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The application of Rydberg atoms to the study of electron attachment at subthermal energies

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Rice University, 1989
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THE APPLICATION OF RYDBERG ATOMS TO THE STUDY OF ELECTRON ATTACHMENT AT SUBTHERMAL ENERGIES

by

RAVINDRA W. MARAWAR

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE MASTER OF ARTS.

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Abstract

The Application of Rydberg Atoms to the Study of Electron Attachment at Subthermal Energies.

By

Ravindra W. Marawar.

Low energy electron interactions with C₂Cl₄ and C₆F₆ molecules have been studied by using Rydberg atoms. It is observed that the electron attachment process occurs through various channels. Collisions of Rydberg atoms with C₂Cl₄ molecules result in the formation of Cl⁻ ions and C₂Cl₄⁻ ions. The data suggest the presence of the long lived C₂Cl₄⁻ ions and that the C₂Cl₄⁻ ions undergo rapid autodetachment forming an electron and a neutral C₂Cl₄ molecule. Similar reactions with the C₆F₆ molecules result in the formation of both long lived C₆F₆⁻ ions and short lived C₆F₆⁻ ions, that suffer rapid autodetachment forming an electron and a neutral molecule. The present data are compared with the previous data obtained by Swarm and Threshold Photoelectron Spectroscopy techniques.
ACKNOWLEDGEMENT

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I. Introduction

A. Purpose of the Research.

Subthermal energy electron attachment to neutral molecules has been a topic of considerable interest in the last few years. The intense research activity in this area has been stimulated by both fundamental and practical considerations\(^1\).

Fundamentally, electron-molecule interactions have provided basic knowledge on the properties of molecules and about the fates of the electronic excitation energy, charge transfer states and complexes formed in reactions. They have aided the understanding of chemical reactions, of the nature of the intermediates and of fast reactions in radiation chemistry\(^2\).

Much of the fundamental work stated above has applications in a wide range of areas such as chemical and electrical engineering, life and radiation sciences, atmospheric and environmental sciences.

The presence of free electrons contributes to the combustion processes which take place in flames. Compounds that reduce the concentration of free electrons through electron attachment are good flame retardants. Halons are the prime candidates because of their large electron attachment cross sections. These compounds are also used to suppress electrical breakdown in high voltage equipment where spurious electrons that might initiate a discharge are removed through attachment.
In gas lasers, the excited states in the gas are most commonly produced by e-beam or e-beam assisted gas discharge. Again the knowledge of electron capture cross sections has been fundamental in the development of Electronic Transition lasers, Vibrational excitation lasers and Excimer lasers².

In biosciences, the information about electron attachment interactions has found applications in the screening of toxic substances. This is expected to lead to an electron-capture-based 'toxicity index'. Cell biologists have observed that some molecules capture electrons from donor enzymes and release a negative ion in the cell plasma. The free ion may have an adverse effect on the cell's metabolism and may act as a carcinogen³. Electron attaching perfluorocarbons have also been used to trace the sources (SO₂ and NO₂) of acid rains in the United States and Canada⁴.

Thus, there is a considerable interest in the investigation of low energy electron attachment to molecules. There are certain difficulties though, in these investigations, especially involving the use of free electrons. A beam of thermal energy electrons is difficult to produce due to space charge effects: like charges in a beam repel each other and the beam rapidly diverges. Further, any stray electric field can rapidly change the kinetic energy of free electrons. Several free electron techniques such as Swarm and TPSA (Threshold Photoelectron Spectroscopy by Electron Attachment) have been developed each with its own advantages and disadvantages. In
our laboratory we use Rydberg atoms to study electron attachment at subthermal energies.

Rydberg atoms have one electron excited to a state of high principal quantum number \( n \). The excited electron moves in a large orbit around the central core of essentially unit charge. The separation between the ionic core and the excited electron is so large that, for sufficiently high values of \( n \) they can be treated as independent particles. The collisions between the target molecule and either the weakly bound Rydberg electron or the ionic core can then be treated independently.

Thus studies of collisions dominated by the electron-target interaction provide a means to study electron attachment and can provide information on electron capture processes at energies of 1-10 meV. This thesis reports use of K(nd) Rydberg atoms to investigate low energy Rydberg electron attachment to \( \text{C}_2\text{Cl}_4 \) and \( \text{C}_6\text{F}_6 \) molecules. Interaction of the Rydberg atoms with \( \text{C}_2\text{Cl}_4 \) results in the formation of \( \text{C}_2\text{Cl}_4^- \) and of \( \text{Cl}^- \) via the electron transfer reaction

\[
\text{K (nd)} + \text{C}_2\text{Cl}_4 \rightarrow \text{K}^+ + \text{C}_2\text{Cl}_4^- \quad \text{I.1}
\]

\[
\rightarrow \text{K}^+ + \text{C}_2\text{Cl}_3 + \text{Cl}^- \quad \text{I.2}
\]

K (nd) is a potassium Rydberg atom with principal quantum number \( n \) and angular momentum \( l = 2 \). Collisions of \( \text{C}_6\text{F}_6 \) molecules with the Rydberg atoms produce \( \text{C}_6\text{F}_6^- \) ions via the reaction

\[
\text{K (nd)} + \text{C}_6\text{F}_6 \rightarrow \text{K}^+ + \text{C}_6\text{F}_6^- \quad \text{I.3}
\]
The rate constants for the formation of the various negative ions were obtained. Direct free electron production was also observed, suggesting that collisions also populate short lived negative ions that undergo rapid autodetachment reverting to a neutral molecule and an electron. Rate constants for the formation of free electrons in such processes were obtained. The lifetimes of the long-lived negative ions were estimated.

To appreciate the wealth of information provided by collisions between Rydberg atoms and molecules, it is essential to review the important properties of Rydberg atoms.

B. Properties of Rydberg Atoms.

As stated earlier Rydberg atoms are obtained by exciting the outermost electron to a state of high principal quantum number. These atoms named after Swedish spectroscopist Johannes Rydberg, exhibit some unique properties. What makes them so special is...

1. their size. The mean atomic radius increases as \( n^2 \) and their geometrical cross section scales as \( n^4 \). There is evidence now that Rydberg atoms with 'n' as high as 600 exist in interstellar space. The size of such atoms is as large as a biological cell. Several other properties which follow are essential artifacts of the strikingly large size of Rydberg atoms.

2. the low binding energy of the Rydberg electron which scales as \( n^{-2} \). For ground state atoms, binding energies are a few eV whereas a Rydberg electron is typically bound by just a few meV.
3. Rydberg atoms are fragile and can be ionized by applying very small electric fields, especially as compared to the electric fields required to ionize a ground state atom. This provides a convenient means to detect high Rydberg atoms and to monitor their excited state distribution.

4. Their long lifetimes against radiative decay. Lifetimes scale approximately as \( n^3 \) for states of low \( l \). Rydberg atoms with lifetimes up to a few milliseconds can be produced in the laboratory. This is more than sufficient to permit the studies of collisions involving Rydberg atoms on a laboratory time scale.

Other important features of Rydberg atoms include closely spaced energy levels. The spacing between energy levels changes as \( n^{-3} \). Thus at high \( n \), even black body radiation can cause state changing or ionization. Also, one has to keep in mind that the electron orbiting around ion core has a very small rms velocity which is inversely proportional to \( n \).

The energy levels of a Rydberg atom are given by

\[
E_{n,l} = - \frac{1}{2(n-\delta l)^2}
\]

where \( \delta l \) is a quantity known as the quantum defect. It is a measure of the penetration and polarization of the ionic core by the Rydberg electron. The ion core, though small compared to the orbit of the electron, has finite size. At low \( l \), the Rydberg electron penetrates the core to a greater extent than at high \( l \). This makes the screening of the nuclear charge by core electrons less complete and thus leads
to a higher binding energy. Since the quantum defect depends on the properties of the core, it provides a qualitative measure how much any Rydberg state differs from the corresponding state of the hydrogen atom.

