Analysis of the Dynamics of Heavy Rydberg Ion Pair Formation Through Studies of Electron Capture Reactions

by

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ABSTRACT

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Scattering of K(np) Rydberg atoms by electron-attaching molecules can result in the formation of positive-negative ion pairs through electron transfer reactions. These reactions can involve the dissociation of a transient intermediate negative ion into a smaller negative ion and a neutral fragment, or they can result in the parent molecule forming a metastable negative ion, with the excess energy being distributed among its internal modes. For Rydberg atoms of intermediate \( n \), it is possible for these ion pairs to orbit each other at large separation, weakly bound by their mutual electrostatic attraction, forming what are known as heavy-Rydberg states. Measurements of the binding energy and velocity distributions of the ion pairs are used to probe the dynamics of electron transfer reactions. The data are analyzed using a semiclassical Monte Carlo collision code to explore the lifetime of the intermediate, the nature of its dissociation, the distribution of the excess energy of reaction, and the branching ratio of the various reaction channels.

Results obtained using a variety of electron-attaching targets, including CF\(_3\)I, CCl\(_4\), SF\(_6\), CH\(_2\)Br\(_2\), 1,1,1-C\(_2\)Cl\(_3\)F\(_3\), CCl\(_3\)Br, Fe(CO)\(_5\), and CH\(_3\)NO\(_2\), have demonstrated both the wide variety of different behaviors that can accompany electron capture as well as the different behaviors of the product ion-pair states themselves.
Remarkably, despite previous work showing that it was possible for CH$_3$NO$_2$ to form long-lived valence-bound negative ions through Rydberg electron transfer, the present work showed that such collisions do not result in the formation of long-lived bound ion-pair states. Rather, the data show that collisions lead to very strong Rydberg atom scattering through formation of transient ion-pair states. These results are consistent with theoretical work that predicts significant collisional quenching of Rydberg atoms by highly polar molecules and highlight a new mechanism for Rydberg atom scattering.
Acknowledgments

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Chapter 1

Introduction

When electrons collide with molecules with significantly positive electron affinities, it is possible for the electron to attach to the molecule and form an excited transient negative ion. These ions exist as temporary resonant states, having lifetimes significantly longer than the time needed for the electron to traverse the width of the molecule. These resonances can exist through the production of a quasi-bound state trapped by a centrifugal barrier imposed by the angular momentum of the collision, or they can exist through coupling between the energy of the electron and rotational and vibrational degrees of freedom of the molecule. These transient negative ions can autodetach into a free electron and a neutral molecule, they can stabilize through redistribution of the excess energy among the rotational and vibrational modes of the molecule, or they can decay through dissociation of the transient negative ion into fragments, with some of the excess energy having been converted into translational energy. How long the resonant states live, the cross sections for the attachment reaction, and how the excess energy of reaction is distributed have been the subjects of much investigation over the past several decades, with measurements typically being conducted via electron beam or electron swarm experiments.

Of particular interest is the scattering of electrons with thermal and subthermal energies by molecules. Electrons with small kinetic energies have very large de Broglie wavelengths ($\lambda_B \sim 120$ Å at 10 meV and $\sim 3900$ Å at 10 µeV.) Wavelengths of this size are comparable to the range of most electron-molecule reactions. Previous work
has shown that at very low energies electron capture is primarily an s-wave process and that, for energy $E \to 0$, the s-wave electron-capture cross section interpolates to $1/E^{1/2}$ behavior [3, 4]. In addition, inelastic collisions can lead to changes in the rotational states of the molecule. For example, when a slow electron inelastically scatters off a rotating polar molecule, the molecule can undergo dipole-allowed rotational deexcitation [5].

$$e^- + ABC(J) \to e^- + ABC(J - 1) + \Delta\varepsilon$$ (1.1)

Finally, low-energy electron scattering from atoms and molecules is one of the most important fundamental processes in gaseous environments such as gaseous dielectrics, discharges, arcs, gas lasers, and the earth’s atmosphere. Therefore, further study of thermal-energy electron scattering is of both fundamental and practical interest.

