}P_{1/2} \rightarrow ns^{2}S_{1/2}$ or $nd^{2}D_{3/2}$ transition, or 2) the $3p^{2}P_{3/2} \rightarrow ns^{2}S_{1/2}$ or $nd^{2}D_{3/2,5/2}$ transition with radiation around $4100 \, \AA$. The value of $n$ depends on the intermediate $3p$ state chosen and on the blue wavelength selected. As implied the dipole selection rules govern which final states are accessed.

The excitation process just described can be made efficient because both the resonance radiation (5896 $\AA$ and 5890 $\AA$) and the 4100 $\AA$ radiation are producible by dye lasers which are relatively intense, tunable sources of light. In fact the absorption oscillator strengths for the D lines are so large (0.327 for the transition to the $2P_{1/2}$ state and 0.655 for the transition to the $2P_{3/2}$ state; see Wiese et al. (1969)), it is possible to saturate these transitions with the output of the yellow laser. As mentioned at the outset of this thesis, it is the use of such lasers in this and other Rydberg atom production methods that has stimulated the broad interest in the study of Rydberg atoms.

In the present experiment the requirements of the
two-step laser excitation technique are met by the use of two tunable dye lasers pumped by a single nitrogen laser (see Sec. 4.5). Although the dye lasers are pulsed due to the use of a nitrogen pump laser, the required degree of simultaneity between the yellow and blue outputs is satisfied since only one nitrogen laser is used.\footnote{Since the lifetimes of the intermediate 3\textit{p} \textsuperscript{2}P\textsubscript{1/2} and 3\textit{p} \textsuperscript{2}P\textsubscript{3/2} states are only 16 nsec (see Wiese \textit{et al.} (1969)), it is necessary that the two sources of radiation operate together in time to within that lifetime.}

The high Rydberg state portion of the sodium energy level diagram is shown in Fig. 4-5 for arbitrary \textit{n} and low values of the orbital angular momentum quantum number, \textit{l}. For large values of \textit{n} the quantum defects, \(\delta_\textit{l} \), of these low \(\textit{l}\) states (ignoring fine and hyperfine structure) are:

- 1.34 for \textit{s} states,
- 0.85 for \textit{p} states,
- 0.014 for \textit{d} states,
- 0.0016 for \textit{f} states, and
- 0.0004 for \textit{g} states.\footnote{The \textit{s}, \textit{p}, and \textit{d} state quantum defect values may be obtained by extrapolation of values calculated from the term energies given by Moore (1971); for the \textit{f} and \textit{g} state values see Gallagher \textit{et al.} (1976b).}

As shown in Fig. 4-5 these quantities are equal to the fractional depression of the sodium \textit{n}\textit{l} levels from the hydrogenic \textit{n} level in terms of the \textit{n} to (\textit{n}-1) energy spacing in hydrogen. Gallagher \textit{et al.} (1976b) show that, for values of \(\textit{l} > 2\), \(\delta_\textit{l} \) scales as \(\textit{l}^{-5}\) while, for \(\textit{l} \leq 2\), \(\delta_\textit{l} \) is larger than that
Fig. 4-5 Rydberg state portion of sodium energy level diagram for low $\ell$ values. Dotted lines are hydrogen energy levels.
predicted by the $\lambda^{-5}$ curve. This dependence indicates (Freeman and Kleppner (1976)) that both core penetration and core polarization determine the value of $\delta_\lambda$ for $\lambda \leq 2$, while only core polarization ($\propto \lambda^{-5}$) is responsible for the value of $\delta_\lambda$ for $\lambda > 2$. This behavior is in keeping with the dramatic decrease in $\delta_\lambda$ as $\lambda$ exceeds the maximum value of $\lambda$ of the core electrons as noted by Freeman and Kleppner (1976). It is seen from Fig. 4-5 that the states accessed in this experiment, ns and nd, lie in the pairs ns, (n-1)d as regards their energy spacings.

The fine structure of sodium Rydberg states for n values in the teens has been examined for $\lambda$ values up to $\lambda = 5$ (Fabre et al. (1975), Gallagher et al. (1976a, 1976b), Gallagher et al. (1977c)). The fine structure intervals of the sodium p states are regular and, while obeying a hydrogen-like $1/n_{eff}^3$ dependence, are much larger than the corresponding value for hydrogen. The sodium d states exhibit an inverted structure. The d state intervals fit the expression $- (a/n_{eff}^3) + (b/n_{eff}^5)$ where $a$ and $b$ are constants and these intervals are larger in magnitude than the corresponding hydrogen values. The fine structure intervals of the sodium f, g, and h states are regular and agree in magnitude (within experimental uncertainty) with the values for hydrogen.
Radiative lifetimes, $\tau$, for the ns and nd states of sodium around $n = 10$ have been measured and compared to theory by Gallagher et al. (1975b). Power law fits to the data give: $\tau_s = (1.99 \pm 0.33)n^{(2.87 \pm 0.08)}$ nsec for the s states and $\tau_d = (0.965 \pm 0.039)n^{(3.00 \pm 0.02)}$ nsec for the d states.\textsuperscript{1} Within experimental uncertainty the exponents agree with the hydrogenic value of 3.

In the present experiment the intermediate $3p^2p_{3/2}$ state is used exclusively. Values of the blue laser wavelength, $\lambda$, required in the second step of the excitation process are given in Table 4-1 for various values of $n$ along with the differences in wavelength, $\Delta \lambda$, for neighboring states. The value of $\Delta \lambda$ determines the blue laser linewidth required if a given ns or nd state is to be accessed individually on the basis of laser linewidth alone. As already suggested it is the separation between ns and (n-1)d states which places the most stringent limits on this linewidth. Level splitting due to fine structure

\textsuperscript{1} These values probably require correction for the recently discovered (Gallagher and Cooke (1979a)) effects on measured lifetimes due to thermal background radiation. The effects are expected to be greatest for p states where Gallagher and Cooke have observed that, at n=17, 18, the true radiative lifetime (i.e. in the absence of background radiation) can be decreased by a factor of three when 300 K background radiation is present. For s states, a 20% background radiation effect has been observed by Gallagher and Cooke.
<table>
<thead>
<tr>
<th>n</th>
<th>$\lambda_{\text{ns}}$ (nm)</th>
<th>$\lambda_{\text{nd}}$ (nm)</th>
<th>$\Delta \lambda_{\text{ns}}$ (n-1)/d</th>
<th>$\Delta \lambda_{\text{nd}}$ (n-1)/d</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>4184.99</td>
<td>4167.57</td>
<td>17.01</td>
<td>12.61</td>
<td>4.81</td>
</tr>
<tr>
<td>20</td>
<td>4137.67</td>
<td>4113.91</td>
<td>3.01</td>
<td>2.53</td>
<td>0.91</td>
</tr>
<tr>
<td>25</td>
<td>4117.35</td>
<td>4104.83</td>
<td>1.66</td>
<td>1.45</td>
<td>0.51</td>
</tr>
<tr>
<td>30</td>
<td>4106.79</td>
<td>4099.38</td>
<td>1.01</td>
<td>0.90</td>
<td>0.32</td>
</tr>
<tr>
<td>35</td>
<td>4100.60</td>
<td>4095.85</td>
<td>0.66</td>
<td>0.60</td>
<td>0.21</td>
</tr>
<tr>
<td>40</td>
<td>4096.66</td>
<td>4093.43</td>
<td>0.45</td>
<td>0.42</td>
<td>0.15</td>
</tr>
<tr>
<td>45</td>
<td>4094.00</td>
<td>4091.71</td>
<td>0.33</td>
<td>0.30</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Parameters for second step of excitation process. All wavelengths in nm and given for air.
interactions is not distinguished since it is impractical in the present work to obtain a linewidth narrow enough so as to select individual fine structure levels solely on the basis of laser linewidth. Absorption oscillator strengths for the second step of the excitation process can be obtained by extrapolation of the semi-empirical calculations of Anderson and Zilitis (1964) and are also given in Table 4-1.

4.5 Lasers

Production of sodium high Rydberg atoms using the two-step laser excitation technique is accomplished in the present experiment by the use of two tunable dye lasers pumped by a single nitrogen laser. The nitrogen laser is of in-house design and construction.\(^1\) A schematic of this laser is shown in Fig. 4-6. A bank of twelve 3600 pf-30 kV capacitors are charged by a high voltage power supply through four 50 kΩ-225 W current-limiting resistors. Upon receiving a trigger pulse, the spark gap fires causing these capacitors to discharge into about twenty, low-inductance 500 pf-20 kV capacitors which are connected across the nitrogen plasma tube. When the breakdown voltage of the nitrogen in the plasma tube is reached, the

\(^1\) By F. B. Dunning and F. G. Kellert
tube breaks down and the small capacitors, due to their low inductance, rapidly discharge into the nitrogen creating an intense discharge. This discharge produces the required population inversion in the nitrogen gas and lasing action follows. Aluminum electrodes 3 cm apart form the sides of the plasma tube while 3/8" thick plexiglass is used for the top and bottom. The tube is 120 cm long and has a quartz flat at the output end and a UV reflecting mirror at the other end. The laser is operated at a charging voltage of 15 kV (drawing 10 to 15 ma dc average) and a repetition rate of 15 pps with a plasma tube pressure of around 60 torr and a spark gap pressure of about 16 psi. Under these conditions the laser produces an output pulse width of approximately 5 nsec and an average power of ~ 15 mW. This corresponds to ~ 1 mJ a shot and a peak power of ~ 200 kW.

The output beam of the nitrogen laser is split and used to pump the two dye lasers (see Fig. 4-7). Different cavity designs have been employed in the construction of these dye lasers throughout the course of this work but the one which has been used the most and is currently in use for both the blue and the yellow lasers is the design of Shoshan et al. (1977) and Littman and Metcalf (1978). At the center of the cavity is a side-pumped dye cell through which the dye solution is flowed. Using two cylindrical lenses, a portion
Fig. 4-7 Schematic diagram of laser arrangement.
of the nitrogen laser output is brought to a line focus just within the dye solution at the inner surface of the cell's input window. The remainder of the cavity is set-up at right angles to this pumping direction. A 100% reflecting mirror forms one end of the cavity while at the other end a grating-mirror combination for wavelength selective feedback and therefore tuning is located. Light coming from the active medium in the cell strikes the grating at grazing incidence. The light diffracted from the grating in a selected order is intercepted by a 100% reflecting mirror which, by its mounting angle, selects the wavelength to be fed back to the cell. Tuning is accomplished by adjusting the angle of this mirror. The light that is specularely reflected off of the grating is used as the output beam of the dye laser. Beam expansion within the cavity is not used and the resulting cavity length can be short. Linewidth reduction results from 1) the high dispersion obtained by using the grating at grazing incidence, 2) the fact that the light is diffracted twice on each pass through the cavity, and 3) the fact that the beam, crossing the grating at grazing incidence, automatically illuminates all of the grooves of the grating. This last point is important since the resolution achieved with a grating is proportional to the number of grooves on the
grating which are illuminated.

A $5 \times 10^{-3}$ molar solution of Rhodamine 6G in ethanol is used in the yellow laser. For the production of $5890 \ \AA$ light this choice is obvious. Rhodamine 6G is a highly efficient dye and this solution has a fluorescence band from $5680 \ \AA$ to $6050 \ \AA$ with a maximum at $5790 \ \AA$ (Molecron Corporation). The choice of a dye solution for the blue laser is not quite so simple. A mixture composed of 200 ml of a saturated solution of DPS in p-dioxane and 30 ml of a $2.5 \times 10^{-3}$ molar solution of POPOP in p-dioxane is employed. The tuning curve of the saturated DPS solution alone runs from $3960 \ \AA$ to $4160 \ \AA$ with a maximum at $4060 \ \AA$ (Molecron Corporation). The addition of the POPOP solution (which lases at longer wavelengths) pulls the DPS curve to somewhat longer wavelengths.

The complete laser set-up is shown in Fig. 4-7. During normal operation the nitrogen laser output beam is split so that about a third of it is used to pump the yellow laser while the rest is sent to the blue laser. This unequal division is used because Rhodamine 6G is such a high gain dye and because the yellow laser need not be too powerful due to the strong D line absorption in sodium. At the same time, since the oscillator strengths for the second step in the excitation process are small, the blue
laser should be as powerful as possible. The yellow laser employs a 1200 lines/mm grating operating in first order and has an average output power of 225 $\mu$W (equivalent to 15 $\mu$J a shot) with a linewidth of $\sim 0.1$ Å at 5890 Å. An 1800 lines/mm grating operating in first order is used in the blue laser and the average output power of that laser is 500 $\mu$W (equivalent to 30 $\mu$J a shot) with a linewidth of $\sim 0.05$ Å at around 4100 Å. Powers are measured with a calibrated thermopile (The Eppley Laboratory) and linewidths are estimated using an air-spaced etalon (Burleigh Instruments) which has a free spectral range of 30 GHz and a finesse of 19.3. The two dye laser output beams are merged together with a dichroic mirror which passes the blue light and reflects the yellow light. The resulting single beam is transported and aligned into the vacuum apparatus via a mirror and lens combination. At the entrance into the vacuum chamber the size of the yellow beam spot is $\sim 1$ cm in diameter while the blue beam is about 0.3 to 0.4 cm in diameter. These spot sizes along with the 0.7 cm height of the sodium beam ensures complete use of the blue laser power. Also under these conditions the size of the volume in which the Rydberg atoms are excited is determined by the blue laser. As indicated in Fig. 4-7 the (optical) path lengths of the two dye lasers are equal.
This results in the yellow and blue laser pulses arriving at the sodium beam simultaneously. Of course either pulse could be delayed for a given time interval with respect to the other by simply inserting the appropriate extra path length into the beamline of the laser whose pulse is to be delayed.

An important concern regarding the blue laser is the reduction of the amount of (untuned) fluorescence produced in that laser's output. Since this fluorescence light is produced over the entire laser dye's fluorescence curve, it is possible to excite other Rydberg states in addition to the state to which the laser is tuned as well as sodium ions from the photoionization of the 3p intermediate state.¹ The amount of fluorescence contained in the blue pulse can be estimated by observing blue light through the previously mentioned etalon and noting the contrast between the bright and dark rings in the ring pattern.

4.6 Detection of High Rydberg Atoms

As with their production, Rydberg atoms can be

¹ Threshold for this photoionization process is 4084 Å which is approximately where the maximum occurs in the fluorescence band of the blue dye mixture used. It should be noted that if the blue laser is tuned into this photo-ion continuum, a reasonably strong ion signal is obtained. Monitoring this signal allows the yellow laser to be accurately tuned onto the D line transition.
detected in a variety of ways. Two methods - observation of the fluorescence from the excited atom and detection of the charged particles from the ionization of the Rydberg atoms in an electric field - are used predominantly. Fluorescence works well for the lower Rydberg states where the lifetimes are short while field ionization is useful for higher Rydberg states where the field strength required to ionize the atoms is not excessive. An additional advantage of field ionization is that it can be essentially unit efficient. Field ionization is the method used to detect Rydberg atoms in the present work.

The process of field ionization is not completely understood for non-hydrogenic systems and even in the case of hydrogen such an understanding requires lengthy calculations. A rather crude, semi-classical picture of field ionization is given in Fig. 4-8 which shows the unperturbed potential energy field of the Rydberg electron on the left followed on the right by the effective potential energy of this electron upon application of an electric field, \( F \). The electric field produces shifts in the energies of the states and state splitting as zero-field degeneracies are removed. It also produces a saddle point in the effective potential energy of the Rydberg electron (depicted as a maximum in the potential energy, \( V_{\text{max}} \), in the one-dimensional
Fig. 4-8 Potential energy curves of Rydberg electron: unperturbed on left; in an applied electric field on right (parallel to field direction).
picture in Fig. 4-8). Classically, an electron in a state which lies below \( V_{\text{max}} \) will remain bound to the atom indefinitely. However, if the field is increased so that \( V_{\text{max}} \) is depressed past the energy state containing the electron, ionization will occur. The value of the field at which the energy of the state coincides with \( V_{\text{max}} \) is called the classical ionization threshold, \( F_c \), and for hydrogen is given by

\[
F_c = \frac{R}{4e^3 n^4} \quad (4-1)
\]

where \( R \) is the Rydberg constant, \( e \) is the electronic charge, and \( n \) is the principal quantum number of the state.

Field ionization may be applied to detect Rydberg atoms in a variety of ways. In the present work two of these applications are employed. From the discussion just given, it is reasonable to expect that, as \( F \) is increased from zero, Rydberg atoms in states of decreasing excitation are ionized in order. Thus if the electrons liberated in the field ionization process are detected per unit field strength as \( F \) is increased (differential electron signal with respect to electric field), a series of peaks each corresponding to a particular ionized Rydberg state will result. This provides a means of state selective detection and is called selective field ionization (SFI). Alternatively,
a field may be applied in which all Rydberg atoms of importance are ionized and the resulting total ion signal detected irrespective of the particular field strength at which the various atoms were ionized. This provides a measure of the total Rydberg population at the time of field application and will be termed, simply, the "field ionization" or FI technique. In this work the SFI technique is used primarily to detect state changing collisions and to measure the de-population of the laser excited state while the FI technique is used in the study of the electron impact ionization process.