The quantum defect values for high n states of potassium are as follows:

<table>
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<th>l</th>
<th>δl</th>
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<tr>
<td>s (l=0)</td>
<td>2.180</td>
</tr>
<tr>
<td>p(l=1)</td>
<td>1.712</td>
</tr>
<tr>
<td>d(l=2)</td>
<td>0.277</td>
</tr>
<tr>
<td>f(l=3)</td>
<td>0.010</td>
</tr>
</tbody>
</table>

As indicated in the above table, the quantum defect is only sizable for the penetrating s,p,d states. At high l, not the core penetration but core polarization is more significant. There is a very weak n dependence in quantum defect.

C. Interaction of Rydberg atoms with molecules:

Rydberg atoms react with molecules in a variety of different ways. Collisions between a Rydberg atom and a neutral molecule can be discussed using an independent particle model. At high n, the radius of a Rydberg electron's orbit is larger than the effective range of interaction between a charged particle and a molecule. Thus when a high Rydberg atom interacts with a molecule, the electron and the ion core act as independent scatterers. In most collisions involving attachment of the Rydberg electron to molecules, the ion
core acts as a spectator and the Rydberg electron interacts with the target molecule much as would a free electron of same energy. The idea that the Rydberg electron interacts with a neutral species as if it were 'free' is due to Fermi and is known as the 'free electron model' \textsuperscript{5,7}.

With this review, we are now ready to study the various reactions involving high Rydberg atoms which are classified according to end products. \(X(nl)\) indicates a Rydberg atom with principal quantum number \(n\) and angular momentum \(l\). \(AB\) denotes the target gas molecules.


In state-changing collisions, interactions between the Rydberg atom and neutral molecule lead to changes in the quantum state of the Rydberg atom. They are further classified as

1. \(i\)-changing collisions:

These are typified by the reaction,

\[
X (nl) + AB (J) \rightarrow X (nl') + AB (J)
\]

These quasi-elastic collisions result primarily from the Rydberg electron-target interaction. The small changes in internal energy of the high Rydberg atom are provided by the translational kinetic energy of the colliding partners. Collisions normally populate higher \(l\) states with longer lifetimes.
2. n-changing collisions:
These are of the type,
\[ X \,(nl) + AB \,(J) \rightarrow X \,(n' > nl') + AB \,(J' < J) \]  
and result from rotational energy transfer from the molecule to excite Rydberg electron to a higher n state. Again the Rydberg electron plays a major role in energy transfer, usually from a rotational inelastic electron-target collision. The reverse type of reactions are also possible in which the molecule is excited to a higher rotational energy state and the Rydberg electron loses energy being deexcited. Ionization may occur if the energy transfer from the molecule to the Rydberg atom is sufficiently large. Such collisional ionization can be written as
\[ X \,(nl) + AB \rightarrow X^+ + AB + e \]  

C.2. Core Ion Interactions:
In these reactions, typified by associative ionization of the type,
\[ X \,(nl) + AB \rightarrow XAB^+ + e \]  
the primary interaction is between the core ion and the target. The positive ion formed XAB+ in the two body X+- AB reaction is unstable and needs to get rid of some energy for stabilization. Energy transfer to the Rydberg electron results in ionization and in stabilization of the XAB+ ions.

C.3. Electron Transfer Collisions:
In these reactions, the electron is transferred to a molecule forming a negative ion resulting in reaction of the type
\[ X \,(nl) + AB \rightarrow X^+ + AB^- \]  
The negative ion so formed is unstable and may undergo
subsequent autodetachment

\[ AB^-* \rightarrow AB + e \quad \text{I.10} \]

or even dissociate unless stabilized by subsequent collisions leading to dissociative electron attachment reactions of the type

\[ X (nl) + AB \rightarrow X^+ + AB^-* \rightarrow X^+ + A^- + B. \quad \text{I.11} \]

Electron transfer from Rydberg atoms to molecules has been studied theoretically by Matsuzawa using the independent particle model to draw parallels between the Rydberg electron transfer at thermal energies and free electron capture i.e. the process

\[ e + AB \rightarrow AB^- \quad \text{I.12} \]

Matsuzawa argues that at high \( n \) the Rydberg electron can be treated as an essentially free electron. The reaction is viewed in terms of the electron-target interaction and the interaction between the ionic core and the target molecule is neglected. It is assumed that the collisions take place impulsively i.e. over a short period of time compared to the period of the electronic motion. According to the impulse approximation, the electron-core coulomb interaction remains constant over the collision time and does not contribute to momentum transfer. On the basis of this model, Matsuzawa showed that the rate constant for Rydberg electron attachment to the target molecule is equal to the rate constant for the capture of free electrons having the same velocity distribution as that of a Rydberg electron.
A similar treatment can be used to show that the rate constant for the dissociative Rydberg electron attachment\textsuperscript{9} is equal to the rate constant for dissociative free electron capture,

\[ e + AB \rightarrow AB^- \rightarrow A^- + B \quad \text{I.13} \]

provided that the velocity distribution of free electrons is the same as that of the Rydberg electron.

The lifetimes of the negative ions thus formed via reaction (I.9) depend on the nature of the negative ion. To facilitate the understanding of the formation and decay of negative ions we will briefly discuss their properties in the next section.

\textbf{D. Negative Ion Resonances:}

An electron is said to be attached to a molecule if it is 'retained' by the molecule for a time long compared to the time it takes to traverse the molecule. The molecular complex is then said to be in a resonant, metastable state which can subsequently decay by either emitting the acquired electron or dissociating into fragments. The lifetime '\( \tau \)' of this resonance is dependent on electron energy. These resonances have been classified by Bardsley and Mandl\textsuperscript{10} as follows.

\textbf{D.1. Shape Resonance:} Consider a system consisting of a projectile electron and a target molecule. A typical potential energy curve which can cause the shape resonance is illustrated in the figure 1.
FIGURE 1

A typical potential that can support a shape resonance. The region of effective barrier extends between $r_1$ and $r_2$.

FIGURE 2

Feshbach resonance occurs when excited vibrational level of the $AB^-$ ion lies above the ground state of the molecule $AB$. 
The repulsive barrier is provided by centrifugal force due to the orbital angular momentum of colliding particles. If an electron enters the potential well created by the barrier, it will be trapped there unless it can tunnel through the repulsive barrier or the molecule may dissociate if energetically possible. This type of transient negative ion formation is termed a shape resonance. The lifetimes of these resonances range from $10^{-15}$ to $10^{-10}$ seconds$^{11}$.

2. The Feshbach resonance: This resonance occurs when the incident electron loses energy in exciting the target molecule and thus does not have enough energy to escape. The electron has to reabsorb energy before it can be emitted from the molecule. There are two different types of Feshbach resonances. If the incident energy of the electron is used for the excitation of the electronic motion of the molecule, then it is called an electron excited Feshbach resonance. If the kinetic energy of the incident electron is absorbed mostly into the nuclear motion then the resonance is called a nuclear excited Feshbach resonance. The nuclear excited Feshbach resonance frequently occurs in a collision involving complex polyatomic molecules and low energy (< 1 ev) electrons$^{11}$. The lifetimes of these resonances are of the order of microseconds to milliseconds.

The nuclear excited Feshbach resonance has been observed in many electron attachment reactions. A Typical potential energy diagram for a molecule AB and its negative ion AB$^-$ is shown in Figure 2. The ground vibrational state of molecule AB$^-$ is a bound
state and a free electron of energy $\mathcal{E}$ is captured into an excited vibrational state. This state subsequently can decay when the electron recovers the energy $\mathcal{E}$ and the target molecule reverts to its original ground state.