Due to the high energy resolution necessary to study the energy-dependent behavior of thermal energy electrons, however, traditional electron beam and electron swarm experiments have, by and large, proven to be inadequate for high-resolution studies of thermal electron scattering. However, many techniques have been developed specifically to study low-energy electron scattering and measure properties such as attachment cross sections, negative ion lifetimes, and the shapes of resonance peaks in electron scattering. These techniques include novel electron swarm techniques utilizing drift tubes (and flowing afterglows.) Drift tube measurements, however, do not directly provide good energy resolution as the electron swarm under study has a broad, non-thermal energy distribution. As will be discussed, much higher energy resolutions can be obtained using laser photoionization techniques in which the photon energy governs the electron energy and energy spread, and by using Rydberg electron transfer.
1.1 Dynamics of Electron-Molecule Collisions

A resonance is a temporary compound state formed when an incoming electron possessing an energy $E$ that falls within a specific range of energies of width $\Gamma$ is captured into a quasistationary orbital in the field of the target molecule. The average lifetimes, $\tau$, of these states before autodetachment can range from $10^{-15}$ to $10^{-11}$ s, as governed by the equation $\tau = \hbar/\Gamma$. These lifetimes are significantly longer than the time needed for an electron to traverse the width of the molecule ($< 10^{-15}$ s). These resonances are usually caused by one of two mechanisms. In the first, the combination of an attractive polarization potential with a repulsive centrifugal potential can create a significant peak in the effective potential for the radial portion of the electron wave function. This mechanism is known as a shape resonance. A common example of this can be found in electron collisions with N$_2$ molecules [6]. For electrons with thermal energies, however, electron scattering is dominated by the s ($l = 0$) wave. Without angular momentum in the scattering, a shape resonance can not be formed. Therefore, resonant states with thermal and subthermal-energy electrons can only be formed by the second resonance mechanism: a nuclear-excited Feshbach resonance. In this case, the electron loses energy by exciting the rotational and vibrational modes of the target molecule. For slow electrons, the energy interchange is sufficient that the electron can become bound, forming a metastable negative ion. This finite lifetime exists because, statistically, it will take some time for the energy to be concentrated in a mode conducive to autoionization [7].

The possible end results of the collision between an electron with energy $E$ and the molecule XY which results in the formation of the negative ion resonant state
XY$^{-\ast}$ are illustrated by the following equations:

$$\begin{align*}
e^-(E) + XY(n, \nu, J) & \rightarrow XY^{-\ast} \rightarrow XY(n', \nu', J') + e^-(E') \quad (1.2a) \\
& \rightarrow XY^- \quad (1.2b) \\
& \rightarrow X + Y^- \quad (1.2c)
\end{align*}$$

Electrons in resonances typically are captured into a low-lying unoccupied molecular orbital (LUMO), which frequently has anti-bonding character. As a result, the capture of the electron can change the equilibrium internuclear distance of the atoms to the point that by the time the electron autodetaches to produce a neutral molecule and a free electron, the molecule may be in a vibrationally excited state. Alternatively, polar molecules may undergo dipole-allowed rotational deexcitation as described earlier. Both of these cases are illustrated by Equation 1.2a. Alternatively, the molecule may be sufficiently complex that the energy of the molecular ion may be efficiently distributed throughout the rovibrational manifold to the point that the ion becomes metastable, as shown in Equation 1.2b. Finally, the transient intermediate ion can dissociate and fragment, forming a negative ion $Y^-$ and a neutral molecule $X$, as shown in Equation 1.2c [8]. The latter two processes are the subjects of this work.

1.1.1 Non-Dissociative Electron Attachment

For molecules with large positive electron affinities, the transient negative ion is energetically below the state of a free electron and the neutral molecule. In this context, the electron affinity is defined as the difference in energy between the neutral molecule and an electron at rest at infinity and the molecular negative ion in its ground state. However, unless the excess energy of reaction (which consists mainly of the electron affinity and the kinetic energy of the electron) is removed via collisional or radia-
tive processes, the electron will eventually regain sufficient energy to autodetach. However, for complex molecules (e.g. \( \text{SF}_6 \), \( \text{C}_6\text{F}_6 \), or \( \text{C}_{60} \)), the transient intermediate ion can temporarily stabilize through efficient distribution of the excess energy throughout the vibrational manifold of the molecule via a process called intramolecular vibrational redistribution (IVR) [9, 10]. Through this process, the probability that the energy will be reconcentrated in a mode from which autodetachment can take place is significantly reduced, allowing the metastable negative ion \( \text{XY}^- \) to have a lifetime as long as several tens of microseconds or even several milliseconds [11].