**SFI Technique.** Following each laser pulse an electric field which increases from zero to some large value in \( \sim 1 \mu \text{sec} \) (i.e. a field ramp) is applied across the interaction region. As the threshold field for a given Rydberg state is exceeded, atoms in that state are ionized. The direction of the field is arranged so that the electrons released in the ionization process are driven out of the interaction region and toward the electron multiplier where they are detected. The output pulses of the multiplier are amplified, passed through a discriminator, and then fed to a TAC which is triggered at the start of the field ramp. The TAC thus measures the time interval between the beginning of the field ramp and the detection of an
electron and stores the result in a 1024 channel MCA. With a knowledge of the time dependence of the field ramp, the time intervals (i.e. channel numbers) can be correlated with the electric field strengths at which the Rydberg atoms (from which the electrons came) were ionized. The resulting signal on the MCA is a differential electron signal with respect to the ionizing electric field and will be called an SFI spectrum.

In normal operation the first dynode of the multiplier along with Grids 5 and 6 are run at $+200\,\text{V}$\footnote{For the Johnston multiplier, 200 eV is the impact energy resulting in the best detection efficiency for electrons.} and Grid 4 is run at $+80\,\text{V}$. The anode and backplate of the multiplier are operated at a voltage, usually $+4000\,\text{V}$ to $+4200\,\text{V}$, such that the multiplier's output pulses, when amplified, exceed the threshold set on the discriminator.\footnote{The anode-backplate voltage which is sufficient to accomplish this is determined in an auxiliary experiment requiring a constant (on average) source of electrons. In the present work an ionization pressure gauge from which electrons continuously escape is used as this source. The count rate from the discriminator resulting from detecting these electrons is measured as the anode-backplate voltage is increased and at some value of this voltage the count rate will level off indicating that all of the amplified multiplier output pulses exceed the discriminator threshold level.} The amplifiers are set at a gain of 40 (an LRS VV100B amp with...
a gain of 10 in series with an LRS 133B amp with a gain of 4) and the discriminator (EG&G TR204A/N) threshold is set at -100 mV. The discriminator is inhibited at all times except during the time the field ramp is applied. The TAC and MCA are contained in a single unit (LRS 300lqVt). In order to avoid having to float all the counting electronics at the potential of the multiplier's anode and backplate, the multiplier is capacitively coupled to the amplifiers via the circuit shown in Fig. 4-9. The electrons which are detected are released at a variety of field strengths in the interaction region depending on the Rydberg states from which they come. However, it is desired that all the electrons be detected with the same efficiency. This means that each electron should strike the first dynode of the multiplier with the same energy. This is accomplished by maintaining the first dynode of the multiplier at +200 V always and applying equal but opposite polarity voltages to Grids 2 and 3 (negative voltage to Grid 2 and positive voltage to Grid 3) to create the ionizing field ramp. Thus the electrons are released in the interaction region at zero potential regardless of the strength of the ionizing field. A schematic diagram of the
Fig. 4-9 Multiplier coupling circuit.
field ramp generator is shown in Fig. 4-10.\textsuperscript{1} Since the risetime of the field ramp is \(\sim 1.2 \ \mu\text{sec}\), the TAC is adjusted to measure time intervals from \(\sim 100 \ \text{nsec to} \sim 1.4 \ \mu\text{sec}\). Both the TAC and field ramp generator are triggered by a single pulse generator (Datapulse, Inc. 101), however the trigger pulse to the ramp generator is passed through a \(\sim 200 \ \text{nsec delay line first}\). This ensures that the TAC "window" is open when the ramp starts.\textsuperscript{2} A schematic diagram of the entire SFI technique is given in Fig. 4-11 and the sequence of events which occur in the application of the SFI technique is shown in Fig. 4-12. It should be noted that, although the field ramp trigger pulse occurs at time \(t_T\) in Fig. 4-12, the actual ionization of the atoms takes place toward the top of the ramp about 1 \(\mu\text{sec}\) later. Thus the time after the laser pulse at which ionization occurs is \(t_T + 1 \ \mu\text{sec}\). Furthermore the shortest time, \(t_T\), after the laser pulse at which the field can be applied is about 2 \(\mu\text{sec}\) due to noise pick-up from the laser fire.

The number of atoms in a given state which are ionized relative to another state can be obtained by integrating the

\textsuperscript{1} The author thanks Dr. T. F. Gallagher of Stanford Research Institute for information on a basic field ramp generator from which the generator used in the present work was developed.

\textsuperscript{2} Although this is not a necessity, it allows all events along the ramp to be detected.
Fig. 4-10 Schematic of field ramp generator.
Fig. 4-11 Schematic of SFI technique.
Fig. 4-12 Sequence of events in SPI technique.
counts in the SFI signal for each state and comparing the integrals. The absolute number of atoms in a given state which are ionized can be obtained by multiplying the integrated number of counts for the state by the multiplier efficiency.

There are several considerations important to obtaining an accurate SFI spectrum (i.e. MCA output). Perhaps the most important concern is the fact that the TAC is able to measure at most only one time interval per laser pulse and therefore only one electron can be handled per laser pulse. Any electrons arriving after the first electron are ignored. Therefore it is necessary to ensure that the probability of detecting an electron does not reach unity on any given laser pulse before the TAC "window" closes. Due to the statistics of the Rydberg atom excitation process,\(^1\) this means that on the average less than 0.1 electrons can be detected per laser pulse. If higher average count rates are used, the signal amplitude of the SFI spectrum will be progressively diminished in traversing the spectrum.\(^2\)

(Changes in the electron detection efficiency due to the electrons being produced at different field strengths

---

\(^1\) See West (1975)

\(^2\) It is possible to correct for this reduction across the spectrum within limits.
would also affect the SFI spectrum amplitude but this problem has already been addressed.) In order to assign the correct field strength to a given time (i.e. channel number) in the SFI spectrum, it is important to correct for the delay between the time the electron is liberated in the field ionization process and the time the TAC is stopped. This delay results from 1) the electrons' flight time to the multiplier, 2) the pulse transit time in the multiplier, and 3) the electronic delays.

Finally, the factors which determine the achievable state resolution need to be discussed. To begin with, the electrons released in the ionization process are used instead of the ions, because, being much less massive than the ions, they respond faster to the electric field. The next most dominant factor in determining resolution is the slew rate of the field ramp. The faster the field rises, the closer together in time the ionizing thresholds of the various states fall. Also for a given field ramp produced by the ramp generator, the slew rate is not constant (see Fig. 4-11). Therefore resolution varies along the ramp. Since the Rydberg atoms are produced over a finite spatial extent, their vertical distribution (determined by the blue laser beam size) will broaden peaks in the spectrum. The reproducibility of the field ramp will have an effect on
the resolution as well as jitter in the delay times of the electronics and in the multiplier transit time. Finally, electrons liberated at most points along the ramp will undergo a de-acceleration between Grids 3 and 4 (because the voltage on Grid 3 exceeds the +80 V on Grid 4 during most of the ramp). This de-acceleration may affect the ultimate resolution.

**FI technique.** Following each laser pulse, an electric field capable of ionizing Rydberg atoms in all states of interest is applied across the interaction region. The direction of the field drives the field ions toward the multiplier where they are simultaneously detected. The multiplier output is fed to a gated current integrator which yields the total charge leaving the multiplier per laser pulse. This technique constitutes a method for detecting large numbers of Rydberg atoms produced per laser pulse (important in the electron impact ionization of Rydberg atoms experiment; see Sec. 4.9). All that is required is 1) a knowledge of how the multiplier output scales with input, i.e. the relative gain per ion of the multiplier as a function of the number of ions which simultaneously strike the first dynode of the multiplier, and 2) that the

\[^{1}\text{In practice it is desirable that the output scale linearly with the input, i.e. that the gain per ion be independent of the input.}\]
multiplier not be driven into saturation. With this knowledge the relative numbers of atoms detected amongst various measurements can be obtained. To obtain absolute numbers of atoms ionized, it is necessary to know the absolute gain of the multiplier and the multiplier's efficiency. Measurements of the relative gain of the multiplier as a function of the incident ion input will be discussed in Sec. 4.9.

The same ionizing field generator is used in the FI technique as is used in the SFI technique except that the polarity is reversed so that positive voltage is applied to Grid 2 while negative voltage goes to Grid 3. As before with electron detection, this allows for constant efficiency detection of the ions irrespective of the field strength at which the ions are produced. The anode and backplate of the multiplier are run at zero potential while the first dynode (along with Grids 5 and 6) is operated at a large enough negative voltage, usually about - 3000 V, so that the multiplier gain is sufficient to result in a measurable charge signal but not so large as to saturate the multiplier. Grid 4 is held at about 40% of the first dynode voltage. The gated current integrator constitutes another input option on the LRS 3001 qVt unit and is gated with a pulse generator (BNC). This gate pulse is centered on the
multiplier output signal as observed on an oscilloscope. The output of the gated current integrator is converted to a channel number and stored in the MCA. A schematic diagram of the entire FI technique is given in Fig. 4-13 and the sequence of events which occur in the application of the FI technique is shown in Fig. 4-14. As in the SFI technique, although the ionizing field is triggered at a time $t_T$, the actual ionization of the atoms occurs at a mean time of $t_T + 1 \mu$sec. In the FI technique $t_T$ can be set equal to zero if desired.

The high voltage applied to Grids 4, 5, and 6, and the first dynode of the multiplier result in an electric field which penetrates up into the interaction region. In order to minimize this field penetration, a fine nickel mesh (Buckbee Mears Co., 100 wires/inch, 82% transmissive) is used across the hole in the frame of Grid 3 instead of the tungsten wire grids described for the other grids in the grid assembly. The use of this mesh substantially diminishes the field penetration, however, some field still exists. This residual field is eliminated at the Rydberg atom production region by applying a reverse bias voltage to Grids 2 and 3 (negative voltage on Grid 2, equal positive voltage on Grid 3) which creates a field equal in strength but opposite in direction to the penetration field at the
Fig. 4-13 Schematic of FI technique.
Fig. 4-14  Sequence of events in FI technique.
location of Rydberg atom production.\textsuperscript{1} The strength of the reverse bias field that is required is determined by producing sodium ions (i.e. tuning the blue laser so as to photoionize the sodium 3p state) and measuring, on an oscilloscope, the time it takes for these sodium ions to be driven to the multiplier by the penetration field as the reverse bias voltage is increased. When this ion flight time goes to infinity, the penetration field has been cancelled at the point of ion production (same location as the Rydberg atom production) by the reverse bias field. Table 4-2 gives the reverse bias voltage required to cancel the penetration field for various voltages used on the grid assembly and first dynode. The size of the penetration field (obtained by dividing the total reverse bias voltage by the Grid 2 to Grid 3 spacing) is also given for each case. The reverse bias voltage is produced by a battery circuit built into the ionizing field generator (see Fig. 4-10).

It should be noted that the SFI and FI techniques are not independent measurements. The SFI signal is essentially the derivative with respect to the field of the FI signal,\textsuperscript{1}

\textsuperscript{1} Since the penetration field is non-uniform while the reverse bias field is uniform, the cancellation of the penetration field can only occur at one location.
Table 4-2
Reverse bias voltages and fields required
in FI technique and ion measurements.

<table>
<thead>
<tr>
<th>Voltage on multiplier first dynode and grids 5 and 6</th>
<th>Voltages on Grid 4</th>
<th>Reverse bias voltage on Grid 2</th>
<th>Reverse bias voltage on Grid 3</th>
<th>Reverse bias field</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 2500 V</td>
<td>- 1000 V</td>
<td>- 0.56 V</td>
<td>+ 0.56 V</td>
<td>0.44 V/cm</td>
</tr>
<tr>
<td>- 3000 V</td>
<td>- 1200 V</td>
<td>- 0.65 V</td>
<td>+ 0.65 V</td>
<td>0.51 V/cm</td>
</tr>
<tr>
<td>- 3500 V</td>
<td>- 1400 V</td>
<td>- 0.74</td>
<td>+ 0.74</td>
<td>0.58 V/cm</td>
</tr>
</tbody>
</table>
i.e. if a series of FI measurements are taken each at a slightly larger value than the previous one, then, when the differences between the consecutive ion signals are taken and divided by the field increment used between measurements, an SFI spectrum of sorts results. On the other hand integrating an SFI spectrum over the ionizing field is equivalent to an FI measurement. The SFI technique is convenient for use in detecting state changing collisions and in measuring the de-population of the laser excited state. The FI method is convenient for use in the study of electron impact ionization of Rydberg atoms where it is necessary to detect large numbers of Rydberg atoms produced per laser pulse (see Sec. 4.9).

Results of the detection of Rydberg atoms by field ionization. At this point it is useful to look at some SFI spectra of atoms in various Rydberg states because 1) the field ionization process has been found to be more complicated than the semi-classical model indicates, and 2) the better the field ionization process is understood,  

1 These statements about the relationship between the SFI and FI measurement techniques hold in general only if the same or at least similar ionizing field ramps are used for both measurements. This requirement results from the field dependence of the adiabatic vs. diabatic paths which a Rydberg atom can take to ionization, as will be discussed next.
the better the signal due to the various state changing processes can be identified (since selective field ionization is used to identify this signal). SFI spectra for several nd and ns states (taken at $t_T = 2 \mu\text{sec}$) are shown in Figs. 4-15a and 4-15b respectively. It is immediately evident that not all of the Rydberg atoms produced in the present work by laser excitation exhibit single peaks (i.e. single ionization thresholds) when they are field ionized. From Fig. 4-15a it is seen that the d state spectra exhibit two distinct thresholds separated by quite a large field strength interval with the second peak increasing in magnitude and getting closer to the first peak as n is increased. In addition the first threshold in each of the d state spectra appears to contain structure. In contrast to the d state spectra, it is seen in Fig. 4-15b that the s state spectra consist of only a single main ionization threshold. While most of these s state thresholds appear to be single peaks, structure is contained in the 3ls state threshold.\footnote{Although not shown, there is evidence that several other s states also show multiple peak structure within their main ionization thresholds.} Shown in Fig. 4-16 is a composite of the first ionization thresholds of several d states taken under better field resolution (solid curves) and of the spectra of several s states (dotted curves). It is
Fig. 4-15a SFI spectra of several nd states. All spectra obtained with the same field ionization ramp.
Fig. 4-15a contd. SPI spectra of several nd states. All spectra obtained with the same field ionization ramp.
Fig. 4-15b  SFI spectra of several ns states. All spectra obtained with the same field ionization ramp.
seen that atoms in an ns state ionize at closely the same field strengths as do those (n-1)d state atoms which ionize at the first of the two main d state thresholds. Additionally it should be noted that the first ionization threshold of the 30d state, located at the same field strength as the anomalously behaving 31s state threshold, also exhibits a character which is different from that of the other d state first thresholds shown in Fig. 4-16.

While ionization of s state atoms and d state atoms at the first ionization threshold of the d states have been observed before (Ducass et al. (1975); Gallagher et al. (1976c); Gallagher et al. (1977d); Vialle (1978); and Vialle and Duong (1979)), the data obtained during this work (Fig. 4-15a) reveal for the first time the existence of a second main threshold of ionization for atoms in d states (see Jeys et al. (1980)). This second threshold, in addition to its significance in the understanding of the field ionization process, has important consequences in the detection of Rydberg atoms. This is evident in the present work in both the measurement of the number of Rydberg atoms created and the interpretation of state changing data.

The field ionization data presented above can only be partially explained by the classical model of ionization discussed earlier. The classical model predicts that ns
Fig. 4-16 Composite of several SFI spectra:

- First ionization thresholds for several nd states obtained under high field resolution;
- SFI spectra of several ns states.
All spectra obtained with the same field ionization ramp.
and \((n-1)d\) states should be ionized at roughly the same field strengths since they lie close together in energy. This prediction is supported by the data in the case of the first ionization thresholds of the \(d\) states, however the model does not explain the second \(d\) state ionization threshold occurring at much larger field strengths. Also the model predicts that all states which are non-degenerate in the presence of the field (even though they may be degenerate in the absence of the field), will possess single, separate ionization thresholds. In the present case, \(^2S_{1/2}\) and \(^2D_{3/2,5/2}\) states are excited. While the \(^2S_{1/2}\) state yields only a single state in the presence of a field, the \(^2D_{3/2,5/2}\) states split into three states. Thus, structure in a \(d\) state ionization threshold, such as that seen in the first \(d\) state thresholds in the data, should perhaps be expected. However, this does not explain the structure in the 31s state spectrum. The semi-classical model, while in essence correct, is not complete. In an attempt to understand all of the features of the data it is necessary to examine the ionization process more closely.

It is useful to begin by looking at the hydrogen atom in a uniform electric field. Ignoring fine and hyperfine interactions, the field-free states belonging to a given value of \(n\) are degenerate. As an electric field is applied,
these degenerate states are immediately mixed together forming Stark states which are characterized by their principal quantum number, n, two parabolic quantum numbers, \( n_1 \) and \( n_2 \), and the absolute value of the azimuthal quantum number, \( |m_\ell| \).\(^1\) These quantum numbers are not all independent and are coupled together by the expression:

\[
n = n_1 + n_2 + |m_\ell| + 1.
\]

Furthermore, these Stark states split apart in energy. This splitting, according to perturbation theory, is initially linear in the field strength, \( F \), i.e. linear Stark effect, and is independent of the value of \( |m_\ell| \). Fig. 4-17 shows the \( n = 10 \) Stark state manifold versus \( F \) for values of \( F \) where the linear Stark effect holds. As the field strength is increased, higher order terms (proportional to higher powers of \( F \)) in the perturbation calculation must be included, all of which are dependent on \( |m_\ell| \).\(^2\) As the Stark states split apart in energy from each other, they each become broader in energy also. This is because it is possible as soon as a field is applied, for the Rydberg electron in a state still below \( V_{\text{max}} \) to tunnel into the continuum on the "up-field" side of the atom (see Fig. 4-8). Thus the atom acquires a

\(^1\) See, for example, Bethe and Salpeter (1957).