E. Techniques to study Electron Attachment.

Apart from Rydberg atom collision studies, two other techniques are commonly used for investigating electron attachment processes at subthermal energies.

1. Electron Swarm Method\textsuperscript{12}.

2. Threshold Photoelectron Spectroscopy by Electron Attachment (TPSA)\textsuperscript{13}.

E.1. Electron Swarm method: In the electron swarm method, electrons are produced by either photoionization, particle ionization or thermionic emission in the presence of a buffer gas at high pressure. These electrons then travel under the influence of an applied electric field $E$ through a buffer gas at a pressure $P$ and attain an equilibrium energy distribution. The distribution of electron energies is characterized by a distribution function $f(\mathcal{E}, E/P)$ where $\mathcal{E}$ is the electron energy and the quantity $E/P$ is the 'pressure reduced electric field'. $f(\mathcal{E}, E/P) \, d\mathcal{E}$ gives the number of electrons in the energy range $d\mathcal{E}$ about $\mathcal{E}$. If an attaching gas is then added to the buffer gas in small quantities, the energy distribution is still characteristic of the buffer gas alone. The attachment coefficient $\alpha(E/P)$, which is the probability of capture per centimeter travelled in the field direction per torr of attaching gas and $\Omega(E/P)$, the
electron swarm drift velocity are measured. Their product gives the absolute rate of electron capture. The attachment rate $\alpha \omega$ and the electron attachment cross section $\sigma$ are related by,

$$\alpha(E/P) \times \omega(E/P) = N \int_0^\infty \sigma(v) f(v, E/P) \, dv \quad \text{I.14}$$

where $N$ is the number of attaching gas molecules per torr and $v$ is the velocity corresponding to energy $E$ of the electron. Thus the swarm method determines absolute total electron attachment cross sections but fails to identify the different channels by which attachment occurs. Also these experiments measure quantities over a large distribution of velocities and it is difficult to deconvolute the data to obtain $\sigma(v)$.

**E.2: Threshold Photoelectron Spectroscopy by Electron Attachment:** In this technique free low energy electrons are produced by near threshold photoionization of Krypton atoms in the presence of target gas. These free electrons attach to target gas molecules in a field free region. The attachment products may correspond to one or several attachment or dissociative attachment channels. The product ions are then extracted, mass analyzed and the ion signal is recorded as a function of photoelectron energy. The energy resolution in these experiments is 5-8 meV. The absolute cross sections are then obtained by normalization to the thermal attachment rate constant as measured in swarm experiments (under multiple collision conditions). This procedure sometimes may lead
to a systematic error. In certain electron attachment reactions, a fraction of the product negative molecular ions undergo rapid autodetachment. This typically happens under single collision conditions where stabilization due to further collisions is not possible. In Swarm type techniques (multiple collisions) energy transfer to buffer gas molecules can stabilize 'short lived' ions before autodetachment occurs. Thus swarm and TPSA cross sections may not correspond to the same reaction channels. Another limitation is that even a very small field in the interaction region can easily perturb the energy of the electrons and cause another systematic error in the measurement.
II. Experimental Investigation:

The apparatus used for experimental investigation of collisions between Rydberg atoms and molecules is shown schematically in figure 3. Briefly, an effusive beam of ground state potassium atoms is produced in an alkali oven. The ground state alkali atoms are then optically excited to a high Rydberg state in a field free region in the presence of a target gas. After a specified interaction time, a time of flight mass spectrometer (TOFMS) is used to extract and identify the product ions. The selective field ionization (SFI) technique is used for Rydberg state determination and lifetime measurements. The apparatus and the experimental techniques are described in this chapter.

A.1: Vacuum System: The vacuum system consists of two differentially pumped chambers, one of which contains the total ion collector (TIC) and the other alkali oven. A base pressure of $5 \times 10^{-8}$ Torr is maintained inside the TIC chamber.

The reactant gases are admitted to the main experimental chamber (that contains the TIC) through an inlet manifold. The inlet lines are heated and gases pass through a sintered plug to dissociate any dimers that might otherwise enter the chamber. The target gas pressure inside the chamber is measured using a Bayard-Alpert type thermionic ionization gauge. Such gauges have different sensitivities for different gases and hence must be calibrated against some absolute pressure gauge. This calibration is done with the help of a diaphragm type capacitance manometer. The diaphragm forms
FIGURE 3

Schematic diagram of the apparatus shows that the laser beam perpendicularly intersects the alkali atom beam producing Rydberg atoms. Time of flight mass spectrometers which consist of a drift region and a multiplier are used to detect and identify the negative ions.
one plate of a capacitor. A change in the diaphragm position due to a change in pressure changes the capacitance which is then detected with the help of a sensitive bridge. The ion gauge is calibrated in the 1-10 *10^-5 torr range. This calibration is assumed to be valid at the target gas pressures used in the experiment i.e. 10^-6 torr range. This is a possible source of systematic error in our experiment. Partial pressures of residual gases in the chamber are determined by a quadrupole type Residual Gas Analyzer.

A.2 Alkali Oven: Alkali metals have been very commonly used in Rydberg atom research. They are an obvious choice because of their simple ground state configuration which consists of an outermost shell with one 'ns' electron surrounding a rare gas type core. Also the amount of energy (4-5eV) required for exciting alkali atoms to high Rydberg states via one or multiphoton absorption is in the range of commercially available tunable dye lasers.

In the present investigation we used potassium with a ground state configuration of

\[ 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^1 \]

It occurs in two isotopic forms, with masses 39 and 41. The melting point of potassium is 63.3 °C and the boiling point is 760 °C. The major impurities in commercially available potassium are Na, Rb, Ca and Fe (all less than 100 ppm).
The present two stage oven has a reservoir ('body') where potassium is heated to about 300 °C. At this temperature the vapor pressure is enough to form an effusive beam that exits an aperture in the 'nose'. The beam is then collimated by another aperture and the cross section of the beam at the interaction region (IR) is about 0.5 x 0.3 cm². The beam density is measured with the help of a hot wire detector. Under normal operating conditions the number density of potassium atoms in the beam is about 3 x 10⁸ cm⁻³ in the IR¹⁴.

A.3 Laser System: Optical excitation is one of the most accurate and convenient means of producing state selected Rydberg atoms. The advent of tunable dye lasers in the mid-seventies greatly stimulated research activity in the field of Rydberg atoms. The present laser system consists of an ion-laser-pumped dye laser. The pump laser is a Coherent - Innova UV20, argon ion laser. It is a fixed frequency laser which outputs about 10 Watts at 514.5 nm. Radiation from this laser then excites molecules of the organic dye (Rhodamine 6G) used in the dye laser. These molecules decay by emitting radiation in the yellow-red region of the spectrum. The range of wavelength for this particular dye is between 570 and 605 nm. Typical output power, which depends on frequency, is about 1 Watt. The maximum power is obtained at 580 nm.

The Coherent 699 ring dye laser is an actively stabilized, single frequency laser. By electronically locking the laser frequency to an external temperature controlled reference interferometer,
frequency drift is minimized. Compensation for high frequency jitter is done by a 'tweeter' mirror mounted on a piezo-electric crystal. Low frequency drift is compensated by a galvo driven quartz plate called the 'Brewster plate'. This electronic control results in a line width of only 250 KHz and long term frequency drift of about 50 MHz/hr.

There are three different tuning elements in this laser. A birefringent filter is used for coarse tuning. Finer tuning is accomplished by a thin etalon (FSR 225 GHz) and a thick etalon (FSR 10 GHz). For continuous manual or computer controlled scanning over 30 GHz, the angle of the Brewster plate is changed. This alters the optical length of the laser cavity which in turn resonates at a different frequency.