Figure 1.1: Schematic energy diagrams for nuclear-excited Feshbach resonances with a positive EA.
1.1.2 Dissociative Electron Attachment

In dissociative attachment, the transient negative ion fragments into a negative ion and a free neutral molecule. For this process to be energetically possible, the fragment to receive the negative charge must have a large positive electron affinity, so it is typically a halogen or a pseudohalogen (e.g., CN.) The dissociative process is two-fold. Firstly, the electron attachment results in a Franck-Condon transition into a repulsive excited state, during which the positions and velocities of the nuclei are considered unchanged because of how quickly the transition occurs ($\sim 10^{-13}$ s [12]) relative to the nuclear motion. Secondly, if the asymptotic energy level of the repulsive resonant state lies below that of the neutral molecule, the state can dissociate to form a neutral X and a free negative ion Y$^-$.

![Potential Energy Diagrams](image)

Figure 1.2: Schematic potential energy diagrams for dissociative electron attachment.

The heavy dependence of the behavior of the temporary negative ion on the shapes of the potential energy curves is illustrated in Figure 1.2. In Figure 1.2a, the potential energy curve of the temporary negative ion is entirely repulsive, and the asymptote lies below that of the neutral molecule for internuclear separation $R > R_c$ by an
amount equal to the electron affinity of Y. As a result, electron attachment to form
the $\text{XY}^{-*}$ resonant state leads only to dissociation. However, for $R < R_c$, the negative
ion curve is still above that of the neutral molecule, so exothermic autodetachment
is still energetically possible. However, Figure 1.2b shows an ionic potential curve
which allows for both dissociative and nondissociative electron attachment. The
$\text{XY}^{-*}$ curve has a local minimum, but when the transition occurs at an internu-
clear separation $R < R_{th}$, the resulting transient negative ion has enough energy to
dissociate [8].

1.2 Previous Experimental Methods

The majority of earlier electron scattering experiments have been conducted through
use of the electron beam [13, 14, 15, 16, 17, 18] or electron swarm [19, 20, 21, 22, 23,
24, 18] experiments. In an electron beam experiment, a flux of electrons is generated,
usually by thermal emission from a hot filament, and is sent to collide with a target
in vacuo. Through the use of a target either consisting of an effusive molecular beam
or a beam produced through supersonic expansion, electron attachment processes to
either single molecules or to molecular clusters, respectively, can be studied through
mass spectrometry. Typically, electron sources based on thermionic emission produce
electrons with an energy distribution ranging from 0.5-1 eV, governed by the filament
temperature and by the potential difference across it. However, this energy distribu-
tion can be significantly reduced through the implementation of a monochromator,
typically consisting of crossed perpendicular electric and magnetic fields, which allow
only electrons within a small energy range to pass through to collide with the target.
Allan, through the use of an apparatus which employs hemispherical monochroma-
tors, has produced electron beams with energy resolutions as low as 6.6 meV [25, 26].
In electron swarm experiments, electrons are produced through photoemission from a cathode, through radioactive decay, or through corona discharges. These electrons are propelled by a constant electric field from their source at the cathode through a drift tube filled with buffer gas to the anode. By measuring the time it takes for a pulse of electrons to traverse the drift tube while colliding with the buffer gas, the drift velocity of the electrons can be determined together with the energy loss per collision and the mean free path. Electron-attaching targets are then added to the buffer gas. By measuring the attenuation of the potential induced in the anode by the drifting electrons as a result of attachment to the target gas, the target gas’ electron attachment cross section can be calculated.