\(^2\) This perturbation expansion should not be used beyond fourth order (see Zimmerman et al. (1979))
Fig. 4-17 Linear Stark effect for the $n = 10$ states of hydrogen. The Stark states are labeled using the parabolic coordinate system quantum numbers, i.e., $|n, n_1, n_2, m_\ell \rangle$. 
finite lifetime against field ionization corresponding to this tunneling probability and the Stark energy levels are broadened.\(^1\) For a given Stark state in a hydrogenic Stark manifold, the lifetime against field ionization is a decreasing function of the electric field while the corresponding ionization rate increases with the field. At some field strength the lifetime will become short in comparison with the temporal resolution available in the experiment (about 1 ns in the present work) and ionization of the atom can be considered to occur at this point. Stated another way the ionization rate (probability) will, at a given field strength, reach infinity (unity) for all practical purposes and the atom will be ionized. The functional dependence of the ionization rate (or lifetime), while monotonic for states in hydrogenic manifolds, is highly nonlinear. For field strengths below the classical threshold field for ionization, \(F_c\), the ionization rate remains negligible for all states in a Stark manifold. Once \(F_c\) is exceeded and ionization becomes energetically possible in the classical sense, it is necessary to consider each Stark state individually and the spatial distribution of that state's wavefunction. The lowest lying Stark state

\(^1\) Of course this lifetime and level broadening is in addition to that dictated by the radiative lifetime of the state.
in a given manifold is associated with a wavefunction which is concentrated on the "up-field" side of the atom toward $V_{\text{max}}$. With the high probability of the Rydberg electron being located in the vicinity of the saddle point in the field, the ionization rate of the atom in this state increases exponentially at the classical threshold for ionization, $F_c$. This exponential increase in the ionization rate defines a small increment of field strength in which ionization of the atom occurs. The value of the field at the center of this increment may be termed the critical field for ionization of the atom in this state. Meanwhile the highest lying Stark state in the manifold is associated with a wavefunction which is concentrated on the "down-field" side of the atom away from $V_{\text{max}}$. Consequently the probability of the Rydberg electron being located near the saddle point in the field is small and thus the ionization rate for this state remains low out to field strengths well beyond $F_c$. However, at some point in this larger field, the ionization rate will, as before, undergo an exponential increase with field strength allowing a critical field for ionization to be assigned to this state.

The critical fields of the two extreme components of the manifold just described define the field limits between which all the remaining states in the manifold ionize. The
critical fields for all of the states in the \( n = 10 \) manifold of hydrogen as calculated by Herrick (1976) are shown in Fig. 4-18.\(^1\)

In addition to allowing a critical field for ionization to be defined, it is the rapid rise of the ionization rate of a state over a small interval of field strengths which permits the detection of Rydberg atoms by field ionization to be state selective (yielding the SFI detection technique). This behavior of the ionization rate also helps ensure that field ionization is unit efficient in practice.

So far attention has only been given to individual hydrogenic Stark state manifolds. In the Rydberg state regime, manifolds corresponding to different values of \( n \) overlap and it is important to ascertain what effect this has upon the ionization process. Fig. 4-19 shows this overlap for the \( |m_A| = 0 \) portions of the Stark manifolds of the \( n = 8, 9, \) and 10 states of hydrogen. A similar diagram exists for the \( |m_A| = 1 \) portions of the manifolds, the \( |m_A| = 2 \) portions, etc. In general states having the

\(^1\) The calculation of ionization rates as a function of field strengths is quite complicated and has had a long history. See, for example, Bethe and Salpeter (1957) for a review of the work until 1957; for more recent work, see, for example, Rice and Good (1962), Bailey \( \text{et al.} \) (1965), and Damburg and Kolosov (1976, 1977, 1978a, 1978b, and 1979) in addition to Herrick (1976).
Fig. 4-18 Field ionization of the $n = 10$ states of hydrogen (Herrick (1976)).
Fig. 4-19 Schematic representation of the $|m_s| = 0$ portions of the manifolds of the $n = 8$, 9, and 10 states of hydrogen.
same value of $|m_\lambda|$ interact and repel each other (undergo avoided crossings) while states of different $|m_\lambda|$ do not interact (undergo allowed crossings). However, in hydrogen, due to the special nature of the Coulomb field, there is no interaction between states of the same $|m_\lambda|$ and all crossings are allowed. As a result, the development of hydrogenic Stark states as a function of field strength is not influenced by the presence of other states of the same value of $|m_\lambda|$. Thus, in hydrogen, the presence of other Stark state manifolds of the same $|m_\lambda|$ overlapping with a given manifold does not affect the ionization process in that manifold.

In sodium the situation is complicated by two features: 1) states having the same value of $n$ are not degenerate, and 2) the field experienced by the Rydberg electron is not a pure Coulomb field and therefore avoided crossings occur between states of the same $|m_\lambda|$ value. Fig. 4-20 schematically depicts the $|m_\lambda| = 0$ Stark structure for sodium in the neighborhood of $n = 9$. Again similar features exist for the $|m_\lambda| = 2$, $|m_\lambda| = 3$, etc. portions of the manifolds. The non-degeneracies of the states of a given value of $n$ cause some interesting differences from hydrogen. For instance, as the field is increased, an initially field-free $ns$ state develops into the lowest component of the $(n-1)$ Stark
Fig. 4-20 Schematic representation of $|m_l| = 0$ portions of the manifolds around the $n = 9$ state of sodium.
manifold: \(|(n-1),0,(n-2),0>|. The initially field-free np states develop into the highest components of the \((n-1)\) Stark manifold: \(|(n-1),(n-2),0,0>\) and \(|(n-1),(n-3),0,1>\). The initially field-free nd states develop into the low lying components of the n Stark manifold: \(|n,0,(n-2),1>, |n,1,(n-2),0>,\) and \(|n,0,(n-3),2>\). This process may be continued until all of the nl states are assigned to Stark states.\(^1\)

Fig. 4-20 also schematically shows the occurrence of avoided crossings between \(|m,0>\) states in the region where Stark manifolds belonging to different n values overlap.\(^2\) The manner in which an atom passes through an avoided crossing depends on the slew rate of the field and on the size of the energy gap between the interacting states at the crossing (i.e. the magnitude of the interaction between the states). If the slew rate is large and/or the energy gap small, the atom can cross across the gap retaining its initial Stark state character (diabatic passage). If the slew rate is small and/or the gap large, the atom can avoid the crossing causing the character of its state to

---

\(^1\) These assignments assume that the states develop in an adiabatic fashion.

\(^2\) As the value of n is increased the number of avoided crossings that occur also increases. For actual data at values of n in the teens see Littman et al. (1976a) and Zimmerman et al. (1979).
change to that of the other state (adiabatic passage). These two types of passage of an atom from low fields to ionizing fields provide an explanation of the two main ionizing thresholds exhibited in the d state SFI spectra. Consider an atom in the field-free 9d state in Fig. 4-20. If such an atom passes to high field strengths along an adiabatic path (shown by darker curve in the figure), it will cross the classical threshold curve at the point marked A. The atom will have changed its character at every avoided crossing and the character it has at point A will, in general, not have a high ionization rate associated with it and therefore not be ionized. However, as it continues to yet higher fields it will sooner or later come to an avoided crossing (point B) with a Stark state extending down from a higher manifold (illustrated in Fig. 4-20 as a dashed line from the n = 10 manifold). Since this intersecting state lies low in the higher manifold and, at B, it is beyond the $F_C$ curve, it will have a very high ionization rate associated with it. As the atom assumes the character of this state at point B it will also acquire the high ionization rate and will ionize at that point.\(^1\)

If, on the other hand, an atom initially in the 9d

---

\(^1\) For more information on this topic of induced ionization by state mixing see Littman et al. (1976b)
state progresses to high fields along a diabatic path, it will cross the $F_C$ curve at point C. Since the atom will have retained its original character throughout the passage—namely, that of a Stark state lying near the bottom of the $n = 9$ manifold—it will be ionized by the field at a point just past C. Thus it is seen that the adiabatic and diabatic passage of an atom to high fields can result in two distinct thresholds for ionization. If this discussion is applied to the Rydberg states of interest in the present work, it is found that there is quantitative agreement between the locations of the two main d state thresholds in the SFI spectra and the predictions of such locations on the basis of a figure similar to Fig. 4-20. This agreement is shown in Fig. 4-21. From this it is concluded that the first and second main peaks in the d state spectra result from adiabatic and diabatic passage of atoms to ionization respectively.

Further evidence supporting this conclusion as well as more insight into the field ionization process is given by the following. Unless otherwise stated, all Rydberg atoms laser excited in this work are produced under conditions in which both yellow and blue laser beams are polarized perpendicular to the ionizing field direction. Consideration of the dipole selection rules and the appropriate correlation
Fig. 4-21 Comparison of adiabatic and diabatic paths to ionization for nd states with nd state SFI spectra.
scheme connecting the $|m_J|$ field-free states (produced by
the lasers) with the $|m_\lambda|$ states existing in the field
(Gallagher et al. (1976c) and Gallagher et al. (1977d)),
shows that for d states, $|m_\lambda| = 0, 1, \text{ and } 2$ Stark states
will result under such polarization conditions. Littman
et al. (1976a) have shown that intermanifold interactions
are strongly $|m_\lambda|$ dependent. The larger the value of $|m_\lambda|$
the smaller the interaction between states of identical
$|m_\lambda|$ at the level crossings. Thus the probability of
diabatic passage for a given electric field slew rate should
increase as $|m_\lambda|$ increases. This implies that the second
d state threshold should be due mainly to $|m_\lambda| = 2$ states.
That this is indeed the case is shown by the fact that the
second d state ionization threshold in each spectrum shown
in Fig. 4-21 occurs at the field strength appropriate to
quantum mechanical ionization for the lowest member of the
$|m_\lambda| = 2$ Stark manifold. Furthermore, when both lasers are
polarized parallel to the direction of the ionizing field,
then theoretically no $|m_\lambda| = 2$ states can result and, in
this case, a dramatic decrease in the signal obtained at the
diabatic threshold is obtained. Finally, states of higher
principal quantum number also exhibit less interaction at
level crossings. Thus, the probability of diabatic passage
for a given field slew rate should increase as n increases.
As seen in the figures, the diabatic signal does increase as the value of \( n \) is increased as already noted.

Only \( |m_\lambda| = 0 \) states can result from laser excited \( s \) states no matter what the laser polarization is. Thus atoms in \( s \) states are expected to ionize in an adiabatic manner. Examination of Fig. 4-20 (viewed for arbitrary \( n \)) shows that adiabatic ionization of an \( s \) state would require it to ionize at about the same field as the adiabatic component of the \((n-1)\) \( d \) state atoms. As already observed, this does in fact occur.

The structure present in the \( d \) state adiabatic peaks and in the \( 3ls \) state peak is not completely explained as yet. In the \( d \) state case, the structure, which typically consists of three peaks, is undoubtedly associated with the three \( |m_\lambda| \) states, however, there is evidence that the situation is more complicated.

4.7 Ion Detection

As mentioned in Chapter III, electron impact ionization of Rydberg atoms is detected by measuring the resulting sodium ion signal. The method of detecting sodium ions is identical to the FI technique except that the ionizing field used in the FI technique is replaced with a small ion collection field which is too weak to ionize any Rydberg atom of importance remaining in the interaction region. The
collection field is produced by the ionizing field ramp generator (Fig. 4-10) under conditions where the positive and negative output voltages (which go to Grids 2 and 3 respectively) are small. The collected sodium ions are detected by the electron multiplier whose output is integrated by the gated current integrator as in the FI technique. Again a knowledge of the relative gain per ion of the multiplier as a function of the number of ions which strike the first dynode of the multiplier is needed (see Sec. 4.9). Statements made, in discussing the FI technique, concerning relative and absolute ion measurements apply equally well here. Finally, as before, although the collection field is triggered at time, $t_T$, the actual collection occurs somewhat later ($t_T + 1 \mu\text{sec}$ is used). However, the selection of the integration gate employed here is more difficult than in the FI technique since, in the weak collection field, the sodium ions are somewhat spread out in time. This problem will be addressed in Sec. 4.9 along with the selection of the magnitude of the collection field used. With the replacement of the ionizing field by a collection field, Fig. 4-13 and Fig. 4-14 are also applicable to ion detection.

4.8 Electron Beamline

The following basic requirements dictated the design
of the electron beamline constructed for this experiment.
1) The beam must intersect the sodium beam at the point of Rydberg atom excitation and have a large enough cross sectional area at that point so that the beam-cell analysis is applicable. 2) There must be a uniform electron density in the beam. 3) The beam energy should be in the vicinity of 100 eV\(^1\) while no strict constraints exist on the energy spread in the beam (resolution to several eV is sufficient). 4) The beam current density should be on the order of 1 \(\mu\)A/cm\(^2\). 5) The background density of low energy electrons (where low energy means less than the beam energy and especially energies on the order of tenths of an eV) must be very small. Although not an original requirement in the design, the ability to pulse the beam on and off through the interaction region became a necessity when the study of state changing collisions was undertaken.

The first two requirements follow directly from the considerations developed in Chapter III. In order to ensure that the Rydberg atoms are entirely immersed in electrons, the beam is designed to be coaxial with the laser

\(^1\) It has already been noted that the beam energy used in this work is 25 eV. However, the electron beamline was originally designed to handle a 100 eV beam. As the experiment progressed it became desirable to operate at lower energies. The quality of the beam was examined at 25 eV and 10 eV and it was found that the beamline could be operated at 25 eV but not at 10 eV. Therefore 25 eV was employed.
beam (thus it is centered on the Rydberg atom production region) and to have a large cross section. In addition, during the entire interaction time with electrons, the Rydberg atoms must travel through a uniform density electron target. The requirement that the low energy electron background be small results from the fact that the maxima in the cross sections for the processes being investigated in this work occur at energies below 25 eV. Consequently low energy electrons (e.g. from secondary electron ejection from surfaces) can contribute to the measured signal. In fact, this contribution can be large. For example, in the electron impact ionization measurements, a low energy electron background whose density is 1% of the primary beam density may increase the signal by as much as 10% to 100%!

Finally, pulsing the electron beam on and off is required by the use of the SFI Rydberg atom detection technique. Since the electrons from the field ionized Rydberg atoms are detected in this technique, the electron beam must be turned off before the ionizing field ramp begins.

The electron beamline consists of three major parts: the beam source, the detector, and the beam profiling device which determines the beam position, size, and uniformity. Each of these components is described in detail below and attention is given to the ways in which the beam
requirements listed above are met.

**Beam source.** The beam source, shown in Fig. 4-22, is composed of an electron source and a "housing" in which the electron source and a variety of beam apertures, etc., are mounted. In order to produce an electron beam with a uniform number density and a large cross section at the interaction region, it was decided to employ an electron source which would emit a rather divergent beam of electrons and then use a defining aperture which would allow only those electrons emitted in a small solid angle about the beam axis to pass on to the interaction region. The actual electron source employed is a conventional planar triode emission system (cathode, control grid, and anode) such as the type used in cathode-ray and television tubes. Specifically the source consists of the first three elements of a black-and-white television tube electron gun which is obtained commercially (Southwest Vacuum Devices, Inc., GE-62). The triode gun is shown in Fig. 4-23. In normal operation the grid is biased slightly negative with respect to the cathode while the anode is run at a positive voltage with respect to the cathode. Electrons, thermally emitted from the indirectly heated oxide cathode, are accelerated toward the anode by the electric field distribution in the gun. This field distribution also focuses the electrons to
Fig. 4-22 Electron beam source. Scale drawing; all dimensions in inches.
Fig. 4-23  Electron gun. (First three elements of GE-62, Southwest Vacuum Devices, Inc.). Scale drawing; all dimensions in inches.
a "cross over" point in the vicinity of the anode as shown in Fig. 4-23. After traveling through the cross over, the electrons separate forming a divergent beam. In the cathode-ray or television tube an electron lens system follows the triode gun and this system re-focuses the beam so that the cross over point is imaged on the tube screen. In the present application, however, a divergent beam is desired and consequently the lens system is removed.\footnote{In the design and construction of these guns the lens system is usually built in as an integral part of the gun and the complete unit is sold.} For the gun in use the divergence half-angle is $\sim 13^\circ$.

The electron gun is mounted at the end of the gun housing which is, in turn, attached to the side of the box containing the grid assembly and electron multiplier (see Figs. 4-22 and 4-1). The housing serves the dual purpose of providing a structure on which the gun and various beam apertures may be mounted and of forming a complete enclosure around the gun and apertures. This enclosure, when appropriately biased (see below), prevents electrons emitted from the heater filament and secondary or scattered primary electrons produced in the gun or at the beam apertures from easily escaping into the interaction region. The housing is of modular design, consisting of a concentric
series of alternating stainless steel and Delrin rings.\textsuperscript{1}

The various beam apertures are mounted on the metal rings while the Delrin rings serve to electrically isolate each metal ring. The assembly is held together by four lengths of thread stock running along the outer circumference of the rings at 90\degree intervals as shown in Fig. 4-22. The definition of a beam 1 cm in diameter at the interaction region is accomplished by the circular first and second beam defining apertures.\textsuperscript{2} The first defining aperture allows only a small portion of the emission leaving the gun to pass, in keeping with the stated method of producing a uniform beam. The second defining aperture is geometrically equivalent to the first, i.e. diameter of DA2 = diameter of DA1 \times (3.35/0.8) (see Fig. 4-22). This aperture acts as a beam skimmer removing electrons that have been scattered at wide angles at the first defining aperture (such electrons would constitute a beam penumbra). The four elements located in

\textsuperscript{1} This design easily allows re-arrangement of the various elements and the addition to or removal of elements from the structure as desired.