The continuous wave output of the dye laser is changed to short pulses (1-5 µsec) of definite time duration for the present experiments. An Electro-Optic Modulator (EOM) coupled with a linear polarizer is used. By controlling the 'ON' and 'OFF' times of a switching transistor, the pulse duration and frequency can be adjusted over a wide range. The laser beam is then guided and focussed into the interaction region. There it crosses the ground state potassium atom beam. In the IR the laser beam waist is about 7µm and the photon density is sufficient to achieve multiphoton excitation. By simultaneous absorption of two photons, Rydberg atoms are produced. Using Rhodamine 6G dye, the laser is capable
of exciting potassium atoms to states with values of \( n = 7 \) and above. The selection rule for two photon excitation require that \( l = 0, +2 \). This implies that the excited state configuration is either \( ns (j = 1/2) \) or \( nd (j = 3/2, 5/2) \).

A.4 Total Ion Collector (TIC) : The time evolution of the Rydberg atom population and the growth of the product ion signal formed in collisions is monitored using the TIC. It essentially consists of two time of flight mass spectrometers (TOFMS) which can be used for the identification of the positively and negatively charged ions formed in the interaction region. Details are shown in figure 4.

The IR is bound by two parallel fine mesh (70 lines per inch) grids. Voltages applied on these grids determine the direction in which the ions will travel and their initial acceleration. Upon leaving the IR, the ions enter a drift region. This region is a metal tube and has electrically connected grids at each end. This field free region serves to distinguish masses of ions according to their flight times. After traversing the drift region the ions are detected by a Johnston MM-1 particle multiplier. These are focussed mesh type 20 stage particle detectors. When an ion or an electron strikes the first dynode, secondary electrons are emitted. These secondary electrons then impact on the next dynode. The cascade of electrons finally reaches the anode resulting in an output pulse. The normal potential difference between the first dynode and the back plate is 5kV. The gain of these multipliers, which is typically \( 10^6 \) to \( 10^8 \) and
FIGURE 4

SIDE VIEW OF THE TOTAL ION COLLECTOR (TIC)

FLANGE

MM-1

INCHES   CMS

0.43   1.09

TOP DRIFT

4.77   12.11

INTERACTION REGION

1.04   2.64

0.4   1.02

0.79   2.01

BOTTOM DRIFT

2.005   5.09

0.3   0.8

NOT TO SCALE.
may drop with use. Thus they are regularly reactivated. Also they are routinely checked for saturation.

A.5 Electronics: The first task is to amplify and discriminate the pulses received from the particle multiplier. A LeCroy MVL 100 amplifier and discriminator is used for this purpose. The threshold discriminator voltage can be set with the help of a trimmer potentiometer. This makes it quite convenient to filter noise and do troubleshooting.

In our experiments it is very important to know and catalog the arrival times of the observed ions. This is achieved by using time to digital converters (TDC). This device converts arrival times of ions into a number to be read by the computer. Depending upon the desired resolution and the time intervals, one of the three different TDCs is used:
1. Elapsed Time Counter (ETC): Span 500 μsec, resolution 100 nsec.
3. Multi Channel Analyser (MCA): Operated in Time mode, it can be used as a TDC. Span 1μsec, resolution 1nsec.

Data acquisition and analysis was accomplished with the help of a DEC LSI 11/23 computer. It was interfaced with the TDCs via a CAMAC (Computer Automated Measurement And Control) bus.
B. Experimental Techniques:

The apparatus described in the previous sections of this chapter enables us to carry out different types of investigations. We can determine the rate constants for several types of Rydberg atom-molecule reactions, the effective lifetimes of Rydberg atoms and can obtain information on the lifetimes of negative molecular ions. The techniques used to accomplish this will be described in detail in this section.

Every data acquisition session starts by tuning the laser to excite a selected Rydberg state. The laser is tuned to a desired wavelength by use of a Fizeau wavemeter. This instrument is accurate to about 1 ppm\textsuperscript{16}. The laser linewidth permits us to selectively excite potassium atoms in 'ns' or 'nd' states up to a value of $n>100$. Rydberg atom production as a function of frequency is shown in figure 5 over a small frequency range in the vicinity of K(9d). The fine structure splitting due to spin-orbit coupling together with hyperfine splitting resulting from the interaction between total electron angular momentum and nuclear angular momentum of the ground state is displayed. The isotope shift is due to the two different isotopic masses of potassium.

B.1 Time Of Flight Mass Spectrometry: This technique identifies ionic products formed after some specified collision times in Rydberg atom-molecule collisions. A negative voltage pulse is applied to the top grid to push any ion formed in the IR towards the bottom drift region. Ions are accelerated as they enter the drift
Scanning of 9D states of potassium.
region. Once inside the drift region they do not experience any electric field. By increasing the flight times, the drift region helps to separate different ions according to their masses. At the end of drift region they are again accelerated so that their impact on first dynode will cause secondary electron emission. The voltages on the various components of spectrometer are adjusted to provide temporal focusing for ions so that all ions of the same mass arrive at the same time irrespective of the initial position within the IR when the extraction pulse was applied. Detailed flight time calculations for the same spectrometer have been published earlier\textsuperscript{17}.

The QET records the arrival times of the different ions. This signal versus flight time data needs to be converted to signal as a function of mass. This is accomplished by fitting a \textit{n}th order polynomial to calculated flight times.

Under the typical operating conditions the laser pulse lasts about 3 $\mu$sec and the interaction time of Rydberg atoms with target gas molecules is between 3$\mu$sec to 10 $\mu$sec. The extraction pulse -160 V is applied to the top grid of the IR. At the same time the QET starts counting time. The drift region is biased at + 325 V and the first dynode is operated at 2700 V. Ion impact causes secondary electron emission and the output pulse from the MM-1 finally stops the QET. Normal repetition rates for these experiments are about 15 KHz.
It should be realized that the TDC can register only one event in one time cycle. Thus if more than one negative ion is formed in a cycle then we may miss some signal. Calculations involving the velocity and the number density of ground state potassium atoms in the IR and the photon density at the point of intersection, have shown that much less than one Rydberg atom is created for every laser pulse. Thus chances of production of more than one negative ion in a cycle are negligible.

B.2 Selective Field Ionization (SFI): In field ionization an electron is stripped from an atom by the application of an electric field. Since Rydberg atoms in different 'n' and 'l' states ionize at different field strengths, measure of field at which field ionization occurs provides a means to study the excited state distribution of Rydberg atoms. This makes SFI a very effective tool for determining state distributions and their time development in Rydberg atom collision studies\textsuperscript{18,19}. The process of ionization in alkali atoms is qualitatively understood as follows.

When an atom is placed in an electric field, its energy levels are split into different Stark states. In the case of alkali atoms there are nonhydrogenic terms in the Hamiltonian due to core penetration and the spin orbit effect. These terms couple states of the same $m_1$ resulting in the appearance of avoided crossings where states of the same $m_1$ from different manifolds approach one another. (See fig 6)
Stark manifolds for m=0, 8 < n < 11. The dashed line path represent adiabatic passage, while the heavy solid curve corresponds to diabatic passage.
Each avoided crossing is traversed either adiabatically or
diabatically depending on the slew rate of the applied electric field
and energy gap at the crossing. If the energy gap at the avoided
crossing is large and slew rate of the electric field is small then the
state will traverse the gap primarily adiabatically. In this event the
state changes its character at every avoided crossing until the atom
is ionized at an electric field very close to that expected classically.
In potassium states with $m_l < 4$ ionize predominantly adiabatically.