Both of these methods have shortcomings when considering measurement of the products of thermal electron attachment. In the case of electron beam experiments, even when beams with both low energy and high resolution can be produced, the difficulty of determining the collision volume of beam-beam experiments as well as determining the solid angle between the collision volume and the detector can make it difficult to determine the absolute cross section. Observed cross sections are usually normalized by comparing them with a known cross section [7]. Unlike electron beam experiments, which are conducted at pressures that only allow single collisions, electron swarm experiments are conducted at pressures that allow for secondary collisions, producing secondary products. These secondary products can complicate efforts to calculate electron attachment cross sections [18]. Furthermore, the distribution of electron energies is broad making it difficult to extract detailed energy dependent cross sections.

In the face of these difficulties with electron beam and electron swarm experiments, additional methods have been developed to improve upon and/or complement the
results obtained via these methods. Electron experiments can be improved through the implementation of afterglows. In static afterglow experiments [27, 28, 29], a gas mixture containing a small fraction of the target gas is ionized by an x-ray burst. The light intensity produced following a delayed RF discharge will be proportional to the remaining free electrons. In flowing afterglow experiments [30, 31, 32, 33], helium is excited by a microwave discharge. Electrons in the discharge products are thermalized by collision, and argon gas quenches excited helium metastables. The electrons are then allowed to collide with a target gas downstream. A Langmuir probe measures the density of surviving electrons at varying points downstream to measure the time evolution of the electron population and determine the electron attachment rate constant.

Another method, used primarily to study scattering of electrons with thermal and subthermal energies, involves the photoionization of ground state krypton and xenon atoms with UV radiation from a continuum helium discharge lamp that is passed through a monochromator [34, 35, 36]. The electron energy is equal to the difference between the energy of the radiation and the threshold ionization energy of the atom. The atoms are photoionized in the presence of a small amount of the target gas. The resulting negative ions are collected through the application of a weak DC electric field and analyzed through mass spectrometry. This method is typically used to produce electrons with energies in the range 0-200 meV. By feeding the lamp radiation through a monochromator, energy resolutions of $\sim 5 - 9$ meV can be produced. However, recent improvements in this approach using laser photoionization has been shown to produce electrons with energy widths as low as a fraction of an meV [37, 38, 39, 40], allowing detailed study of a variety of electron attachment processes in the s-wave limit.
Chapter 2

Heavy-Rydberg States and Rydberg Electron Transfer

A Rydberg atom is an atom in which the outermost electron is excited to a very high principal quantum number \( n \gtrsim 10 \). As excitations to increasingly large \( n \) are performed, the properties of the atom undergo significant changes, such as a greatly increased size and cross-sectional area, and a greatly reduced ionization energy. The electron is so far from the nucleus that even small external electric fields can cause substantial shifts in the energy levels and can even ionize the atom. At sufficiently high values of \( n \) \( (n \gtrsim 50) \), the Rydberg atom is so large and the binding energy so small that the Rydberg electron can be considered as an essentially free, independent particle. The atom functions as a low-energy electron trap and provides an effective laboratory for studying electron capture by polyatomic molecules at thermal and sub-thermal energies. Collisions frequently result in the formation of a pair of unbound ions. However, with the Rydberg atom excited to intermediate \( n \) \( (12 \lesssim n \lesssim 50) \) the ions that result from electron transfer in collisions can remain electrostatically bound, forming a heavy-Rydberg ion-pair state in which the ions orbit each other at large separation. The replacement of the electron with a much heavier negative ion greatly increases the reduced mass of the system, dramatically increasing the value of the ion pair principal quantum number \( n_H \). Study of the physical and chemical properties of such heavy-Rydberg species and their dependence on parameters such as \( n_H \), the nature of the negative ion, and the initial collision conditions forms the basis of the
Besides bound ion-pair states, recent research has discovered other unusual weakly-bound, long-range molecular systems formed from Rydberg atoms. Pairs and triplets of Rydberg atoms can form long-range bound states through strong $l$-state mixing. Known as Rydberg macrodimers and macrotrimers, these bound states can have internuclear separations as large as $1 \mu$m [41, 42, 43]. Another class of ultra-long-range Rydberg molecules can form when a ground-state atom is embedded within the wave function of a Rydberg electron. This binding mechanism, resulting from the scattering of the low-energy Rydberg electron from an atom with a negative scattering length, can produce molecules with internuclear separations of several thousand Bohr radii [44, 45, 46, 47]. Along with ion pairs, these Rydberg states are the subject of much interest because they blur the separation between classical and quantum mechanics and they provide a useful way to investigate the transition between the two realms.