\textsuperscript{2} The size of the defining apertures is determined by viewing the electrons as coming from a point source located at the aperture in the gun anode. It is assumed that the beam cross over is such a point source and is located near the anode. Problems could arise if the cross over location is not near the anode or if its size does not constitute a point source, however, beam profiles (see Sec. 4.9) indicate a well-defined beam at the interaction region at a beam energy of 25 eV.
between the defining point comprise an electron lens which can be used to adjust the size of the beam. The purpose of the exit aperture will be explained shortly. All apertures are made from 0.001" thick shim stock.

The electron beam travels a distance of 5.8" from the anode aperture to the interaction region. In this distance the earth's magnetic field can deflect a 100 eV beam by as much as 1.6 cm and even more for a 25 eV beam. Such a deflection would make good overlap with the Rydberg atom production volume difficult to achieve and increase the possibility of the beam striking surfaces.\footnote{In addition it is difficult to determine what the deflection really is since the beam and the earth's field are not at right angles to each other and since there are magnetic materials in the vicinity of the apparatus.} Therefore the entire electron beam source, grid assembly, and multiplier are enclosed in a mu-metal box (0.040" thick mu-metal obtained from Eagle Magnetic Co.) (see Fig. 4-1). Also the use of magnetic material within the mu-metal box is minimized. Non-magnetic grades of stainless steel are used predominantly, brass thread stock is used in the grid assembly and gun housing, brass shim stock is used for the beam apertures, and Grids 2 and 3 are made out of copper.

Detector. The electron beam is detected in a Faraday cup. The design of this cup is rather unconventional
since it must a hole completely through it along the electron beam in order to let the laser beam pass. Thus it was to electrostatically deflect the electron beam to the beam axis onto a collecting surface using the cylindrically symmetric design shown in Fig. 4-24. The deflection is accomplished by running the backplate and wedge at zero potential while maintaining the back cylinder at a positivatial and therefore establishing an electric field between the wedge and the back cylinder. At the same time penetration of this deflecting field out of the cup into the interaction region must be kept as low as possible. Therefore the front cylinder, held at zero potential, defines a buffer region to prevent any field penetrat of the cup. The electron beam current is deduced by measuring the electron current to the entire cup with an electrometer (Keithley, 610B). The voltages applied to the various cup elements, using well-insulated batoxes, are adjusted until the current to the cup exhibits a current indicating complete capture and detection of the microscopic beam.

Producing the electron beam with a small low energy electron beam proved to be, as expected, a difficult problem. In the gun housing and Faraday cup went through two in dealing with this background. Major
Fig. 4-24 Faraday cup and mu-metal shield. Scale drawing.
considerations in this regard are 1) escape out of the gun housing of secondary electrons produced at the beam apertures, 2) escape of secondary electrons and reflected primary electrons out of the Faraday cup, and 3) scattering of wide angle primary electrons off surfaces around the interaction region and off the front of the Faraday cup. The first item is addressed by floating all the beamline elements in the housing from the anode to the exit aperture at a positive voltage above whatever their operating voltages may be. Therefore any secondary electrons produced within the gun housing will be suppressed from entering the interaction region. It is because this voltage is applied that the exit aperture exists. As mentioned earlier, the gun house is attached to the wall of the box which surrounds the grid assembly. Since the interaction region is maintained at ground potential, this box is held at ground. As a result, a lens is formed between the last element in the gun house (held at a positive voltage) and the wall of the box. To avoid aberrations in this lens, the beam should not fill the lens apertures. The hole in the wall of the box is large (1" in diameter, see Fig. 4-22) but in the absence of an exit aperture the last element of the gun house would be the second beam defining aperture which is filled by the beam. Therefore the exit aperture
(larger in diameter than the beam) is added. The second consideration - escape of electrons out of the Faraday cup - turned out to be probably the most crucial concern. Even though it may be possible to bias the components of the cup so as to obtain a measurement of the total beam current to the cup which is saturated with respect to these operating voltages, a small amount of current - say 1% of the beam current (which is undetectable in the total beam current measurements) - may still escape back out of the cup. A rule of thumb used in cup design is that the depth of the cup should be about ten times longer than the diameter of the cup's entrance aperture. In the present case, due to the large beam diameter, this is not quite possible even though all the space available in the main chamber is used (see Fig. 4-1). The cup is mostly shielded in a mu-metal cylinder (Ad-vance Magnetic) to prevent magnetic deflections of the beam into the side of the cup before the beam is electrostatically deflected and collected on the back cylinder of the cup. In addition, all inner surfaces of the cup are coated with soot to aid in capturing the electrons. Concerning the scattering of wide angle primary electrons, the use of a second beam defining aperture as a skimmer aperture (as already discussed) helps to eliminate electrons traveling on wide angle trajectories (beam penumbra). Also
the front of the first element of the Faraday cup is coated with soot to help absorb any electrons incident upon it.

The low energy electron background existing in the interaction region when the gun is on is estimated by running a low current electron beam (10^{-10} \text{ amps}) continuously and operating the multiplier in an electron counting mode. Along with low energy electrons already directed toward the multiplier, the field penetration into the interaction region from the voltages on Grids 4, 5, and 6 and the multiplier (Grids 1, 2, and 3 at ground) attracts the low energy electrons to the multiplier where they are detected. The count rate obtained is used as a measure of the background. The operating parameters of the beamline are then adjusted until both the required macroscopic properties of the beam (i.e. beam position, size, and uniformity and saturation of the total beam current in the cup) are achieved and the count rate due to the background is minimized. For the cw operation of a 25 eV beam the following conditions are used:

\[ V_{fil} = 6.3 \text{ V}, \quad V_C = -25 \text{ V}, \quad V_G = -26.5 \text{ V}, \quad V_A = V_{DA1} = V_{LC1} = \]
\[ V_{LA1} = V_{LA2} = V_{LC2} = V_{DA2} = V_{EA} = +20 \text{ V}, \quad V_F = V_{FC} = V_{BW} = 0 \text{ V}, \quad \]
\[ V_{BC} = +150 \text{ V} \]

where the notation is defined in Figs. 4-22, 4-23, and 4-24. At these settings the count rate due to the background is 2 \times 10^4 \text{ counts/sec} at a beam current of about 2 \times 10^{-10} \text{ amps}. This should be compared to the
$10^3$ electrons/sec count rate that is expected on the basis of electron impact ionization of the background gas by the beam electrons at this beam current. An alternative comparison is to convert the measured count rate to a density of low energy electrons in the interaction region and to compare this density with the beam density. If the most probable energy of a secondary electron under these conditions is $\sim 2$ eV,\(^1\) then the background electron density is about $3 \times 10^{-5}$ electrons/cm\(^3\) as compared with a density of primary electrons in the beam of about 5 electrons/cm\(^3\) at the above beam current.\(^2\)

The electron beam can be pulsed on and off by first holding the grid of the gun at about 15 V more negative than its normal operating potential thus keeping the gun in a cut-off condition and then applying a + 15 V pulse to the grid (through a coupling capacitor) turning the gun on at its normal operating condition. The gun remains on for the duration of the pulse to the gun grid. This is the

---

\(^1\) See Hachenberg and Brauer (1959)

\(^2\) It should be noted that all of these numbers are order of magnitude estimates only. Unit collection and detection efficiency of the background electrons has been assumed. A $10^{-16}$ cm\(^2\) electron impact ionization cross section has been used. Also it is assumed that this background electron production scales linearly up to the beam currents ($\sim 1$ μamp) used in the actual collision experiments. This linear scaling appears to hold at the low beam currents (around $10^{-10}$ amp).
conventional method of switching an electron gun on and off. Since the gun used in the present work is designed for a television tube, it is expected that the response time of the gun to the grid pulse should be fast (i.e. < 1 μsec). When operating the beamline in the pulsed mode, the beam current during the pulse is obtained by measuring the average current to the Faraday cup over a series of beam pulses and then dividing this result by the beam's duty factor.

It is possible that the + 20 V on the exit aperture and the + 150 V on the back cylinder of the Faraday cup may, through field penetration, perturb the Rydberg atoms produced. However, SFI spectra of Rydberg atoms taken with and without these voltages applied indicate that the application of the voltages has no effect on the atoms (see Sec. 4-10). In this connection it should also be noted that the electric field created by a 1 μamp, 25 eV electron beam can at most be about 10 mV/cm and therefore has a negligible effect on the Rydberg atoms which are laser excited in this work.

**Beam profiling device.** It has been stated that the electron beam must be coaxial with the laser beams, be 1 cm in diameter at the interaction region, and be uniform in number density. These conditions must, of course, be satisfied in selecting the operating conditions of the beamline
as discussed above. It is the purpose of the beam profiling
device to determine to what extent these conditions are met.
A variety of two-dimensional beam profiling methods exist.
The one used here is relatively simple in design and fits
the space limitations of the main chamber. The device
consists of a flag containing two 0.1 cm wide slits at right
angles to each other (see Fig. 4-25). The flag pivots about
a point 3.5" from the intersection of the two slits and can
be rotated through the electron beam in a plane oriented at
right angles to the beam axis. In the case where there is
an infinite separation between the point of rotation of the
flag and the intersection of the slits, when the flag is
rotated through the electron beam from below, one slit
traverses the beam from right to left while remaining
vertical (therefore called the vertical slit) and the other
slit crosses the beam from bottom to top while remaining
horizontal (therefore called the horizontal slit). In the
present case where the rotation arm is 3.5" (maximum allowed
by the chamber size), only approximations to the motions
just described are realized. Nonetheless, it is possible
to make adjustments for some of the deficiencies of the
present design in the analysis of the profile measurements.
The flag is located between the end of the mu-metal box and
the entrance to the Faraday cup (see Fig. 4-1).
Fig. 4-25 Flag of electron beam profiling device. Scale drawing; all dimensions in inches.
As mentioned above, this device yields a two-dimensional profile of the beam in a cross sectional plane of the beam. Aside from the constant decrease in the beam density due to the beam divergence, it is assumed that the beam is uniform along its axial dimension. Although it is possible to determine the uniformity and size of the beam without any absolute calibration of the flag position, it is necessary to fix the flag's rotation angle absolutely if beam position is to be determined. This is accomplished by rotating the flag through the laser beam while Rydberg atoms (or photoions) are being produced. The angles at which the laser beams pass through the flag slits thus allowing Rydberg atoms (or photoions) to be made fix the flag rotation scale and the position of the laser beams. The position of the electron beam should coincide with the position of the laser beams so measured. Of course, the electron and laser beams could intersect at the same point in the plane of the flag and still not be coaxial as required but this situation is felt to be unlikely. Fig. 4-26 shows what the profile of a uniform electron beam of the correct size and position would look like using the flag profiling device. Examples of actual profiles of the beam will be given in the next section when the final conditions under which the electron beamline must operate for each type of signal measurement
made are described. These final conditions will be seen to include the operation of the beamline in the pulsed mode with various voltage applied to the grid assembly and electron multiplier. It should be noted that beam profiles are always taken under cw operation of the beam. It is assumed that the results of such profiles apply to the pulsed beam also.

The important overall dimensions of the electron beamline are given in Fig. 4-27.

4.9 Signal Measurements

*Signal analysis formulae.* At the end of Chapter III it was pointed out that several processes in addition to the electron processes are coupled together in determining the time development of the laser excited Rydberg atom and related populations following the laser pulse. These processes consist of first order processes (single events), second order processes (second processes in double events), and so on. First order processes include radiative decay of the laser excited Rydberg atoms, state changes of the laser excited Rydberg atoms by background gas and radiation and by electrons, and ionization of the laser excited
Fig. 4-27  Geometry of electron beamline.
All dimensions in inches.
Rydberg atoms by background gas and radiation and by electrons.\footnote{1} Second order processes include radiative decay of the mixed state Rydberg atoms,\footnote{2} further state changes of the mixed state Rydberg atoms by background gas and radiation and by electrons (including transfer of excitation back to the laser excited state), and ionization of the mixed state Rydberg atoms by the background gas and radiation and by electrons. Thus the fate of a laser excited Rydberg atom in composed of radiative decay, state changes, and ionization. The mixed state atoms may, in turn, decay radiatively, undergo state changes again (including back to the laser excited state), or be ionized.

The situation described above can be modeled in a variety of ways. The following model has been chosen for the present work. All atomic species of importance are divided into four populations: 1) the laser excited Rydberg atoms (designated $N_L(t)$), 2) all Rydberg atoms whose states have been changed from the laser excited state, i.e. all other Rydberg atoms, (designated $N_M(t)$), 3) sodium ions

\footnote{1}{It is seen that Rydberg atom-Rydberg atom collision processes have been neglected here. This is because, for the Rydberg atom densities produced in this experiment, these processes are expected to be negligible.}
\footnote{2}{Rydberg atoms which have had their state changed from the laser excited state will be referred to as mixed state Rydberg atoms.}
resulting from the ionization of the Rydberg atoms (designated \( N_I(t) \)), and 4) all sodium atoms in low-lying, non-Rydberg states that are produced from the radiative decay of Rydberg atoms (designated \( N_G(t) \)). The model views all mixed state Rydberg atoms as composing the single reservoir, \( N_M(t) \), no matter what the state designation or how the atom was placed in that state. Thus state changing between the mixed states is ignored. Average values of the parameters describing the mixed state atoms, such as radiative lifetimes, collisional ionization rates, etc., may be assigned to this reservoir. In a similar fashion state designation is not distinguished in the \( N_I(t) \) and \( N_G(t) \) reservoirs.

In order to lessen the amount of notation in the equations that will follow, rate coefficients are used. For a two-body collision process, the rate coefficient for particle 1 incident on a group of particles 2 having uniform number density, \( n \), is

\[
\text{rate coefficient} = n \int_0^{\infty} \sigma(v_r) v_r f(v_r) dv_r = nk \quad (4-2)
\]

where \( \sigma(v_r) \) and \( k \) are the cross section and rate constant respectively for the interaction, \( v_r \) is the relative velocity between particle 1 and particle 2, and \( f(v_r) \) is the normalized relative velocity distribution. For a photon-particle interaction, the rate coefficient for the particle is
\[ \text{rate coefficient} = \int_{0}^{\infty} \sigma(\lambda) c n(\lambda) d\lambda \] (4-3)

where \( \sigma(\lambda) \) is the cross section for the process, \( c \) is the speed of light, and \( n(\lambda) \) is the photon number density at the wavelength \( \lambda \). For the radiative decay of an atom, the rate coefficient is just the inverse of the radiative lifetime of the state occupied by the atom.

The following notation will be used in the equations:

- \( \tau_L \) = radiative lifetime of laser excited Rydberg atom
- \( \alpha_g, \alpha_p, \alpha_e \) = rate coefficients for state changing process from laser excited state to mixed state reservoir due to background gas, background radiation, and electrons respectively
- \( \beta_g, \beta_p, \beta_e \) = rate coefficients for ionization of laser excited Rydberg atoms due to background gas, background radiation, and electrons respectively.