If an atom is initially in a high $m_l$ state, the gaps at the avoided
crossing are small and avoided crossings are typically traversed
diabatically. Fast slew rates and high $m_l$ values are prerequisites for
diabatic ionization. Field required for diabatic ionization is roughly
twice as much as adiabatic ionization. In hydrogen, as one would
expect, Stark states of same $m_l$ cross each other and ionization is
purely diabatic. In an SFI experiment a negative going ramp is
applied to a grid of the IR. At the same time the MCA is triggered.
The SFI pulse rises from 0 to 2000 V in approximately 1 μsec
corresponding to a slew rate of $2 \times 10^9$ V/cm-sec. This pulse is
capable of ionizing Rydberg atoms with principal quantum numbers
as low as 22. When the Rydberg atom in the IR is ionized, the
electron is accelerated directly towards the multiplier. The output
pulse from the MM1 is then used to stop the MCA. The MCA shows
the field ionized signal as a function of time. To determine the
excited state distribution, we must have data in the form of signal as
a function of ionizing electric field. The time dependence of the
voltage pulse is determined by a ramp digitizer\textsuperscript{20}. Our main purpose of using this technique though, was to obtain the rate constants for ionization of Rydberg atoms by a target gas. We also checked for $n$-changing and $l$-changing of the Rydberg state due to collisions. To obtain these rate constants, experiments were performed in which the time development of Rydberg atom population was measured with and without target gas. Comparison of the two time developments yielded the rate constants. Analysis of SFI data will be described in the next chapter.

B.3 DC Bias Experiment: These experiments are carried out to measure the rate constants for the formation of free electrons in Rydberg atom-molecule collisions. A small DC electric field (2V/cm) was applied in the IR to direct electrons towards the multiplier as soon as they were formed. The drift region was maintained at a few tens of volts. As the flight times of electrons to the multiplier are much shorter than those of product negative ions, these signals can be separated.

The small drift region voltage combined with low extraction field in the IR makes the ion flight times quite long. The ETC was therefore used for recording the flight times of different ions. Figure 7 displays a typical arrival time spectrum obtained with C\textsubscript{2}Cl\textsubscript{4} as the target gas. The early time signal corresponds to the arrival of free electrons that may have contributions from several sources like
Production of free electrons, Cl\(^-\) ions and C\(_2\)Cl\(_4\)\(^-\) ions is observed when potassium high Rydberg atoms collide with C\(_2\)Cl\(_4\) molecules. The flight times of the negative ions are much longer as compared to those of electrons and thus arrive much later at the multiplier.
autodetachment of short lived negative ions, black body or laser radiation induced photoionization and collisional ionization with background or the target gas. The two peaks which follow are due to arrival of Cl\(^-\) and C\(_2\)Cl\(_4\)\(^-\) ions respectively. This experiment is carried out with and without target gas. The electron signal due to the presence of target gas is obtained by subtracting the latter from the former. Details of the analysis are given in the next chapter.

One unusual feature of the DC bias method is the presence of the electric field at the time of excitation of the Rydberg atoms. The obvious concern is, how much does the electric field affect the Rydberg state excitation? It has been observed that even at high n (say, n=60) there is not a major Stark shift in the Rydberg state, at a field of 2V/cm. Thus conclusions drawn from these experiments will be characteristic of those corresponding to zero bias.

Before we proceed to discuss experimental results, we mention a few precautions that always need be taken in Rydberg collision experiments. Collisions with target gas can lead to rapid mixing of the original Rydberg state. Thus even if we may excite single Rydberg state, collisions can result in a complex, time dependent population distribution in the IR. Hence the rate constants characteristic of a particular Rydberg state can only be obtained by limiting target gas densities (<10\(^{11}\) cm\(^{-3}\)) to ensure that only a small percentage of the parent population undergoes state changing during the time of the experiment.
III. Data Analysis and Results:

Time Of Flight Mass Spectrometry (TOFMS), Selective Field Ionization (SFI) and DC bias techniques are used to measure different parameters and investigate varying aspects of Rydberg atom-molecule collisions. In this chapter we will first elaborate upon the measurement procedures. Quantitative results will be presented later.

A.1 Analysis of the SFI data: In an SFI experiment the rate constants for collisional ionization and state changing collisions are obtained by monitoring the time development of the Rydberg atom population in the IR. If $N(t)$ is the total number of Rydberg atoms in the IR at time $t$ after excitation, then,

$$N(t) = N(0) \exp\left(-\frac{t}{\tau}\right)$$  \hspace{1cm} \text{III.1}

where $N(0)$ is the number of Rydberg atoms initially excited which depends on laser power, focus and mode, alkali beam density and principal quantum number $n$. $\tau$ is the lifetime of the Rydberg state in the presence of target gas. The time evolution of the Rydberg population is influenced by the electron attachment to the target gas, spontaneous decay, state changing collisions, laser or blackbody induced photoionization and other black body radiation stimulated processes. We can isolate the effect of electron attachment by writing $\tau$ as,

$$\frac{1}{\tau} = \rho k_i + \frac{1}{\tau_{\text{eff}}}$$  \hspace{1cm} \text{III.2}

where $\rho$ is the number density of the target gas molecules.
$k_i$ is the total rate constant for ionization of Rydberg atoms due to the presence of a target gas and $\tau_{\text{eff}}$ represents the lifetime due to the processes other than electron attachment. $\tau_{\text{eff}}$ is determined in a subsidiary SFI experiment in which target gas is allowed into the chamber ($\rho = 0$). Thus by measuring $\tau$ and $\tau_{\text{eff}}$, one can obtain the rate constants for total collisional ionization $k_i$ in the presence of target gas. The SFI data can also be analyzed to obtain the rate constants for 'n-changing' and 'l-changing' collisions of Rydberg atoms. The n and l state of a Rydberg atom can be inferred from knowledge of the electric field required to ionize the atom. Thus the electron signal from n and l changed Rydberg states can be separated from that due to the parent (initial) state. Comparison of the data obtained with and without target gas can be used to obtain rate constants for state changing collisions.

A2. Analysis of TOFMS Data: The reactions studied during the course of this work were,

$$K(\text{nd}) + C_2\text{Cl}_4 \rightarrow K^+ + C_2\text{Cl}_4^- \quad \text{III.3}$$

$$\rightarrow \quad K^+ + \text{Cl}^- + C_2\text{Cl}_3$$

$$K(\text{nd}) + C_6\text{F}_6 \rightarrow K^+ + C_6\text{F}_6^- \quad \text{III.4}$$

Product ions formed in these reactions were identified and measured by TOFMS. The number of product ions formed at time t, $N_{\text{AB}}(t)$ is given by,
\[ N_{AB}^- (t) = N(0) \rho \ k_{AB}^- \ \tau (1- \exp(-t/\tau)) \]  

where \( k_{AB}^- \) is the rate constant of formation of negative ions \( \text{AB}^- \), \( \rho \) is the target gas number density, \( N(0) \) is the number of Rydberg atoms initially excited and \( \tau \) is the lifetime of the Rydberg state. For \( n>20 \), \( N(0) \) can be determined directly by SFI, but at lower \( n \), SFI cannot be performed because of the large electric field required to ionize the Rydberg atoms. If we measure the ratio of number of product ions formed by collisions with the target gas of interest relative to the number of product ions formed by collisions with a second target gas, whose rate constant for collisional ionization are previously known, then determination of \( N(0) \) is not necessary. This is the basis of the 'Mixed Gas Ratio Technique'. A small amount of \( \text{SF}_6 \) is allowed into the chamber along with target gas \( \text{AB} \). \( \text{SF}_6 \) attaches Rydberg electrons via the reaction,

\[ K(\text{nd}) + \text{SF}_6 \rightarrow K^+ + \text{SF}_6^- \]

Absolute rate constants for this reaction have been previously determined in this laboratory\(^{21} \). Measurement of the ratio \( \frac{N_{AB}^-}{N_{\text{SF}_6^-}} \)-normalized to equal target gas densities gives absolute rate constants for electron attachment to the target molecule \( \text{AB} \), as follows,

\[ \frac{N_{AB}^-}{N_{\text{SF}_6^-}} = \frac{k_{AB}^-}{k_{\text{SF}_6^-}} \rho_{\text{AB}^-} \eta_{\text{AB}^-} \]
where \( k \) denotes the rate of formation of respective negative ions,
\( \rho \) denotes the number density of respective target and
\( \eta \) denotes the multiplier detection efficiency of the ions.