### 2.1 Rydberg Atoms

To a first approximation, the binding energy of the valence electron in an atom in a Rydberg state is given by [48]

$$E_B = -\frac{R_\infty}{n^2}$$

(2.1)

where $R_\infty = 109737.32$ cm$^{-1}$ is the Rydberg constant and $n$ is the principal quantum number. However, the application of two corrections can significantly improve the accuracy of this expression. First, this formula approximates the mass of the atomic nucleus as infinite compared to the mass of the Rydberg electron. To improve the result for the energy, the equation can be modified by inserting a reduced mass
correction:

\[ E_B = -\frac{R_M}{n^2} \]  

(2.2)

where

\[ R_M = \frac{R_\infty}{1 + m_e/M} \]  

(2.3)

with \( m_e \) and \( M \) representing the masses of the electron and atomic nucleus, respectively.

A second correction involves the interaction of the Rydberg electron with the core electrons, particularly for low angular momentum states. With lower angular momentum states, the probability increases for the Rydberg electron to penetrate inside the core and “see” more of the nuclear charge, reducing the effectiveness of the charge screening by the core electrons. Thus, lower angular momentum states have lower energies than higher angular momentum states for the same principal quantum number. To address this, Equation (2.1) is written

\[ E_B = -\frac{R_M}{(n - \delta_{nlj})^2} \]  

(2.4)

where \( \delta_{nlj} \) is the quantum defect of that state. The value of the quantum defect depends on the quantum numbers of the Rydberg state of interest, where \( s \) states have the largest quantum defects as they feature the most significant core penetration.

The values of the quantum defects can be calculated using

\[ \delta_{nlj} = \delta_0 + \frac{\delta_2}{(n - \delta_0)^2} + \frac{\delta_4}{(n - \delta_0)^4} + \frac{\delta_6}{(n - \delta_0)^6} + \frac{\delta_8}{(n - \delta_0)^8} + \cdots \]  

(2.5)

where the values of \( \delta_0, \delta_2, \) etc. for potassium are listed in Table 2.1 [1].

Rydberg atoms demonstrate unusual properties that reveal themselves ever more dramatically as the principal quantum number increases. Several of these properties scale by powers of the principal quantum number \( n \). For instance, the mean orbital
Table 2.1: Potassium quantum defect parameters for Eq. (2.5) (taken from [1])

<table>
<thead>
<tr>
<th>Series</th>
<th>$\delta_0$</th>
<th>$\delta_2$</th>
<th>$\delta_4$</th>
<th>$\delta_6$</th>
<th>$\delta_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ns$_{1/2}$</td>
<td>2.180197(15)</td>
<td>0.136(3)</td>
<td>0.0759</td>
<td>0.117</td>
<td>-0.206</td>
</tr>
<tr>
<td>np$_{1/2}$</td>
<td>1.713892(30)</td>
<td>0.2332(50)</td>
<td>0.16137</td>
<td>0.5345</td>
<td>-0.234</td>
</tr>
<tr>
<td>np$_{3/2}$</td>
<td>1.710848(30)</td>
<td>0.2354(60)</td>
<td>0.11551</td>
<td>1.105</td>
<td>-2.0356</td>
</tr>
</tbody>
</table>

Table 2.2: Dependence of Properties of Hydrogen Rydberg Atoms on $n$ (taken from [2])

<table>
<thead>
<tr>
<th>Property</th>
<th>Scaling(a.u.)</th>
<th>$n = 1$</th>
<th>$n = 20$</th>
<th>$n = 40$</th>
<th>$n = 60$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Radius</td>
<td>$n^2$</td>
<td>0.05 nm</td>
<td>20 nm</td>
<td>85 nm</td>
<td>190 nm</td>
</tr>
<tr>
<td>Orbital Period</td>
<td>$n^3$</td>
<td>0.15 fs</td>
<td>1.2 ps</td>
<td>9.8 ps</td>
<td>33 ps</td>
</tr>
<tr>
<td>Binding Energy</td>
<td>$\frac{1}{n^2}$</td>
<td>13.6 eV</td>
<td>34 meV</td>
<td>8.5 meV</td>
<td>3.8 meV</td>
</tr>
<tr>
<td>Energy Spacing</td>
<td>$\frac{1}{n^2}$</td>
<td>10.2 eV</td>
<td>3.2 meV</td>
<td>0.4 meV</td>
<td>0.1 meV</td>
</tr>
<tr>
<td>Classical Field</td>
<td>$\frac{1}{16n^4}$</td>
<td>$3.2 \times 10^8$ V/cm</td>
<td>2008 V/cm</td>
<td>125 V/cm</td>
<td>25 V/cm</td>
</tr>
<tr>
<td>Ionization Threshold</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