Since the processes due to the background gas and radiation cannot be distinguished from each other in this work, they will be regarded as a single background process in the case of state changes and in the case of ionization, i.e.,

\[ \alpha_g + \alpha_p = \alpha_b \] and \( \beta_g + \beta_p = \beta_b \). However, with the background gas pressure attained in the present work, the background radiation process is expected to dominate in each case, i.e., \( \alpha_b \approx \alpha_p \) and \( \beta_b \approx \beta_p \).
In the absence of electrons (i.e. electron gun turned off), the rate equations, written to first order, for the four populations are:

\[
\frac{dN_L}{dt} = -N_L \left( \frac{1}{\tau_L} + \alpha_b + \beta_b \right) \tag{4-4a}
\]

\[
\frac{dN_M}{dt} = N_L \alpha_b \tag{4-4b}
\]

\[
\frac{dN_I}{dt} = N_L \beta_b \tag{4-4c}
\]

\[
\frac{dN_G}{dt} = N_L \frac{1}{\tau_L} \tag{4-4d}
\]

Solutions of these equations are:

\[
N_L(t) = N_L(0) e^{-\left( \frac{1}{\tau_L} + \alpha_b + \beta_b \right) t} \tag{4-5a}
\]

\[
N_M(t) = N_L(0) \frac{\alpha_b}{\frac{1}{\tau_L} + \alpha_b + \beta_b} \left( 1 - e^{-\left( \frac{1}{\tau_L} + \alpha_b + \beta_b \right) t} \right) \tag{4-5b}
\]

\[
N_I(t) = N_L(0) \frac{\beta_b}{\frac{1}{\tau_L} + \alpha_b + \beta_b} \left( 1 - e^{-\left( \frac{1}{\tau_L} + \alpha_b + \beta_b \right) t} \right) \tag{4-5c}
\]

\[
N_G(t) = N_L(0) \frac{1/\tau_L}{\frac{1}{\tau_L} + \alpha_b + \beta_b} \left( 1 - e^{-\left( \frac{1}{\tau_L} + \alpha_b + \beta_b \right) t} \right) \tag{4-5d}
\]

---

This analysis applies when the laser pulse is short compared to the characteristic times of the system (see Sec. 3.3). Such is the case in this work. The laser pulse lasts \( \sim 5 \) nsec while the characteristic times for the system are \( > 1 \) \( \mu \)sec.
In the presence of electrons (i.e. electron gun turned on), the rate equations, written to first order, for the four populations are:

\[
\frac{dN_L}{dt} = -N_L \left( \frac{1}{\tau_L} + \alpha_b + \beta_b + \alpha_e + \beta_e \right) \tag{4-6a}
\]

\[
\frac{dN_M}{dt} = N_L (\alpha_b + \alpha_e) \tag{4-6b}
\]

\[
\frac{dN_I}{dt} = N_L (\beta_b + \beta_e) \tag{4-6c}
\]

\[
\frac{dN_G}{dt} = N_L \frac{1}{\tau_L} \tag{4-6d}
\]

Solutions of these equations are:

\[
N_L(t) = N_L(0) e^{-\left(\frac{1}{\tau_L} + \alpha_b + \alpha_e + \beta_b + \beta_e \right)t} \tag{4-7a}
\]

\[
N_M(t) = N_L(0) \frac{\alpha_b + \alpha_e}{\tau_L + \alpha_b + \alpha_e + \beta_b + \beta_e} \left(1 - e^{-\left(\frac{1}{\tau_L} + \alpha_b + \alpha_e + \beta_b + \beta_e \right)t} \right) \tag{4-7b}
\]

\[
N_I(t) = N_L(0) \frac{\beta_b + \beta_e}{\tau_L + \alpha_b + \alpha_e + \beta_b + \beta_e} \left(1 - e^{-\left(\frac{1}{\tau_L} + \alpha_b + \alpha_e + \beta_b + \beta_e \right)t} \right) \tag{4-7c}
\]

\[
N_G(t) = N_L(0) \frac{1/\tau_L}{\tau_L + \alpha_b + \alpha_e + \beta_b + \beta_e} \left(1 - e^{-\left(\frac{1}{\tau_L} + \alpha_b + \alpha_e + \beta_b + \beta_e \right)t} \right) \tag{4-7d}
\]

It is immediately apparent that the sets of rate equations with and without electrons are formally the same.
set of equations and can be made to look alike if the following definitions are used \( \alpha = \alpha_b + \alpha_e \) and \( \beta = \beta_b + \beta_e \).
(Of course in the absence of electrons, \( \alpha = \alpha_b \) and \( \beta = \beta_b \).)
Thus the solutions with and without electrons formally exhibit the same type of time behavior which is shown schematically in Fig. 4-28a. If second order processes are included in the above sets of equations, the time development of the four populations will be that exhibited in Fig. 4-28b. The early time development shown in Fig. 4-28b is closely similar to that of Fig. 4-28a, but at later times \( N_L(t) \) loses its single exponential behavior due to the re-populating of the laser excited state from the mixed state reservoir and \( N_M(t) \) decays to zero due to loss processes. The four populations, either with or without electrons, are not all independent. Their sum at any given time equals \( N_L(0) \). Therefore, with a knowledge of \( N_L(0) \), at most only three of the populations need to be measured with and without electrons in order to determine all of the salient parameters: \( \tau_L, \alpha_b, \beta_b, \alpha_e, \) and \( \beta_e \). In the present work the capability exists to measure, with and without electrons present, \( N_L(t)/N_L(0) \) and \( N_M(t)/N_L(0) \) using the SFI technique and \( N_I(t)/N_L(0) \) using a combination of the FI technique and ion detection. The measurements of these three population ratios in the absence of electrons allows
Fig. 4-28  Time development of $N_L(t)$, $N_M(t)$, $N_I(t)$, and $N_G(t)$ populations.
Schematic only: (a) including first order processes only, (b) including second order processes.
\( \tau_L, \alpha_b, \) and \( \beta_b \) to be determined from (4-5a, b, and c).

Then, using \( \tau_L, \alpha_b, \beta_b \), and the measurements of any two of the population ratios measured in the presence of electrons, \( \alpha_e \) and \( \beta_e \) can be determined from (4-7a, b, or c). From a knowledge of the electron beam current and geometry, the electron impact state changing and ionizing cross sections can be obtained from \( \alpha_e \) and \( \beta_e \). The unused population ratio may be employed in a consistency check calculation.

For the maintenance of single collision conditions, it is important to select the experimental conditions, i.e. interaction time and/or collision partner densities (when variable), so that the occurrence of second order processes is negligible. It should be noted in this regard that the radiative lifetimes of the mixed state Rydberg atoms are, of course, constant and the densities of the background gas in the chamber and of the background radiation photons are fixed. The pressure in the apparatus is probably about as low as can be achieved without modifications to the design. Since the effects of background radiation on Rydberg atoms were only first appreciated during the course of this work, no provision in the design was made for cooling down the environment of the Rydberg atoms in order to reduce the
radiation processes.\footnote{It is felt that the background radiation processes constitute the second largest competing process involving Rydberg atoms in comparison to the electron processes. The largest is radiative decay of the Rydberg atoms.} Thus it is necessary to establish single collision conditions commensurate with these limits. One way to judge whether or not second order processes are important for a given set of experimental conditions is to set up and solve the model rate equations through second order. By using reasonable estimates of the rate coefficients for the second order terms, the importance of such terms can be examined.

**SFI measurements.** These measurements, which employ the selective field ionization technique discussed in Sec. 4.6, are used to determine $N_L(t)/N_L(0)$ and $N_N(t)/N_L(0)$ with and without electrons present. First of all, an SFI spectrum for $N_L(0)$ is obtained (measurement $\#1$) by applying the SFI technique immediately following the laser pulse (i.e. $t_T = 2 \mu$s in Fig. 4-12). Next, an SFI spectrum is obtained without electrons present at a time $t$ after the laser pulse (measurement $\#2$). Upon comparison with the first spectrum ($\#1$), this second spectrum reveals the remaining laser excited Rydberg atom population and also the mixed state signal due to the background processes. Then measurement $\#2$ is repeated with electrons present (measure-
ment #3). This last spectrum contains the mixed state signal due to both background and electron processes along with the remaining laser excited Rydberg atom population. At this point both background state changing and electron state changing processes can be identified. In order to determine the population ratios, the two mixed state portions of the SFI spectra (i.e. from #2 and #3) are integrated to get \( N_M(t) \) with and without electrons present. Also the two portions of the spectra comprising the remaining laser excited state populations (i.e. again from #2 and #3) are integrated to get \( N_L(t) \) with and without electrons present. As discussed in Sec. 4.6, the four numbers resulting from these integrations are only equal to \( N_M(t) \) and \( N_L(t) \) with and without electrons to within the multiplier efficiency factor. This efficiency factor, however, cancels out when the numbers are divided by the integral of the \( N_L(0) \) spectrum (i.e. #1) which also is only equal to \( N_L(0) \) to within the multiplier efficiency factor. Thus the population ratios are obtained. This cancellation of the multiplier efficiency factor is a nice feature of the present experiment since, as a result, absolute cross sections may be obtained without having to calibrate the multiplier.

Two features must be considered in making these
measurements: 1) the selection of the appropriate field ramp size, and 2) the effect of the presence of the electron beam on the SFI technique.

(1) The criterion used to determine the field ramp size is that the laser excited state is resolved as well as possible from the mixed state signal in the SFI spectrum. Resolution of the individual mixed states is also desirable. Since it generally is not possible to select a ramp which will provide adequate state resolution for all possible state changing processes, the procedure is to concentrate on one aspect of the process ($m$-changing, $n$-$m$-changing, etc.) and then, using a figure similar to Fig. 4-20 for high values of $n$ (see, for example Fig. 4-37) to determine at what field strengths such mixed states will be field ionized, pick the appropriate field ramp size.

(2) Since electrons are detected in the SFI technique, it is apparent that, in order to avoid burying the ionization signal in an electron background from the beam, the electron beam must not be on when the field ramp is applied. Also due to the ever present stray electron background when the electron beam is on (see Sec. 4-8), operating the beam continuously at the current levels used in the experiment would probably damage the electron multiplier (which is on all the time). Therefore the electron beam is pulsed
in the manner described in Sec. 4-8. It is turned on just before each laser pulse\(^1\) and turned off before the field ramp is applied. The time interval between laser fire and the end of the electron pulse is then the interaction time for the electron-Rydberg atom collisions.

Even with the electron beam operating in a pulsed mode so that the electrons liberated in the field ionizing events can be detected after each pulse, the electron multiplier itself may still be saturated during each pulse. Since it takes the multiplier on the order of tens of microseconds to recover from saturation, it is necessary to prevent the saturation from occurring. This is accomplished by switching Grids 5 and 6, which are normally held at +200 V, to -40 V and Grid 4, which is normally at +80 V, to -16 V during the gun pulse interval. This "grid pulse" rather effectively prevents electrons from reaching the electron multiplier. The circuit used to perform this task is shown in Fig. 4-29. A complication arising from the application of the grid pulse is that it takes ~4 \(\mu\)sec for grids 4, 5, and 6 to return to their normal voltage after the grid pulse is removed. Furthermore it takes about the same amount of time for the multiplier anode lead, which

\(^1\) Turning the beam on before the laser pulse allows the beam to stabilize (if necessary) before the Rydberg atoms are produced.
Fig. 4-29 Grid pulse circuit.
experiences a baseline shift due to the grid pulse, to return to 0 V. Therefore, the SFI spectrum is not taken until 4 μsec after the electron gun (and thus the grid pulse) is turned off. This 4 μsec interval, in turn, causes a problem in the use of the signal formulae derived earlier. There the assumption had been that the various collision partners (electrons, background gas, and radiation) all interact with the Rydberg atoms for the same length of time, $t$, following which SFI spectra are taken to analyze the results. Now it is seen that, when electrons are present, the Rydberg atoms will interact with the electrons for a given time, denoted $t_e$, and with the background gas and radiation for a longer time, $t_b = t_e + 4 \mu s + 1 \mu s$ (the 1 μsec is for the rise time of the field ramp which is triggered at $t_T = t_e + 4 \mu s$. (Even in the absence of the 4 μsec delay it is apparent that this interaction time problem exists because of the 1 μsec rise time of the field ramp.) However, it is not difficult to modify the signal equations to handle this situation and the results are given as follows. In the presence of electrons, the equations are:

$$N_L(t) = N_L(0) e^{-(\alpha_e + \beta_e)t_e - \left(\frac{1}{T_L} + \alpha_b + \beta_b\right)t_b}$$

(4-8a)
\[ N_M(t) = N_L(0) \frac{\alpha_b \epsilon^{-(\alpha_e + \beta_e) t_e}}{1 + \alpha_b + \beta_b} \left( e^{-\left(\frac{1}{\tau_L} + \alpha_b + \beta_b\right) t_e} - e^{-\left(\frac{1}{\tau_L} + \alpha_b + \beta_b\right) t_b} \right) \]
\[ + N_L(0) \frac{\alpha_e + \alpha_b}{\tau_L + \alpha_b + \beta_b + \alpha_e + \beta_e} \left( 1 - e^{-\left(\frac{1}{\tau_L} + \alpha_b + \beta_b + \alpha_e + \beta_e\right) t_e} \right) \]

(4-8b)

\[ N_I(t) = N_L(0) \frac{\beta_b \epsilon^{-(\alpha_e + \beta_e) t_e}}{1 + \alpha_b + \beta_b} \left( e^{-\left(\frac{1}{\tau_L} + \alpha_b + \beta_b\right) t_e} - e^{-\left(\frac{1}{\tau_L} + \alpha_b + \beta_b\right) t_b} \right) \]
\[ + N_L(0) \frac{\beta_b + \beta_e}{\tau_L + \alpha_b + \beta_b + \alpha_e + \beta_e} \left( 1 - e^{-\left(\frac{1}{\tau_L} + \alpha_b + \beta_b + \alpha_e + \beta_e\right) t_e} \right) \]

(4-8c)

\[ N_G(t) = N_L(0) \frac{(\frac{1}{\tau_L}) \epsilon^{-(\alpha_e + \beta_e) t_e}}{1 + \alpha_b + \beta_b} \left( e^{-\left(\frac{1}{\tau_L} + \alpha_b + \beta_b\right) t_e} - e^{-\left(\frac{1}{\tau_L} + \alpha_b + \beta_b\right) t_b} \right) \]
\[ + N_L(0) \frac{1/\tau_L}{\tau_L + \alpha_b + \beta_b + \alpha_e + \beta_e} \left( 1 - e^{-\left(\frac{1}{\tau_L} + \alpha_b + \beta_b + \alpha_e + \beta_e\right) t_e} \right) \]

(4-8d)

In the absence of electrons, the equations are the same as
(4-5a, b, c, and d) with t replaced by \( t_b \): ¹

\[
N_L(t) = N_L(0) e^{-\left(\frac{1}{\tau_L} + \alpha_D + \beta_D\right)t_b}
\]  

(4-9a)

\[
N_M(t) = N_L(0) \frac{1}{\tau_L + \alpha_D + \beta_D} \left(1 - e^{-\left(\frac{1}{\tau_L} + \alpha_D + \beta_D\right)t_b}\right)
\]

(4-9b)

\[
N_I(t) = N_L(0) \frac{\beta_D}{\tau_L + \alpha_D + \beta_D} \left(1 - e^{-\left(\frac{1}{\tau_L} + \alpha_D + \beta_D\right)t_b}\right)
\]

(4-9c)

\[
N_G(t) = N_L(0) \frac{1/\tau_L}{\tau_L + \alpha_D + \beta_D} \left(1 - e^{-\left(\frac{1}{\tau_L} + \alpha_D + \beta_D\right)t_b}\right)
\]

(4-9d)

Finally, the electron beam produces a noise signal in the SFI spectra in the following manner. During the electron pulse, the electrons ionize some of the background gas in the chamber. These ions, which have only a thermal velocity, are still present in the interaction region when the field ramp is applied and are consequently driven up into Grid 2 where they release secondary electrons. If the field

¹ As far as the calculations for obtaining the various rate coefficients are concerned, it is not necessary that the time at which the SFI spectra are taken in the measurements without electrons present equals the time used in the measurements with electrons present. However, in order to compare measurements #2 and #3 to separate electron induced state changing signal from the background radiation and gas induced state changing signal and therefore to be able to identify what type of electron impact state changing processes are occurring, these two times should be equal.
ramp in use is large enough, this process occurs in a short time and the secondary electrons which are accelerated by the field down to the multiplier, are detected and appear as an additional signal in the SFI spectrum. As implied this is only a problem for the larger ramp sizes since for small ramps the ions are accelerated slowly and do not reach Grid 2 before the ramp has reached its maximum. In order to decrease this noise signal, the frame of Grid 2 contains a 2" in diameter hole with 0.001" diameter tungsten wire stretched across it at a 0.1" pitch. Meanwhile the hole in Grid 3 is a narrow rectangle 0.40" wide and 1.0" long with its long axis parallel to the sodium beam. The design of Grid 2 minimizes the surface area exposed to the ions while the design of Grid 3 decreases the field of view of the multiplier so that fewer secondary electrons can reach it. Of course the multiplier is still able to completely view the interaction region.\(^1\) Since the noise process is not completely eliminated by this grid design, there is a contribution from this process in measurement #3. Therefore a noise SFI spectrum (which consists of measurement #3 repeated with sodium beam blocked) must be taken

\(^1\) The secondary electron noise also depends on the electron beam energy since the cross section for electron impact ionization of the background gas is a function of this energy.
(measurement #4) and subtracted channel by channel from the spectrum of measurement #3.

The sequence of events used in making the four measurements just described are shown in Fig. 4-30a, b, and c. The electron-Rydberg atom interaction time, $t_e$ employed is 6 μsec while the SFI spectra used to analyze the products of the collision processes are taken 11 μsec (equals $t_b$) after the laser pulse. These times are consistent with the upper limits placed on $t_e$ and $t_b$ by the system geometry. Using the average velocity of a Rydberg atom and the radius of the electron beam, it is found that a Rydberg atom produced at the center of the excitation region will exit the electron beam in $\sim 7.5$ μsec after the laser pulse. Similarly using the dimensions of the rectangular hole in Grid 3, it is found that this same Rydberg atom will leave the field of view of the multiplier in $\sim 19$ μsec. Finally, the SFI spectrum obtained for $N_L(0)$ (measurement #1) really yields a number proportional to $N_L(3 \mu\text{sec})$ as discussed in Sec. 4.6. However this number is easily converted to a number proportional to $N_L(0)$ by using the equation

$$N_L(0) = N_L(3 \mu\text{sec}) e^{\frac{1}{T_L}(3 \times 10^{-6})}$$

(4-10)

obtained from (4-5a).

At this point it is important to check the electron
Fig. 4-30a  Sequence of events - SFI measurement #1.
All times in μsec.
Fig. 4-30b Sequence of events - SFI measurement #2.
All times in μsec.
Fig. 4-30c  Sequence of events - SFI measurement #3 and SFI measurement #4 (sodium off).
All times in \( \mu \text{sec} \).
beam's position, size, and uniformity under the conditions used for SFI measurements when electrons are present. As noted the beamline is operated in the pulsed mode. The conditions specified for a cw 25 eV beam in Sec. 4.6 are used with the exceptions that $V_{Fil} = 7.2 \text{ V}$ and $V_G = -23.5 \text{ V}$ during the pulse. These different settings allow a higher beam current to be obtained. It is hoped that the different settings do not dramatically increase the low energy electron background. Also for these measurements the voltage on the first dynode of the multiplier is $+200 \text{ V}$ while during the electron beam pulse the voltage on Grids 5 and 6 is $-40 \text{ V}$ and the voltage on Grid 4 is $-16 \text{ V}$. Therefore all of these voltages are applied cw to the apparatus and the beam profile, shown in Fig. 4-31, is taken. It is seen that the position, size, and uniformity of the beam are reasonable.