As mentioned previously, the sensitivity of an ionization gauge is different for different gases. Thus the absolute target gas pressure must be obtained by calibrating the ionization gauge against a capacitance manometer for every different gas used in the experiment. The number density \( \rho \) can then be obtained by multiplying the ion gauge indicated pressure by an absolute sensitivity factor for that gas.

In this experiment it was found that under normal operating conditions \( \text{Cl}^- \) ions were detected 15% more efficiently than \( \text{SF}_6^- \) ions. Considering the similar masses of \( \text{C}_2\text{Cl}_4^- \) and \( \text{SF}_6^- \) ions, the relative efficiencies for these two ions are taken to be equal. The internal self consistencies within the data will later prove the correctness of this assumption.

A.3 DC Bias Data Analysis: This experiment determines the rate constants for the formation of free electrons in Rydberg atom molecule interactions. As described in the previous chapter free electrons are separated from the product ions with a combination of small extraction voltage and small drift region voltage. To obtain the desired free electron signal the contribution due to photoionized electrons is subtracted by performing an experiment without the presence of target gas under identical conditions. The number of
free electrons formed due to collision with target gas molecules in time $t$, can be written as

$$N_e(t) = N(0) \rho k_e \tau(1 - \exp(-t/\tau))$$  \hspace{1cm} \text{III.8}$$

where $\rho$ is the number gas density of the target gas molecules, $N(0)$ is the number of Rydberg atoms initially excited and $\tau$, the lifetime of the Rydberg state is obtained from an SFI experiment performed under similar conditions. Thus $k_e$, the rate of formation of free electrons can be obtained.

B. Rydberg Electron Attachment to C$_2$Cl$_4$.

The collisions of Rydberg atoms with C$_2$Cl$_4$ result in the formation of long lived C$_2$Cl$_4$\(^-\), dissociatively produced Cl\(^-\) and free electrons$^{22}$. The rates of formation of long lived C$_2$Cl$_4$\(^-\) and Cl\(^-\) ions were obtained using the mixed gas technique described earlier. The investigations were carried out for principal quantum numbers $n$, in the range 12 to 100. The ratios $N_{C_2Cl_4^-}/N_{SF_6^-}$ and $N_{Cl^-}/N_{SF_6^-}$ normalized to equal gas densities are presented in Table III.1. It also includes the rate constants $k_{C_2Cl_4^-}$ and $k_{Cl^-}$ for the formation of negative ions, calculated from the ratios and the known rate constants of SF$_6^-$ formation.

To test for systematic errors, the target gas number density was varied and no pressure dependence was observed in these ratios. Product ions were extracted from the IR at three different times, up to 8 $\mu$sec after excitation. SF$_6^-$ is known to have lifetimes
TABLE III.1

Rate Constants for the formation of negative ions $\text{Cl}^{-}$ and $\text{C}_2\text{Cl}_4^{-}$

<table>
<thead>
<tr>
<th>n</th>
<th>$R_{\text{Cl}^-}$</th>
<th>$R_{\text{C}_2\text{Cl}_4^-}$</th>
<th>$k_{\text{Cl}^-} \times 10^{-8}$</th>
<th>$k_{\text{C}_2\text{Cl}_4^-} \times 10^{-8}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.07</td>
<td>0.31</td>
<td>0.3</td>
<td>1.2</td>
</tr>
<tr>
<td>14</td>
<td>0.1</td>
<td>0.24</td>
<td>0.8</td>
<td>1.9</td>
</tr>
<tr>
<td>16</td>
<td>0.13</td>
<td>0.24</td>
<td>1.8</td>
<td>3.4</td>
</tr>
<tr>
<td>20</td>
<td>0.16</td>
<td>0.23</td>
<td>4.3</td>
<td>6.2</td>
</tr>
<tr>
<td>25</td>
<td>0.21</td>
<td>0.28</td>
<td>7.1</td>
<td>9.2</td>
</tr>
<tr>
<td>28</td>
<td>0.21</td>
<td>0.27</td>
<td>7.9</td>
<td>10.4</td>
</tr>
<tr>
<td>30</td>
<td>0.22</td>
<td>0.28</td>
<td>8.5</td>
<td>11.1</td>
</tr>
<tr>
<td>32</td>
<td>0.2</td>
<td>0.22</td>
<td>8.1</td>
<td>8.7</td>
</tr>
<tr>
<td>35</td>
<td>0.2</td>
<td>0.22</td>
<td>7.9</td>
<td>8.7</td>
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<td>0.16</td>
<td>0.19</td>
<td>6.5</td>
<td>7.4</td>
</tr>
<tr>
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<td>0.15</td>
<td>0.17</td>
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</tr>
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<td>0.16</td>
<td>6.1</td>
<td>6.3</td>
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<td>45</td>
<td>0.14</td>
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<td>6.0</td>
<td>5.2</td>
</tr>
<tr>
<td>60</td>
<td>0.14</td>
<td>0.13</td>
<td>5.7</td>
<td>5.1</td>
</tr>
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<td>5.2</td>
</tr>
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<td>80</td>
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<td>6.0</td>
<td>5.4</td>
</tr>
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<td>0.15</td>
<td>0.16</td>
<td>5.8</td>
<td>6.5</td>
</tr>
<tr>
<td>100</td>
<td>0.14</td>
<td>0.14</td>
<td>5.5</td>
<td>5.6</td>
</tr>
</tbody>
</table>

$n =$ Principal quantum number of the Rydberg atom

$R =$ Pressure normalized ratios $N_{\text{Cl}^-}/N_{\text{SF}_6^-}$ and $N_{\text{C}_2\text{Cl}_4^-}/N_{\text{SF}_6^-}$

$k =$ Rate of formation of a negative ion. Units are $\text{cm}^3\text{sec}^{-1}$. 
FIGURE 8

Rate constants $k(C_2Cl_4^-)$ (○) and $k(Cl^-)$ (●)

Rate constants $k(C_2Cl_4^-)$ (○) and $k(Cl^-)$ (●)

Rate constants $k(C_2Cl_4^-)$ (○) and $k(Cl^-)$ (●)
greater than 100 \mu \text{sec} from previous experiments\textsuperscript{23}. Pressure normalized ratios $N_{\text{C}_{2}\text{Cl}_{4}}/N_{\text{SF}_{6}}$ and $N_{\text{Cl}^-}/N_{\text{SF}_{6}}$-remained constant for interaction times up to 8\mu\text{sec} indicating that $\text{C}_{2}\text{Cl}_{4}^-$ ions have long lifetimes and showing that the negative ions are not exiting the IR before the extraction pulse is applied. Final ratios at every $n$ were obtained by averaging over the three different interaction times.

The present data are displayed in figure 8. At high $n$ ($n>40$) the rate constants are independent of $n$, but they drop sharply at low $n$. This results because, at low $n$, the radius of the Rydberg atom is small and the negative molecular ion is formed sufficiently close to the $\text{K}^+$ ion that the ion pair is bound by electrostatic attraction. If the kinetic energy of the negative molecular ion is insufficient to overcome the force of attraction, then the ions remain undetected. The drop in $k_{\text{Cl}^-}$ at low $n$, suggests that a significant fraction of the $\text{K}^+\text{-Cl}^-$ ion pairs possess insufficient kinetic energy to break and escape the complex\textsuperscript{24}.

Direct free electron production was also observed in $\text{K(n,d)} - \text{C}_{2}\text{Cl}_{4}$ collisions. The DC bias method used for this investigation has been described earlier. For $n=35$ and 50, the rate constants for this process were $1.1 \times 10^{-7}$ cm$^3$ sec$^{-1}$ and $8.0 \times 10^{-8}$ cm$^3$ sec$^{-1}$ respectively. To investigate the origin of the free electrons, SFI studies were carried out. These showed that collisions do not populate states of higher $n$ at an appreciable rate. Thus it is unlikely that the observed free electron signal results from ionization caused
by collision induced transfer of molecular rotational energy because such processes are normally accompanied by collisional population of Rydberg states of higher n. Thus it can be concluded that the free electrons result from formation of short lived $\text{C}_2\text{Cl}_4^-$ ions that undergo rapid autodetachment.

Collisions with $\text{C}_2\text{Cl}_4$ molecules can also result in $l$ changing

$$K(n,d) + \text{C}_2\text{Cl}_4 \rightarrow K(n,l>2) + \text{C}_2\text{Cl}_4$$

(III.9)

By analysis of the SFI data at $n=35$ and 50 the rate constants for this reaction were found to be about $3 \times 10^{-7}$ cm$^3$ sec$^{-1}$. It is evident, though, that state changing collisions do not deplete the Rydberg atom population. The time development of the total Rydberg atom population can provide rate constants for collisional ionization. Rate constants for collisional ionization at $n=35$ and 50 are, $3 \times 10^{-7}$ cm$^3$ sec$^{-1}$ and $1.6 \times 10^{-7}$ cm$^3$ sec$^{-1}$. Within experimental error these rate constants are equal to the sum of the corresponding rate constants for the formation of Cl$^-$ ions, $\text{C}_2\text{Cl}_4^-$ ions and direct free electron production. This demonstrates internal self-consistency among the measurements and justifies the assumption about the equal detection efficiencies of $\text{C}_2\text{Cl}_4^-$ and SF$_6^-$.

The uncertainty in these measurements is about 30%. The error in the individual pressure measurements of the target gas is estimated to be 10%. The assumption of the equal detection efficiency is accurate to about 10%. There is a statistical error between 5% to 10% depending on a particular set of data.
Motivated by the determination of lifetimes for the long lived negative ions, time developments were monitored to longer times after Rydberg atom excitation (up to 40 µs) using the mixed gas technique. The time developments of Cl\(^-\), C\(_2\)Cl\(_4\)\(^-\) and SF\(_6\)\(^-\) ions produced at n=50 are shown in figure 9. The growth of SF\(_6\)\(^-\) is consistent with that expected for production of a very long lived negative ion (eq III.5). No evidence suggesting decay of SF\(_6\)\(^-\) is observed. The Cl\(^-\) signal though drops at later times because the velocities of Cl\(^-\) ions are sufficient that the ions escape the IR. C\(_2\)Cl\(_4\)\(^-\) and SF\(_6\)\(^-\) ions have comparable velocities and thus the drop in C\(_2\)Cl\(_4\)\(^-\) signal cannot be attributed to ions leaving the IR. It is thus concluded that this drop at later times is due to decay of C\(_2\)Cl\(_4\)\(^-\) ions. Model fits to the data suggest C\(_2\)Cl\(_4\)\(^-\) lifetimes of the order of 30-40 µsec. These are longer than those measured in earlier free electron studies 14 µsec\(^{25}\). This difference may be due to lower initial electron energies of the electrons attached in the Rydberg atom experiment.

In chapter I, theoretical models of Rydberg electron attachment and dissociative electron attachment were discussed. The essential conclusion was that the rate constants for negative ion formation measured in Rydberg atom collisional studies at high n should equal those for the capture of free electrons having the same velocity distribution as the Rydberg electron i.e.,
FIGURE 9

Time development of the Cl\(^-\), C\(_2\)Cl\(_4\)\(^-\) and SF\(_6\)\(^-\) populations in the interaction region produced by collisions of K (50d) atoms with a mixed C\(_2\)Cl\(_4\)/SF\(_6\) target gas.
k = \int_{0}^{\infty} v \sigma_e(v) f(v) \, dv \quad \text{III.10}

where \( k \) is the free electron attachment rate constant, \( f(v) \) is the Rydberg electron velocity distribution (determined by its quantum state) and \( \sigma_e(v) \) is the free electron attachment cross section. Fig III.1 shows that \( k_{C2Cl_4^-} \) and \( k_{Cl^-} \) are independent of \( n \) at high \( n \). According to Eq III.10, this independence requires that the corresponding free electron cross sections \( \sigma_e(C2Cl_4^-) \) and \( \sigma_e(Cl^-) \) be inversely proportional to the electron velocity pointing to 's' wave capture. The free electron cross sections obtained from Rydberg data, \( \sigma_e = \beta/v \) (\( \beta_{Cl^-} = 5.9 \pm 1.8 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1} \), \( \beta_{C2Cl_4^-} = 5.4 \pm 1.6 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1} \)) are shown in figure 10.

To compare Rydberg atom data with available free electron data velocity averaged free electron cross sections can be calculated by using the expression,

\[ \sigma_e = \frac{k}{v_{rms}} \quad \text{III.11} \]

where \( v_{rms} \) is velocity corresponding to the average kinetic energy of the Rydberg electron. The velocity averaged cross sections \( \sigma_e(C2Cl_4^-) \) and \( \sigma_e(Cl^-) \) along with cross sections obtained in free electron studies using swarm-unfolded\textsuperscript{26} and TPSA\textsuperscript{27} techniques are shown in fig III.3.
FIGURE 10

Electron attachment to C₂Cl₄.

Velocity averaged cross section \( \sigma(C₂Cl₄^-) \): O
Velocity averaged cross section \( \overline{\sigma}(Cl^-) \): O
Free electron cross section \( \sigma(C₂Cl₄^-) \): ---
Free electron cross section \( \sigma(Cl^-) \): ---
TPSA data: ---
Swarm data: \( \Delta \)
The TPSA cross sections for $\text{C}_2\text{Cl}_4^-$ formation lie higher than the present data. This can be explained as follows. The TPSA data is normalized to the swarm measured rate constants for thermal electron attachment. This assumes that the reaction results in the production of only $\text{Cl}^-$ ions and relatively long lived $\text{C}_2\text{Cl}_4^-$ ions. The present data however suggests that at least at electron energies below 10meV, electron attachment also results in the formation of $\text{C}_2\text{Cl}_4^-$ ions that undergo rapid autodetachment. If this is also true at higher electron energies, the rate constant measured in swarm experiments may not correspond directly to that for the formation of long lived negative ions in TPSA and Rydberg studies. Swarm measurements are performed under multiple collision conditions and short lived negative ions may be rapidly stabilized by collisions with the buffer gas and contribute to the total measured electron attachment rate. In TPSA and Rydberg atom studies such stabilization is not possible due to single collision conditions. If significant collisional stabilization of short lived $\text{C}_2\text{Cl}_4^-$ ions occurs in the swarm measurements, then the TPSA data should be renormalized to only that part of the total swarm measured thermal electron attachment rate constant that is associated with direct formation of long lived negative ions. This would lower the TPSA cross sections for $\text{C}_2\text{Cl}_4^-$ formation and result in better agreement with the present data.
C. Electron Attachment to C₆F₆ (Perfluorobenzene):

Rydberg electron attachment to C₆F₆ (eq III.4) showed the formation of two types of C₆F₆⁻ ions: relatively long lived C₆F₆⁻ ions and short lived C₆F₆⁻ ions that undergo rapid autodetachment forming a neutral C₆F₆ and an electron. The mixed gas technique was used to obtain the rate constants for the formation of long lived C₆F₆⁻ ions. The rate constants kC₆F₆⁻ obtained using equation III.7 are included in Table III.2. As expected the measured ratios were independent of target gas densities and collision times up to 8 µsec. The relative detection efficiencies for C₆F₆⁻ and SF₆⁻ ions were taken to be equal.