Combination FI and ion measurements. These two measurements are used together to obtain the population ratio $N_I(t)/N_L(0)$ with and without electrons present. It has been stated several times that it is the ions released in ionization events involving Rydberg atoms (i.e. electron impact ionization, photoionization by the background radiation, etc.) which are detected and not the released electrons. The ions must be used since the released
Fig. 4-31 Electron beam (25 eV) profile taken under SFI measurement conditions.
electrons, with their high velocities, would rapidly escape from the interaction region while the ions, traveling with the sodium beam velocity can be produced over a long interaction time period (up to 19 μsec, see above) and yet be collected and detected just as can the various Rydberg atoms in the SFI measurements. While this may seem obvious, it is an important consideration because the detection of ions allows a large background process to come into play—electron impact ionization of the background gas in the chamber. This process, which is not directly detected in the SFI measurements, immediately places constraints on the electron-Rydberg atom ionization experiment. This noise, which can be measured without Rydberg atoms present, must be subtracted from a signal plus noise measurement where the signal is composed of ions resulting from Rydberg atom ionization events. Since the difference in the densities between the number of Rydberg atoms produced and the background gas more than compensates for the difference in the cross sections for the Rydberg atom and background gas ionization processes, the noise is larger than the signal.

---

1 As has been discussed, this process is indirectly detected in the SFI measurements due to the production of secondary electrons by the ions. However, the number of secondaries detected should be much smaller than the initial number of ions and the whole process is important only when the larger field ramps are used.
(i.e. signal-to-noise ratio < 1). Therefore in order to make the net result of the subtraction statistically significant, it is necessary to increase the signal as much as possible. This can only be accomplished by increasing the Rydberg atom production.\(^1\) Herein lies the reason for designing a technique which is capable of detecting large numbers of both Rydberg atoms simultaneously (FI technique, Sec. 4.6) and ions simultaneously (ion detection, Sec. 4.7).

After a multiplier first dynode operating voltage is chosen and the corresponding reverse bias voltage is applied to Grids 2 and 3, the measurements required to obtain \(N_I(t)/N_L(0)\) are made as follows. First of all, a measure of \(N_L(0)\) is obtained by applying the FI technique immediately following the laser pulse (measurement \#5, \(t_T = 0\) in Fig. 4-14). Next a measurement is made which is proportional to \(N_I(t)\) at a time \(t\) after the laser pulse for the case in which electrons are absent (measurement \#6). This measurement encompasses ions produced by the ionization of Rydberg atoms by the background radiation and gas. Then measurement \#6 is repeated for the case in which electrons

---

\(^1\) It should be remembered that the increase in ionization signal caused by increasing the Rydberg atom production is not solely due to electron-Rydberg atom ionization events. The contribution to the signal from photoionization of the Rydberg atoms by the background radiation will also increase with increasing Rydberg atom production.
are present (measurement #7). This measurement detects the ions from electron impact ionization of the background gas as well as the ions resulting from Rydberg atom ionizing events. Finally, measurement #7 is repeated with the sodium beam blocked (measurement #8) in order to detect only the background gas ions. The charge obtained in measurement #8 is subtracted from that of measurement #7 to give the net signal due to Rydberg atom ionizing events. Dividing measurement #6 and the difference between measurements #7 and #8 by measurement #5 gives \( \frac{N_I(t)}{N_L(0)} \) without and with electrons present respectively.\(^1\)

Two features of the \( \frac{N_I(t)}{N_L(0)} \) measurement must be examined closely: 1) how the multiplier's output scales with its input, and 2) the size of the collection field and the determination of the appropriate integration gates to be used in the ion detection measurements.

(1) In the determination of \( \frac{N_I(t)}{N_L(0)} \), the multiplier is called upon to detect widely varying numbers of ions. These range from the large numbers of ions resulting from the field ionization of Rydberg atoms (measurement #5) to

\(^1\) If the multiplier's output does not scale linearly with its input, i.e. the relative gain per ion is not independent of the number of ions simultaneously striking the first dynode, then the functional dependence of the gain must be removed from these quotients to get the ion population ratio. As in the SFI measurements the multiplier efficiency cancels out.
the small numbers of ions produced by photoionization of Rydberg atoms by the background radiation (measurement #6). Thus it is important to ensure that the multiplier has a dynamic range sufficient for this detection. It is also necessary to know how the multiplier's output scales with its input in order to make comparisons between results within a given type of measurement (#5, #6, #7, or #8) and between results of different measurements. The multiplier's dynamic range and the manner in which its output scales with its input are determined by using the ion detection technique to detect the ions created in the interaction region by a cw electron beam (100 eV) ionizing nitrogen gas which is leaked into the chamber. A large collection field (essentially an ionizing field although no atoms are ionized) is used and each time this field is applied the electron impact produced ions are driven to the multiplier and detected simultaneously. The multiplier output is then monitored as a function of the nitrogen pressure in the chamber under the assumption that the ion production by the electron beam (and therefore the number of ions incident on the multiplier per field pulse) scales directly with the nitrogen pressure for the pressures employed. Care is taken not to get too close to the chamber's base pressure (i.e. very little nitrogen present) in order to avoid
problems associated with gas composition changes. Fig. 4-32 shows the dependence of the multiplier output on the nitrogen pressure\textsuperscript{1} for three first dynode voltages. The curves exhibit a close to linear output to input scaling factor but they also indicate a tendency for the output to roll over as the pressure is increased. As long as all charge measurements used in the determination of $N_I(t)/N_L(0)$ fall on this graph, then the required knowledge of the multiplier's gain behavior is, in principle, available from the graph.

(2) The constraints on the size of the ion collection field used are that it be large enough to ensure efficient ion collection and yet be small enough so that it does not ionize any Rydberg atoms of importance in the experiment. In the present work a collection field of 22 V/cm is employed. Using (4-1) this field corresponds to the classical threshold field for ionization of the $n = 62$ state. As already mentioned, a collection field of this size produces a large spread in the ion flight times and therefore a large time interval over which they are detected. Under such conditions the determination of the integration gates to be used for measurements #6 and #7 by observing, on an oscilloscope, the

\textsuperscript{1} Actually the nitrogen pressure times the electron beam current is used so as to account for drifts in the current.
Fig. 4-32 Multiplier output as a function of $N_2$ pressure times electron beam current for three multiplier voltages, $V_{MULT}$.

- LRS 3001 qVt gated current integrator used.
- Keithley 610B electrometer used.
detection of the ions versus the time after the collection field is triggered is difficult especially for measurement #7 where the signal ions are obscured by the large numbers of noise ions produced by electrons colliding with the background gas. Therefore a short gate (~ 200 nsec) is traversed step by step through the ion arrival time interval for each of the measurements: #6, #7, and #8. A charge measurement is produced at each step. This results in an ion arrival time spectrum for each measurement. Fig. 4-33a shows the spectrum for measurement #6 (i.e. ions produced by the ionization of Rydberg atoms by background gas and radiation). The open circles in Fig. 4-33b show the spectrum for measurement #7 (i.e. ions from Rydberg atoms plus background gas ions) while the solid circles show the difference between the spectrum for measurement #7 and that for measurement #8 (background gas ions only). This difference spectrum is the arrival time spectrum for ions produced by electron-, background radiation-, and background gas-Rydberg atom ionizing events. From these graphs the location and width of the integration gates necessary for each ion measurement can be obtained.

The sequence of events used in making the four measurements: #5, #6, #7, and #8 are shown in Fig. 4-34a, b, and c. The interaction times $t_e$ and $t_b$ used in these measure-
Fig. 4-33a Ion arrival time spectrum for ion measurement #6.
Fig. 4-33b  Ion arrival time spectrum for ion measurement #7 (o). Ion arrival time spectrum for difference between measurements #7 and #8 (•).
Fig. 4-34a Sequence of events - measurement #5
All times in μsec.
Fig. 4-34c  Sequence of events - measurement #7 and measurement #8 (sodium off).
All times in μsec.
ments are the same as those used in the SFI measurements. Measurement #5 really results in an amount of charge proportional to \([N_L(1\ \mu\sec) + N_M(1\ \mu\sec) + N_I(1\ \mu\sec)]\) instead of \(N_L(0)\). These two quantities are related to each other by

\[
N_L(0) = \frac{[N_L(1\ \mu\sec) + N_M(1\ \mu\sec) + N_I(1\ \mu\sec)] \left(\frac{1}{\tau_L} + \alpha_b + \beta_b\right)}{[\alpha_b + \beta_b + \frac{1}{\tau_L} e^{-(\frac{1}{\tau_L} + \alpha_b + \beta_b)(1\times10^{-6})}]} \tag{4-11}
\]

which is obtained from (4-5a, b, and c). This is difficult to use and can be approximated by

\[
N_L(0) = [N_L(1\ \mu\sec) + N_M(1\ \mu\sec) + N_I(1\ \mu\sec)] e^{\frac{1}{\tau_L} (1\times10^{-6})} \tag{4-12}
\]

when \(\frac{1}{\tau_L} \gg \alpha_b + \beta_b\) as is the case in the present work. Thus the result of measurement #5 can be related to \(N_L(0)\) by using (4-12).

Finally it is necessary to check the electron beam's position, size, and uniformity under the ion measurement conditions. The electron beam is pulsed in the same way as in the SFI measurements. The voltages used on the grid assembly and multiplier (including the reverse bias voltages applied to Grids 2 and 3 which is appropriate to the first dynode voltage) are given in Sec. 4.6. A beam profile taken under these conditions (applied in cw fashion) is shown in Fig. 4-35. Although it is close to the right
Fig. 4-35 Electron beam (25 eV) profile taken under ion measurement conditions (voltage on multiplier first dynode and Grids 5 and 6 = -3000 V, voltage on Grid 4 = -1200 V, reverse bias voltage on Grids 2 and 3 = -0.65 V and +0.65 V, respectively).
position, the beam appears to be focused. This casts doubt on both its overlap with the Rydberg atom region and its uniformity. As it turns out this is only one problem that plagues the measurement of \( N_I(t)/N_L(0) \). Further discussion of this measurement will be given in the next chapter and in an appendix.

4.10 Effects of Small Electric Fields on Rydberg Atoms

It was discussed in Sec. 3.2 and 4.6 that Rydberg states of sodium in zero field develop, upon application of an electric field, into Stark states which are both energy shifted from the original states and of a character that can be viewed as a superposition or mixture of the original zero field states. Since the states of sodium are non-degenerate in zero field, the initial energy shift of a given state is quadratic in field strength until an avoided crossing with a neighboring state is reached. At that point appreciable mixing between the two states occurs and the energy shift between the two states becomes linear with field strength.\(^1\) For a given value of \( n \) this process

\(^1\) It should be remembered (as mentioned in Sec. 4.6) that in the present work (i.e. under the experimental conditions employed and for the Rydberg states excited) the passage through this crossing (and therefore the development of a linear Stark state) from a zero field state is assumed to occur adiabatically. The successful explanation of the ionization thresholds of the various Rydberg states (see Fig. 4-21) is viewed as supporting this assumption.
occurs first for those states possessing the largest values of \( \ell \) in zero field since those states lie closest together in zero field. As the field is increased, states with smaller values of \( \ell \) become involved. Such a development is shown in Fig. 4-20 for the \(|m_\ell| = 0\) states, however, on the scale of that figure, the process is only apparent for the \( s \) and \( p \) states. It is seen from the figure, for instance, that the \( 10p \) state mixes into the \( n = 9 \) linear Stark manifold at a field strength of about 9 kV/cm while a field of about 23 kV/cm is required to mix the \( 10s \) state. For the Rydberg states excited in the present work the field strengths at which initial state mixing occurs are quite small even for the low \( \ell \) states. For instance, for the zero field \( 29d \) state the value is only \( \sim 2 \) V/cm. This indicates that the application of only a small field is required to substantially alter a zero field Rydberg state.

The above discussion can be experimentally demonstrated by laser exciting sodium Rydberg states in the presence of electric fields of various strengths. In zero field \( \ell \) is a good quantum number. This means that each state is associated with only one value of \( \ell \), i.e. the angular momentum character of a state's wavefunction is determined by a single value of \( \ell \). As a result the dipole selection rule places constraints on which states can be
excited in zero field. However, in the presence of a field, the mixing of the zero field states produces Stark states which possess some \( l \) character from each of the zero field states that were mixed together. If excitation to a certain \( l \) state is dipole allowed in zero field, then upon application of a field sufficient in strength to mix this state into other states, excitation of all these other states will be dipole allowed since they each will possess some of the initial state's \( l \) character. The degree to which excitation to any one of these states is allowed is dependent on the amount of the specific \( l \) character that the state contains as a result of the mixing.

As a specific example, the excitation of what is the 29d state in zero field has been carried out in the presence of several small dc fields by applying equal but opposite polarity voltages to Grids 2 and 3 (positive voltage to Grid 2 and negative voltage to Grid 3 using the bias voltage battery in the ionizing field ramp generator). The blue laser, operating with a 0.05 \( \text{A} \) linewidth, produces radiation which is energetically capable of exciting states lying within about \( 3.6 \times 10^{-5} \text{ eV} \) of the zero field 29d state to which the laser is tuned. This includes all of the higher

---

\(^1\) Twice the linewidth is taken as the wavelength interval over which the blue laser emits radiation.
lying \( n = 29 \) states in zero field and, in fact, all of the Stark states into which these higher lying states develop in a field out to a field strength of around 2.5 V/cm (at which point the highest energy Stark states begin to be blue shifted by the field out of the laser radiation bandwidth). However, as has been discussed, none of these higher states will be excited until the field strength is reached at which the 29d state is mixed into the rest of the \( n = 29 \) manifold. This field strength was stated above to be approximately 2 V/cm. The fields in which the excitation was carried out range in strength from what is assumed (for practical purposes) to be zero field in the interaction region to a field of 2.5 V/cm. The Rydberg atoms produced under these conditions are detected using the SFI technique (see Sec. 4.6). The results are shown in Fig. 4-36. The additional signal which appears at non-zero fields to the left of the 29d adiabatic ionization signal indicates that other Rydberg states are being excited in the presence of a field. The initial nonlinear appearance of this signal with field, followed by a constant

---

1 The reader may have noticed that the small field in which the Rydberg atoms are excited is oppositely directed to the ionizing field. This is due to the polarity of the bias voltage battery in the ionizing field ramp generator. Therefore, the atoms experience a field polarity reversal. However, it is not thought that this will affect the results.
Fig. 4-36  SFI spectra obtained following laser excitation of Rydberg atoms in the presence of various fields. The blue laser is tuned in zero field to excite the 29d state.
amount of signal between 2.0 and 2.5 V/cm is consistent with the expected 2 V/cm mixing threshold for the 29d state. According to the discussion above, the "field mixed" signal comes from Rydberg atoms whose states energetically lie throughout the n = 29 Stark manifold. That this is true can be shown by determining the manner in which these states are field ionized. Such information is obtained from Fig. 4-37 which follows the example given by Gallagher et al. (1977d). Only the components at the extreme energies of each of the n = 28, 29, and 30 Stark manifolds are shown. Of the states whose manner of ionization is desired, those with small values of $|m|_k$ will ionize adiabatically. The field strengths between which this adiabatic ionization will occur are found by following the dark curves of the n = 29 manifold to their points of intersection with the classical ionization curve, $F_c$, and reading the field values corresponding to these points, i.e., $F_1$ and $F_2$. It is seen from the figure that $F_1$, the field strength at which the signal should start to appear, should be just larger than that at which the adiabatic ionization threshold of the 30d state (excited in zero field) occurs. Comparison of this 30d threshold, shown in Fig. 4-16, with the present data shows this to be the case. The other extreme, $F_2$, is just smaller than the 29d state adiabatic threshold. Again this
Fig. 4-37 Schematic representation of several extreme components of the $27 \leq n \leq 31$ Stark manifolds. Dark curves represent adiabatic paths to ionization for the $n = 29$, $\ell = 3$ and $\ell = 28$, $|m_\ell| = 0$ states. For the details on the construction of these adiabatic paths, see Jeys et al. (1980).
agrees with the present data.

Several final observations should be made. 1) This example demonstrates that a maximum field strength exists which, if approached, results in a substantial alteration of the excitation process from one occurring in zero field. A method of estimating this field strength is also demonstrated. 2) The method used above in confirming the state composition of the "field mixed" signal is exemplary of the technique used to identify the composition of the mixed state signal resulting from background radiation- and electron-Rydberg atom interactions. 3) Finally, it was stated in Sec. 4.8 that the voltages employed in operating the electron beamline do not create fields which affect the Rydberg atoms. This has been demonstrated as concerns the Rydberg atom excitation process by exciting 29d state atoms under conditions where Grids 2 and 3 are held at ground while \( V_{A-EA} = +20 \text{ V} \) and \( V_{BC} = +100 \text{ V} \). An SFI spectrum obtained for atoms so excited shows no statistical difference from the 0 V/cm field spectrum at the top of Fig. 4-36.
CHAPTER V
RESULTS AND DISCUSSION

5.1 General

An experiment has been outlined in the last two chapters in which the following quantities can be determined for a sodium Rydberg atom in an ns or nd state: $\tau_L$, the radiative lifetime; $\alpha_b \approx \alpha_p$, the rate coefficient for state changing processes primarily due to 300 K background radiation; $\beta_b \approx \beta_p$, the rate coefficient for the ionizing process primarily due to 300 K background radiation; $\sigma_M$, the cross section for the electron impact state changing process at 25 eV; and $\sigma_I$, the cross section for the electron impact ionizing process at 25 eV. Although two sets of data for the laser excited state of 36d were obtained to which the full analysis of the last chapter (i.e. equations (4-8) and (4-9)) could be applied, several problems arose which cast doubt on some of the data. Analysis revealed that the data are not self-consistent (i.e. consistency checks failed). It is necessary, then, to determine which measurements are in error.

One major problem, as mentioned in Sec. 4.9, has been determined to be the inability, at present, to make reliable measurements of the ion signal resulting from both photo-
ionization of the Rydberg atoms by the background radiation and electron impact ionization of the Rydberg atoms. The nature of this problem is discussed in the Appendix. The difficulties encountered have been of sufficient severity to result in the elimination from further analysis of the \( N_I(t)/N_L(0) \) data taken both with and without electrons present.

However, even in the absence of \( N_I(t)/N_L(0) \) data, it is still possible to carry through the analysis on the remaining data and obtain values for \( \tau_L, c_b, c_e \) and \( \beta_e \), given that a reasonable estimate of \( \beta_b \) is employed. Since \( \frac{1}{\tau_L} \gg c_b + c_b \), the results are not very sensitive to the value of \( \beta_b \) chosen. For instance, if \( \beta_b = 1350 \text{ sec}^{-1} \) is used in (4-9a) and (4-9b) along with the 36d \( N_L(t)/N_L(0) \) and \( N_M(t)/N_L(0) \) data taken without electrons present, values obtained for \( c_b \) and \( \tau_L \) are: \( c_b \approx 4100 \text{ sec}^{-1} \) and \( \tau_L \approx 32 \mu\text{sec} \). Then calculation of \( c_e \) and \( \beta_e \) from (4-8a) and (4-8b) using the 36d \( N_L(t)/N_L(0) \) and \( N_M(t)/N_L(0) \) data taken with electrons present, results in \( c_e \approx 3200 \text{ sec}^{-1} \) (\( \sigma_M \approx 4 \times 10^{-10} \text{ cm}^2 \)) and \( \beta_e \approx 8600 \text{ sec}^{-1} \) (\( \sigma_I \approx 1 \times 10^{-9} \text{ cm}^2 \)). These values, obtained without the use of the problematic ion measurement data, require further discussion. Comparison of the above \( \tau_L \) value with the 45 \( \mu\text{sec} \) value calculated from the equation quoted in chapter IV indicates that \( N_L(t)/N_L(0) \) and/or
$N_M(t)/N_L(0)$ may be too small. Furthermore, the value of $\sigma_I$ obtained above is larger than the theoretical value for hydrogen\(^1\) and if the larger value of $\tau_L$ is used (i.e. 45 $\mu$sec), then $\sigma_I$ could become larger. This implies that $N_M(t)/N_L(0)$ taken with electrons present may be too small. Thus it is seen that, even after eliminating the ion measurement data, the remaining data may still give troublesome results. While, at the moment, it is difficult to see how the $N_L(t)/N_L(0)$ measurement taken without electrons can be low, such a possibility does exist for the $N_M(t)/N_L(0)$ measurements. It should be remembered that $\alpha$ represents the rate coefficient for the de-population of the laser excited state by all state changing processes. It is therefore necessary that all of the mixed state signal be detected. For the SFI detection technique, this means that all field strengths must be examined.\(^2\) Detailed discussion of this examination will be given in Sec. 5.3 after the data obtained is presented. However, it is apparent that if

\(^1\) Comparison of $\sigma_I$ with theory is made here rather than a similar comparison for $\sigma_M$ because it is easier. This results from the fact that ionization is a single, clear-cut process while state changing collisions can involve many different processes making comparison difficult.

\(^2\) Since one field ramp usually is not sufficient for this (see Chapter IV), several spectra taken with different field ramps are required.
mixed state signal is overlooked, then \( N_M(t)/N_L(0) \) will be too small and the value obtained for \( \sigma_M \) will only be a lower bound on the total state changing process.

On the other hand, cross sections which are not just lower bounds can be determined for the mixed state signal that is detected. This is accomplished by using the analysis of (4-8) and (4-9) under the thin target assumption. The calculation of such cross sections is, of course, independent of whether or not the observed signal can be identified with a particular state changing process (e.g. n-changing, n&lsquo;-changing, etc.). First of all, (4-8) and (4-9) can be simplified when thin target conditions apply to both the collision and background radiation processes but not to the radiative decay of the laser excited state by employing the condition

\[
\frac{1}{\tau_L} \gg \alpha_b + \beta_b + c_e + \beta_e . \tag{5-1}
\]

This is a pretty good assumption in the present work. The results are, for the measurements in which electrons are present

\[
N_L(t) = N_L(0) e^{-t_b/\tau_L} \tag{5-2a}
\]

\[
N_M(t) = N_L(0) \frac{\alpha_b}{1/\tau_L} \left(1 - e^{-t_b/\tau_L}\right) + N_L(0) \frac{\alpha_e}{1/\tau_L} \left(1 - e^{-t_e/\tau_L}\right) \tag{5-2b}
\]
\[ N_I(t) = N_L(0) \frac{\beta_B}{1/\tau_L} \left( 1 - e^{-t_B/\tau_L} \right) + N_L(0) \frac{\beta_e}{1/\tau_L} \left( 1 - e^{-t_e/\tau_L} \right) \]

(5-2c)

\[ N_G(t) = N_L(0) \left( 1 - e^{-t_B/\tau_L} \right) \]

(5-2d)

while for measurements in which electrons are absent

\[ N_L(t) = N_L(0) \left( e^{-t_B/\tau_L} \right) \]

(5-3a)

\[ N_M(t) = N_L(0) \frac{\alpha_B}{1/\tau_L} \left( 1 - e^{-t_B/\tau_L} \right) \]

(5-3b)

\[ N_I(t) = N_L(0) \frac{\beta_B}{1/\tau_L} \left( 1 - e^{-t_B/\tau_L} \right) \]

(5-3c)

\[ N_G(t) = N_L(0) \left( 1 - e^{-t_B/\tau_L} \right). \]

(5-3d)

It is seen that the collisional and background radiation processes have been de-coupled from each other under this approximation. It is now possible to simply subtract the signals obtained when electrons are absent from those obtained when electrons are present in order to arrive at the net signal due to electrons. This is, of course, in agreement with the discussion in Sec. 3.3. Thus

\[ [N_M(t)]_e = N_L(0) \frac{\alpha_e}{1/\tau_L} \left( 1 - e^{-t_e/\tau_L} \right) \]

(5-4a)

\[ [N_I(t)]_e = N_L(0) \frac{\beta_e}{1/\tau_L} \left( 1 - e^{-t_e/\tau_L} \right) \]

(5-4b)
where $[\cdot]_e$ indicates the net signal due to electrons.\(^1\)

Finally, the approximation can be carried to complete thin target conditions for all processes including radiative decay of the laser excited state by using the condition $\tau_L >> t_e$ and $t_b$. This is not such a good approximation in the present work.\(^2\) Under such conditions $N_L(t) = N_L(0)$ and $N_G(t) = 0$ while for electrons present

\[
N_M(t) = N_L(0) \alpha_b t_b + N_L(0) \alpha_e t_e \quad (5-5a)
\]

\[
N_I(t) = N_L(0) \beta_b t_b + N_L(0) \beta_e t_e \quad (5-5b)
\]

and for electrons absent

\[
N_M(t) = N_L(0) \alpha_b t_b \quad (5-6a)
\]

\[
N_I(t) = N_L(0) \beta_b t_b \quad (5-6b)
\]

So, from (5-5) and (5-6) or from (5-4) directly

\[
[N_M(t)]_e = N_L(0) \alpha_e t_e \quad (5-7a)
\]

\(^1\) This de-coupling approximation allows the various collisional and background radiation processes to be studied independently. Also the radiative lifetime of the laser excited state can be obtained directly, however, as already mentioned, the lifetimes obtained seem small. The main interest in these simplified equations at the moment is to obtain a method for calculating state changing cross sections for the observed mixed state signal.

\(^2\) If thin target conditions do not apply, then this will be reflected in the size of the error bars on the result.
\[ [N_I(t)]_e = N_L(0) \beta_e t_e \]  \hspace{1cm} (5-7b)

in agreement with (3-2) when the thin target approximation is applied to that equation.\(^1\)

5.2 Results of State Changing Processes due to Background Radiation

It is important to understand the effects of the background processes on the Rydberg atoms before dealing with the electron effects. As has been mentioned several times, these background effects are considered to be due primarily to the 300 K background radiation. As an example, Fig. 5-1 shows an SFI spectrum taken at a time \( t_T = 12 \mu\text{sec} \) after the laser pulse (measurement \#2 with \( t_T = 12 \mu\text{sec} \)) where Rydberg atoms in the 29d state are laser excited. This spectrum exhibits the ionization behavior of at least part

\(^1\) There appears to be a discrepancy between (5-4) and (3-2). However, such is really not the case and the resolution to the problem lies in the order of approximation made. Equation (3-2) is derived on the assumption that the electron-Rydberg atom process is the only, or at least the largest process occurring. This situation does not pertain to the present work. For the level of Rydberg atom excitation and the electron density and energy used in this experiment, radiative decay overshadows all other processes. However, the order of the processes can be re-arranged if, for instance, very high \( n \) Rydberg atoms (where \( \tau_L \) is long) are used, or if large densities of low energy electrons are employed. Under such conditions, (3-2) may apply.
Fig. 5-1 Mixed state signal due to background radiation.
The laser excited state is 29d.
of the mixed state atoms present at $t = 13 \mu$sec as well as that of the remaining laser excited atoms which ionize in an adiabatic manner. In order to discern which features are due to the mixed state atoms, Fig. 5-1 should be compared to Fig. 4-16. Using Fig. 4-37 and the dipole selection rule, it is seen that, for laser excited (parent) nd states, the first mixed state peak to the left of the adiabatic parent state peak should result from the ionization of $(n+1)p$ state atoms and the adiabatic ionization of $(n+1)f$ state atoms. This peak should be located at the same place in field strength as the $(n+1)d$ (adiabatic) and $(n+2)s$ state peaks. The second mixed state peak on the left should be due to $(n+2)p$ atoms and the adiabatic component of $(n+2)f$ atoms. It should be located at the same place in field strength as the $(n+2)d$ adiabatic and $(n+3)s$ state peaks. Comparison of Fig. 5-1 with Fig. 4-16 shows good agreement with this description. In the case of laser excited ns states the mixed state peaks to the left of the parent state peak correspond to np, $(n+1)p$, $(n+2)p$, .... atoms in that order. Of course, only p states are made and it is thus possible to obtain an SFI spectrum for a p state by observing the results of background radiation-Rydberg atom state changing processes. Such a result is shown in Fig. 5-2 in which the 30s state is laser excited.
Fig. 5-2  SFI detection of np states due to background radiation-Rydberg atom (30s) state changing process. (The portion of the spectrum to the right of the 30s state is distorted due to the high count rate used.)
An interesting and so far unexplained aspect of this background radiation process is the fact that no mixed state peaks to the right of the laser excited state peak are seen. Such peaks would correspond to stimulated emission from the parent Rydberg state by the background radiation. In the case of laser excited nd states, mixed state peaks to the right of the adiabatic parent state peak would be due to \((n-1)p\) plus \((n-1)f\) (adiabatic component) atoms, \((n-2)p\) plus \((n-2)f\) (adiabatic component) atoms, etc., respectively. For laser excited \(ns\) states, mixed state peaks to the right of the parent state peak would result from \((n-2)p\) atoms, \((n-3)p\) atoms, etc., respectively. A careful search for mixed state signal to the right of the parent state peak has been conducted, but nothing significant has been found. Such a signal, if small, would be difficult to see when a laser excited \(d\) state is used because of the parent state signal which exists between the adiabatic and diabatic peaks of the parent state. Fig. 5-3 shows an SFI spectrum taken at 10 \(\mu\)sec in which 30s is laser excited. This spectrum is taken under conditions where the 30s and 29s state peaks are resolved (and therefore the 30s and 28p state peaks should also be resolved) and at very low count rate (\(\sim 0.05\) counts per laser pulse and therefore no distortion of the peaks is expected). It should be noted that
Fig. 5-3 Search for radiation induced mixed state signal to right of parent state. Arrows indicate where other ns atoms ionize along field ramp.
28p atoms would constitute the first mixed state peak to the right of the 30s peak. As can be seen from the figure, no significant signal exists to the right of the parent 30s peak (compare with the mixed state signal to the left of the 30s peak).

Using (5-3b) or (5-6a) it is possible to estimate rate coefficients, \( \alpha_D \), for the total production of the mixed state signal which is observed (to the left of the parent state). Results are given in Table 5-1.

5.3 Results of State Changing Processes due to Electrons

Mixed state signal due to electron-Rydberg atom collisions has been observed in the present work for several laser excited nd states and is found to occur to the left of the parent state adiabatic peak as shown in Fig. 5-4 through Fig. 5-10. In (b) of each figure, the difference SFI spectrum resulting from the channel-by-channel subtraction of measurement #4 from measurement #3 is shown. This spectrum contains the remaining laser excited Rydberg atom signal and the mixed state signal due to both electron and background state changing processes. In order to identify those features which result from the electron processes alone, the SFI spectrum of measurement #2 is given for comparison in (a) of the figures for each nd state. This latter spectrum contains only the background induced
Table 5-1

Rate coefficients for the production of the observed mixed state signal due to background radiation.

<table>
<thead>
<tr>
<th>State</th>
<th>$\alpha_b(\text{sec}^{-1})^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>36d</td>
<td>3800</td>
</tr>
<tr>
<td>38d</td>
<td>3100</td>
</tr>
<tr>
<td>40d</td>
<td>2400</td>
</tr>
<tr>
<td>41d</td>
<td>2350</td>
</tr>
</tbody>
</table>

* These values are probably only good to a factor of two.
Fig. 5-4 Results of state changing collisions between electrons and laser excited 36d atoms: a) electrons absent, b) electrons present.
Fig. 5-5 Results of state changing collisions between electrons and laser excited 38d atoms: a) electrons absent, b) electrons present.
Fig. 5-6 Results of state changing collisions between electrons and laser excited 40d atoms: a) electrons absent, b) electrons present.
Fig. 5-7 Results of state changing collisions between electrons and laser excited 4d1 atoms: a) electrons absent, b) electrons present.
Fig. 5-8 Results of state changing collisions between electrons and laser excited 45d atoms: a) electrons absent, b) electrons present.
Fig. 5-9 Results of state changing collisions between electrons and laser excited 50d + 51s atoms:
a) electrons absent, b) electrons present. The pair of laser excited states results from
the blue laser linewidth.
Fig. 5-10 Results of state changing collisions between electrons and laser excited \((60 \pm 1)\)d + \((61 \pm 1)\)s atoms: a) electrons absent, b) electrons present. The pair of laser excited states (d and s) results from the blue laser linewidth; the uncertainty in the n values results from difficulty in tuning the blue laser.
mixed state signal along with the remaining laser excited state signal and has been accumulated for the same length of time as the spectrum in (b). It is seen that the mixed state signal due to electron-Rydberg atom state changing processes exists immediately to the left of the parent state adiabatic peak for all nd states shown while a broadening on the high field side of the parent state diabatic peak from mixed state signal occurs for the higher n states (starting in Fig. 5-6).

In order to identify the type or types of state changing processes responsible for this signal and to determine if any other state changing processes are occurring, it is necessary to ensure that all of the different kinds of mixed state atoms produced in the collisions are detected. First of all, it is seen from Fig. 5-4 through Fig. 5-10 that there is no evidence of mixed state signal in between the parent state adiabatic and diabatic peaks. Furthermore, since the TAC window is triggered just before the field ramp starts, each SFI spectrum contains the low field, high quantum state regime (to the left in the figures and continuing to the left off the page). No mixed state signal due to electrons has been observed at lower fields than that shown in the figures at the left of the parent state adiabatic peak. The high field side of the spectrum is limited
by the size of the field ramp employed. While single collisions resulting in changes of state to low lying Rydberg states (detected at high field strengths) are not thought to be likely, Rydberg atoms passing to ionization along diabatic paths may require a high field to be detected. For instance, if, as the result of a state changing process, a Rydberg atom in a high $L$, high $m_L$ state for a given $n$ is produced, that atom may follow a diabatic path to ionization in the upper part of the Stark state manifold for that value of $n$. In such a case the atom would ionize at considerably higher field than those atoms of low $L$ which ionize along adiabatic or diabatic paths at the bottom of the manifold (see Fig. 4-19 and 4-20). As a result the atom may not be ionized (and thus not detected) with the field ramp normally used. Therefore, for two states, 36d and 40d, the state changing experiment was conducted with a field ramp large enough to ionize all atoms having any allowed value of $L$ and $m_L$. Thus such atoms are ionized no matter which path they may take to ionization. It was found that, to the accuracy of the experiment,\(^1\) no mixed state signal exists at higher fields than that shown in Fig. 5-4

\(^1\) Detection of mixed state signal at higher field strengths is complicated by the electron produced noise process discussed in Sec. 4.9 under SFI measurements and therefore is less accurate.
and Fig. 5-6 at the right of the parent state diabatic peak. Finally, it is possible that some mixed state atoms are of such a character so that they ionize at the same field strengths as the parent state (note that this is not just a question of resolution). In such a situation the mixed state signal would most likely be buried in the parent state signal. Only in cases where the mixed state signal is large enough to cause an apparent change of shape in the parent state ionization peaks would this situation be observed. Some of the mixed state signal already pointed out in the figures is occurring nearly in this manner and therefore causes uncertainties in the quantitative evaluation of the signal.