At high n (n > 40), the rate constants kC₆F₆⁻ are independent of n. At low n (10 < n < 40) the rate constants drop with n. This is shown in figure 11. The drop in the rate constant is again due to the small initial separation between the product C₆F₆⁻ and K⁺ ions at low n when post attachment interactions are important²⁴.

DC bias method measurements showed the rate constants ke for the direct formation of free electrons to be 1 x 10⁻⁹ cm³ sec⁻¹ at n= 40-55. Analysis of SFI data again showed that n-changing does not occur at an appreciable rate discounting the possibility of ionization due to collisional transfer of rotational kinetic energy of the molecule. Thus it is concluded that the origin of the free electrons are short lived C₆F₆⁻ ions that undergo autodetachment reverting back to a neutral molecule and an electron.
TABLE III.2

RATE CONSTANTS FOR THE FORMATION OF C₆F₆⁻ IONS

<table>
<thead>
<tr>
<th>n</th>
<th>$k_{C_6F_6^-} \times 10^{-8}$ cm³/sec</th>
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</thead>
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<tr>
<td>15</td>
<td>1.0</td>
</tr>
<tr>
<td>20</td>
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<tr>
<td>25</td>
<td>2.8</td>
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<td>30</td>
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<td>40</td>
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<td>70</td>
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<tr>
<td>80</td>
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</tr>
<tr>
<td>90</td>
<td>5.1</td>
</tr>
<tr>
<td>100</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Notes: $n =$ Principal Quantum Number of Rydberg atom.

$k_{C_6F_6^-} =$ Rate constant for the formation of C₆F₆⁻ ions.
Rate constants for C₆F₆⁻ formation due to collisions of Rydberg atoms and C₆F₆ molecules.
The total rate constant for collisional ionization of Rydberg atom $k_i$, at $n=40$ was, $1.8 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. This is, to within experimental error equal to the rate constant for negative ion formation plus the rate constant for direct free electron production.

A drop in pressure normalized ratios $C_6F_6^-/SF_6^-$ of the signals for longer interaction times (30-50 $\mu$sec) was observed. This drop is attributed to the decay of $C_6F_6^-$ ions because it is unlikely that the ions will leave the IR during that time. Measurements showed that for $n$ 40-60, the lifetime of the $C_6F_6^-$ ions is about 50 $\mu$sec. This is considerably longer than that determined in earlier free electron studies, 13 $\mu$sec$^{28,29}$. The difference may again be due to the lower initial energies of the attached electron.

At high $n$ ($n>40$) post attachment interactions between positive and negative ions are negligible and the free electron model can be applied to discuss Rydberg electron capture by $C_6F_6$. The rate constants are independent of $n$ at high $n$ thus from eq III.10, $n$ independence of rate constant requires $1/v$ dependence of $\sigma_e(v)$ which suggests s-wave capture. The free electron cross sections $\sigma_e(v)$ obtained from the present data are shown in figure 12. This figure also includes velocity averaged free electron cross sections calculated by using the expression III.11.

The present results are compared with other free electron studies data in figure 12. The disagreement between the Rydberg
Figure 12

Velocity averaged cross section $\sigma (C_6F_6^-)$: ∗
Free electron cross section $\sigma (C_6F_6^-)$: ———
TPSA data: ———
Swarm data: △
and the TPSA data\textsuperscript{30} may again be explained by the normalization of the TPSA data to the swarm data\textsuperscript{31} where stabilization of short lived C\textsubscript{6}F\textsubscript{6}\textsuperscript{-} ions is possible. Renormalization of the TPSA data to only that part of swarm cross section that corresponds to formation of long lived C\textsubscript{6}F\textsubscript{6}\textsuperscript{-} ions will result in better agreement between the Rydberg data and TPSA data.
IV. Conclusions:

The work presented in this thesis provides new information on electron attachment to $\text{C}_2\text{Cl}_4$ and $\text{C}_6\text{F}_6$ molecules. It was observed that collisions of Rydberg atoms with $\text{C}_2\text{Cl}_4$ molecules result in the formation of $\text{C}_2\text{Cl}_4^-$ ions, $\text{Cl}^-$ ions and free electrons. The origin of these free electrons was later traced to be short lived $\text{C}_2\text{Cl}_4^-$ ions that decay by rapid autodetachment. Collisions of Rydberg atoms with $\text{C}_6\text{F}_6$ molecules result in the formation of relatively long lived $\text{C}_6\text{F}_6^-$ ions and of short lived $\text{C}_6\text{F}_6^-$ ions that undergo rapid autodetachment. The present data for both gases agree with the TPSA data provided that the TPSA data is renormalized to only that part of the swarm cross section that results from the formation of relatively long lived negative ions. Subsidiary measurements showed that the lifetimes of the relatively long lived $\text{C}_2\text{Cl}_4^-$ and $\text{C}_6\text{F}_6^-$ ions are about 40 $\mu$sec.

Thus it is concluded that the Rydberg atom technique can be effectively used for the investigation of subthermal energy electron attachment to molecules. This technique provides information about all the channels operative in electron attaching collisions. In free electron experiments such as the swarm technique, this information is not available. It is also possible to study the lifetimes of the negative ions by using the Rydberg atom technique.

The present work points out several different areas where Rydberg atom collision techniques can be employed for interesting
future research. The lifetimes of negative ions formed in electron transfer reactions have been measured using free electron techniques but are not in good agreement. For example, in the case of SF$_6^-$ lifetimes varying between a few μsec and a few milliseconds have been reported. High Rydberg studies provide alternative means to investigate these lifetimes. If the negative ions formed in Rydberg electron-molecule interactions are trapped in an ion trap such as a Penning trap, their lifetimes can be determined by simply monitoring the decay of the ion population in the trap. It is expected that the lifetimes of the negative ions depend on the energy of the attached electron. Rydberg atoms, being an ideal source of low-energy electrons, can be used for investigating the electron energy dependence of the lifetimes of negative ions, hopefully removing earlier discrepancies.

It has been observed that only a small fraction of the energy released in dissociative electron attachment appears as the kinetic energy of the negatively charged fragment. However precise measurements of the energy of the negative ion have not been made. The Rydberg atom collision technique is currently being applied to this problem to measure the kinetic energy distribution of the negative ions. In these experiments negative ions are formed in a localized volume and are accelerated towards a position sensitive detector (PSD), their flight times being greater than 20 μsec. The ion arrival positions at the PSD provide a measure of their initial
velocities and thus their kinetic energies. Kinematic studies of this type are not possible using very low energy free electrons.

Another ongoing project in this program is the production of high \( l \) states and the study of their collisional properties. Classically, high-\( l \) states correspond to the Rydberg electron in a circular orbit about the core ion. For an atom in a 'circular state' the probability of finding the Rydberg electron near the core is negligible. Thus collisional properties can be well described by the independent-particle, free electron model. Further the electron momentum distribution is a single, gaussian peak. Thus the velocity spread of the Rydberg electron is very small, permitting more detailed study of energy dependences in electron-molecule collisions and opening the possibility of observing very narrow resonances in the scattering.

Molecules at higher than room temperature are in higher rotational and vibrational states. The cross section for the formation of negative ions may depend on the quantum states of a molecule. Using the Rydberg atom technique, the effect of molecular internal energy on electron attachment and dissociative electron attachment processes and the lifetimes of the negative ions can be investigated.
V. REFERENCES

5. M.Matsuzawa's article in Ref 1.
7. An article by A.P.Hickman, R.E.Olson and J.Pascale in Ref 1.