Based on the current level of understanding of the field ionization process, the mixed state signal observed and shown in Fig. 5-4 through Fig. 5-10 is consistent with the single state changing process of $\lambda$-changing from the laser excited nd state to neighboring higher $\lambda$ states of the same n, i.e., nf, ng, etc. Such a mixed state atom population would contribute an ionization signal extending from the left side of the laser excited state adiabatic peak to smaller field strengths. This signal would be due to the low $m_\lambda$ state atoms following adiabatic paths to ionization. Depending on the values of $\lambda$ which are produced,
this signal could extend down to, but not past, the field strength corresponding to the adiabatic peak of the \((n+1)d\) state. The mixed state atom population must also produce a signal extending from the right side of the parent state diabatic peak. This signal would be due to the high \(m_J\) state atoms following diabatic paths to ionization. Again, depending on the values of \(J\) which are produced, this signal could extend out to the field strength required for the diabatic ionization of the \(J = n-1\) state.

Concerning the \(J\) and \(m_J\) composition of the mixed state atom population, the adiabatic portion of the mixed state signal extends far enough to the left of the laser excited state adiabatic peak (at least for the cases shown in Fig. 5-4, 5-5, and 5-6) to indicate that high values of \(J\) (and low values of \(m_J\)) are being produced in the collisions. However, as already mentioned, the diabatic portion of the signal does not appear, within the experimental accuracy, to extend out to the maximum allowable field limit mentioned above, indicating that either high \(J\) values or, at least, high \(m_J\) values are not being produced. Nevertheless, based on the adiabatic signal, it is felt that high \(J\) states are being produced. Furthermore, according to information obtained in this laboratory during the writing of this thesis, this high field signal may appear to be small in an
SFI spectrum. It should be noted that such a signal would be spread out over a large interval of field strengths. Therefore, mixed state atoms may be ionizing at high field strengths in the present work but, for the cases examined, the signal so produced was not observable over the background noise.

It is not thought that the observed signal is due to electron-induced nd → (n+1)ₗ transitions although the adiabatic portion of the signal could be interpreted as indicative of this process. However, the diabatic portion of a signal corresponding to this process would be expected to exhibit a threshold to the left of the laser excited state diabatic peak. Such a threshold is not observed in the present data.

To summarize, the present conclusion is that the signal observed from the electron-Rydberg state changing collisions is due to an ℓ-changing process only, in which an ensemble of the higher lying ℓ states (including high ℓ states) of the same n are produced. Since this work is conducted under single collision conditions, changes in ℓ of greater than one (Δℓ > 1) in a single collision must occur. This result has important consequences both for theory and for several earlier electron-Rydberg atom collision experiments where there is a question as to whether
the high J states observed were produced in single or multiple collisions (see Chapter II).

Cross sections for the production of the signal observed in the present work can be estimated using (5-4a) or (5-7a). These cross sections can then be compared with the experimental results of Schiavone et al. (1977) and with the available theoretical calculations. Of course, this comparison can provide an independent method for identifying the nature of the state changing process which is responsible for the signal observed in this work. To this end, cross sections for the present results are given along with other experimental and theoretical results for J-changing collisions between non-degenerate states in Table 5-2a and along with theoretical results for sodium nσ- and hydrogenic n-changing collisions in Table 5-2b. In Table 5-2a the results of Schiavone et al. (1977) are obtained from (2-18) for 25 eV. The values of Percival and Richards (1977) are for sodium nd → nf transitions occurring at 25 eV where the values of the radial matrix elements involved are extrapolated from the results of Gounand (1979). The values of Herrick (1978) are for nd → nf transitions occurring at 25 eV in which the quantum defects of the sodium d and f states have been used. In Table 5-2b the present results are shown with 1) the values of Percival and
Table 5-2a

Results of present measurements shown with results of other investigations (see text). Cross sections given in cm\(^2\) and E = 25 eV.

<table>
<thead>
<tr>
<th>n</th>
<th>Present results Using (5-7a)</th>
<th>Present results Using (5-4a)*</th>
<th>Schiavone et al. (1977)</th>
<th>Percival and Richards (1977) nd → nf</th>
<th>Herrick (1978) nd → nf</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>4.6x10^{-10}</td>
<td>4.6x10^{-10}</td>
<td>4.48x10^{-9}</td>
<td>2.08x10^{-9}</td>
<td>2.03x10^{-9}</td>
</tr>
<tr>
<td>36</td>
<td>4.5x10^{-10}</td>
<td>4.5x10^{-10}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>1.2x10^{-9}</td>
<td>1.2x10^{-9}</td>
<td>7.78x10^{-9}</td>
<td>3.60x10^{-9}</td>
<td>3.53x10^{-9}</td>
</tr>
<tr>
<td>40</td>
<td>1.7x10^{-9}</td>
<td>1.7x10^{-9}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>3.0x10^{-9}</td>
<td>2.7x10^{-9}</td>
<td>1.27x10^{-8}</td>
<td>5.85x10^{-9}</td>
<td>5.74x10^{-9}</td>
</tr>
<tr>
<td>45</td>
<td>3.4x10^{-9}</td>
<td>3.2x10^{-9}</td>
<td>1.96x10^{-8}</td>
<td>9.03x10^{-9}</td>
<td>8.86x10^{-9}</td>
</tr>
<tr>
<td>50d+51s(^†)</td>
<td>2.4x10^{-9}</td>
<td>2.3x10^{-9}</td>
<td>4.15x10^{-8}</td>
<td>1.91x10^{-8}</td>
<td>1.88x10^{-8}</td>
</tr>
<tr>
<td>(60+1)d+(61+1)s(^†)</td>
<td>2.4x10^{-9}</td>
<td>2.3x10^{-9}</td>
<td>4.15x10^{-8}</td>
<td>1.91x10^{-8}</td>
<td>1.88x10^{-8}</td>
</tr>
</tbody>
</table>

* The radiative lifetimes employed come from equations given in Chapter IV.

\(^†\) Represents blue laser linewidth and difficulty in tuning. Values given in the last three columns on the right are for n = 50 and n = 60.
Table 5-2b

Results of present measurements shown with results of other investigations (see text). Cross sections given in cm\(^2\) and \(E = 25\) eV.

<table>
<thead>
<tr>
<th>(n)</th>
<th>Present results Using (5-7a)</th>
<th>Present results Using (5-4a)*</th>
<th>Percival and Richards (1977) (nd \rightarrow (n+1)p)</th>
<th>Percival and Richards (1977) (nd \rightarrow (n+1)f)</th>
<th>Gee et al. (1976)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>(4.6 \times 10^{-10})</td>
<td>(4.6 \times 10^{-10})</td>
<td>(8.75 \times 10^{-10})</td>
<td>(4.81 \times 10^{-11})</td>
<td>(2.43 \times 10^{-10})</td>
</tr>
<tr>
<td>36</td>
<td>(4.5 \times 10^{-10})</td>
<td>(4.6 \times 10^{-10})</td>
<td>(8.75 \times 10^{-10})</td>
<td>(4.81 \times 10^{-11})</td>
<td>(2.43 \times 10^{-10})</td>
</tr>
<tr>
<td>38</td>
<td>(1.2 \times 10^{-9})</td>
<td>(1.2 \times 10^{-9})</td>
<td>(1.53 \times 10^{-9})</td>
<td>(8.32 \times 10^{-11})</td>
<td>(4.25 \times 10^{-10})</td>
</tr>
<tr>
<td>40</td>
<td>(1.7 \times 10^{-9})</td>
<td>(1.7 \times 10^{-9})</td>
<td>(1.53 \times 10^{-9})</td>
<td>(8.32 \times 10^{-11})</td>
<td>(4.25 \times 10^{-10})</td>
</tr>
<tr>
<td>45</td>
<td>(3.0 \times 10^{-9})</td>
<td>(2.7 \times 10^{-9})</td>
<td>(2.50 \times 10^{-9})</td>
<td>(1.36 \times 10^{-10})</td>
<td>(6.92 \times 10^{-10})</td>
</tr>
<tr>
<td>50(d+51s)†</td>
<td>(3.4 \times 10^{-9})</td>
<td>(3.2 \times 10^{-9})</td>
<td>(3.88 \times 10^{-9})</td>
<td>(2.12 \times 10^{-10})</td>
<td>(1.08 \times 10^{-9})</td>
</tr>
<tr>
<td>(60(d+1)(d+61s)†</td>
<td>(2.4 \times 10^{-9})</td>
<td>(2.3 \times 10^{-9})</td>
<td>(8.29 \times 10^{-9})</td>
<td>(4.55 \times 10^{-10})</td>
<td>(2.30 \times 10^{-9})</td>
</tr>
</tbody>
</table>

* The radiative lifetimes employed come from equations given in Chapter IV.

† Represents the blue laser linewidth and difficulty in tuning. Values given in the last three columns on the right are for \(n = 50\) and \(n = 60\).
Richards (1977) for both nd → (n+1)p and nd → (n+1)f transitions at 25 eV where the work of Gounand (1979) is again used and 2) the semi-empirical values of Gee et al. (1976) for n → n+1 transitions in hydrogen at 25 eV in which an average over all λ's has been performed for each n state.

The present results should be considered accurate to no more than a factor of two. This factor stems from uncertainties in the degree of beam overlap, electron beam uniformity and current measurement, and in the ability to detect all of the mixed state signal. As mentioned earlier, this last item is only important if the cross section is expected to be representative of a given physical process such as λ-changing collisions (as opposed to being representative of only the mixed state signal which is observed). For example, from the point of view of describing the observed mixed state signal, the cross section given for the (60+1)d + (61+1)s state may be considered as accurate. However, from the point of view of the total λ-changing process, the decrease in this particular cross section compared to the others is considered to be artificial due to the lack of state resolution in the SFI spectrum for the state and the resultant difficulty in extracting the signal.

Finally, several suggestions will be made for future
work in the investigation of electron-Rydberg atom state changing collisions. A reduction in the data accumulation time would result if the laser fire repetition rate and/or the electron beam current could be increased. With respect to the present data, it would probably be useful to conduct a careful search for mixed state signal to the left of the laser excited state diabatic peak in order to test the present conclusion that no nd → (n+1)l collisions are occurring. Of course, performing the experiment at other electron energies, particularly the low energies is important. If the use of field ionization remains the method of detecting Rydberg atoms, then it is apparent that the more this process is studied and understood, the more useful it will be in the collision experiments. Of course, the ionization of Rydberg atoms by electric fields is interesting in its own right and it is one of the topics which has been and is currently being pursued in this laboratory.
APPENDIX

PROBLEMS WITH THE MEASUREMENT OF CROSS SECTIONS
FOR ELECTRON IMPACT IONIZATION OF RYDBERG ATOMS

A variety of problems have resulted in the inability in
the present work to measure cross sections for the ioni-
zation of Rydberg atoms by electron impact. These problems
include 1) uncertainties in the measurement of ion signals,
2) questions concerning both the electron beam's uniformity
and its overlap with the Rydberg atoms, and 3) the presence
of ions made directly by the lasers.

(1) This is essentially an instrumentation problem
concerning both the electron multiplier and the LRS 3001
qVt unit. It is necessary that the ion detection system
have the capability to detect widely varying numbers of
ions while at the same time being very accurate. The
dynamic range of the system as a whole was found to be
somewhat limited. When detecting large numbers of ions
(measurement #5), the multiplier output charge spectrum
(equivalent to the pulse height spectrum) has an extended
tail on the high charge side. Since the LRS unit has a
maximum amount of charge per pulse that it can register,
this broad charge spectrum limits the gain voltage that can
be used on the multiplier. Under such a limitation it turns
out that for the small charge measurements (#7, #8, and
especially #6) the output charge of the multiplier is registered in only the first few channels of the MCA. This suggests that the charge output for small ion measurements may be too small to be registered and therefore is lost.\textsuperscript{1,2}

A second problem with the ion measurements concerns the non-linear input-output characteristics of the multiplier (Fig. 4-32). Although, as mentioned in Chapter IV, this non-linearity can be handled in principle if the functional dependence of the curves in Fig. 4-32 is known, it is much more desirable in practice for the curves to be linear. It should be noted that if corrections to the charge measurements due to the non-linear behavior need to be made, they have to be applied to the three largest measurements relative to the smallest charge measurement.

(2) As noted in Chapter IV, the electron beam profile taken under ion measurement conditions indicates that the

---

\textsuperscript{1} Observation of this effect was attempted when the input-output characteristics of the multiplier (Fig. 4-32) were measured by extending the measurements down to low nitrogen ion production. Any loss of charge would be displayed by a drop-off at the low end of the curves. As seen in Fig. 4-32, this is not observed.

\textsuperscript{2} It is possible to eliminate this problem by making the large charge measurements with one multiplier gain voltage and then increasing the voltage to make the small charge measurements. However, this requires a measurement of the relative multiplier gain between the voltages employed (as a function of ion input) and the use of such a quantity in the data analysis is undesirable.
beam is focused. The cross sectional shape of the beam at
the profiling flag is an oval, its long axis along the
horizontal direction. This implies astigmatic focusing.
The reason for such focusing is probably due to the presence
of the reverse bias field between Grids 2 and 3 which is
applied to nullify the penetration field coming from lower
regions of the grid assembly. This penetration field only
exists above the hole in the frame of Grid 3. At other
regions between Grids 2 and 3, such as where the electron
beam emerges from the gun housing and exits from the grid
assembly, the penetration field is zero but the bias field
still exists (see Fig. 4-3). This field points only in the
vertical direction and can therefore astigmatically focus
the beam. Such focusing causes concern about the uni-
formity of the beam.

The bias field can also deflect the beam and decrease
the beam's overlap with the Rydberg atoms. However, the
fact that the beam is in the correct position at the pro-
filing flag would indicate that either the deflection is not
great or it is counteracted by some oppositely directed
deflection. Since the beam is deflected downward by the
bias field, a counter-deflection could occur as the beam
passes over the hole in Grid 3 since the penetration field
is not completely cancelled out in the region below the interaction region.¹

(3) In measuring the ion signal as a function of time, it became clear that there was a component of the signal at $t = 0$ (when the laser fires). These ions exist when the electron beam is off and require the presence of both laser beams and the sodium beam for their production. It was mentioned in the last chapter that short wavelength fluorescence in the blue laser output could be responsible for photoionizing sodium 3p atoms. However, perhaps the sodium dimers in the sodium beam play a role in this ion formation.

¹The electron beam is found to be deflected upward if the reverse bias voltage is not applied while all other voltages remain on. This is presumably due to the penetration field.
REFERENCES

Abrines, R., I. C. Percival, and N. A. Valentine (1966),

Proc. Phys. Soc. 89, 515


Bailey, D. S., J. R. Hiskes, and A. C. Riviere (1965),

Nucl. Fusion 5, 41

Beigman, I. L., A. M. Urnov, and V. P. Shevel'ko (1970),

Sov. Phys. - JETP 31, 978

Beiting, E. J., G. F. Hildebrandt, F. G. Kellert, G. W.

Foltz, K. A. Smith, F. B. Dunning, and R. F. Stebbings

(1979), J. Chem. Phys. 70, 3551

Bethe, H. A. and E. E. Salpeter (1957), Quantum Mechanics


Cook, III, T. B. (1977), Ph.D. thesis, Rice University,

Houston, TX 77001

Damburg, R. J. and V. V. Kolosov (1976), J. Phys. B 9, 3149;


B 12, 2637


Deech, J. S., R. Luypaert, L. R. Pendrill, and G. W. Series


Devos, F., J. Boulmer, and J.-F. Delpech (1979), J. Physique 40, 215


Flannery, M. R. and K. J. McCann (to be published)


Kochee, C. and A. Smith (1977), Phys. Lett. 61A, 305
L. Marton, Vol. 4, Atomic and Electron Physics, Part A,
Atomic Sources and Detectors, eds. V. W. Hughes and
Littman, M. G., M. L. Zimmerman, T. W. Ducas, R. R. Freeman,
and D. Kleppner (1976a), Phys. Rev. Lett. 36, 788
Littman, M. G., M. L. Zimmerman, and D. Kleppner (1976b),
Phys. Rev. Lett. 37, 486
Soc. Japan 33, 1108
Olson, R. E. (1979), Phys. Rev. Lett. 43, 126
Omont, A. (1977), J. Physique 38, 1335
Prunelé, E. de and J. Pascale (1979), J. Phys. B 12, 2511
Shoshan, I., N. N. Danon, and U. P. Oppenheimer (1977), J. Appl. Phys. 48, 4495


Thomson, J. J. (1912), *Phil. Mag.* 23, 449


West, W. P. (1975), Ph.D. thesis, Rice University, Houston, TX 77001