radius of the atom scales as $n^2$. Conversely, the binding energy scales as $n^{-2}$. The scaling laws for these and other properties are listed in Table 2.2 [2].

2.2 Formation of Rydberg Atoms

Rydberg atoms can be formed through one of three methods: charge exchange, electron impact, and photoexcitation. The equations below illustrate these three respec-
tive methods.

\[ A^+ + B \rightarrow A(nl) + B^+ \] \hspace{1cm} (2.6a)

\[ e^- + A \rightarrow A(nl) + e^- \] \hspace{1cm} (2.6b)

\[ h\nu + A \rightarrow A(nl) \] \hspace{1cm} (2.6c)

This experiment uses photoexcitation, which, unlike the first two methods, allows a specific Rydberg state to be precisely targeted by controlling the wavelength of the incident light. However, also unlike the first two methods, photoexcitation only allows the creation of low angular momentum Rydberg states [1].

2.3 Rydberg Atom-Molecule Interactions

The most striking feature of Rydberg atoms is their large physical size. For \( n = 1000 \), the radius of the atom can reach \( \sim 0.1 \) mm, or about the size of a simple single-celled organism. Their radii are significantly larger than the ranges associated with ion-molecule and electron-molecule interactions. Additionally, the Rydberg electron is very weakly bound (\( \sim 100 \) \( \mu \)eV for \( n = 1000 \)). Even for relatively small values of \( n \) (\( n \gtrsim 10 \)), the Rydberg electron and the core ion are sufficiently separated that upon colliding with a neutral target the Rydberg atom can be treated as two independent particles rather than as an atom, and negative ion formation through collisions with Rydberg atoms can be viewed in terms of electron capture during a binary interaction between the excited electron and the target molecule [49, 5]. The reactions resulting
from such electron transfer include: [8]

\[
A(nl) + XY \rightarrow A^+ + XY^{-*} \rightarrow A^+ + XY + e \quad (2.7a)
\]

\[
\rightarrow A(n'l') + XY 
\quad (2.7b)
\]

\[
\rightarrow A^+ + XY^{-} \quad (2.7c)
\]

\[
\rightarrow A^+ + X + Y^{-} \quad (2.7d)
\]

where \(A(nl)\) represents a Rydberg atom and \(XY^{-*}\) represents an excited transient intermediate state of the target molecule. This state may rapidly undergo autodetachment, separating into the original neutral molecule and a free electron (Equation 2.7a). Alternatively, the electron may remain bound to the original Rydberg atom, and the interaction with the attaching molecule may result in a change of state (Equation 2.7b). The reactions illustrated in Equations (2.7c) and (2.7d) are the subject of this work. The excited intermediate state may transition into a long-lived metastable negative ion via intramolecular vibrational energy redistribution and remain electrostatically bound to the core of the original Rydberg atom (Equation 2.7c). Alternatively, the intermediate may dissociate and fragment, creating a negative ion and a neutral molecule, whereupon the negative ion might remain bound to the Rydberg core ion (Equation 2.7d).

If the nearly-free electron model is correct, then for sufficiently high \(n\), the rate constant for collisional destruction of Rydberg atoms must equal the rate constant for attachment for free electrons having the same velocity distribution:

\[
k_d = \int_0^\infty v \sigma_e(v) f_R(v) \, dv \quad (2.8)
\]

where \(f_R(v)\) is the Rydberg electron velocity distribution and \(\sigma_e(v)\) is the attachment cross section of free electrons with velocity \(v\). Previous Rydberg electron transfer measurements [5] have shown good agreement between the rate constant for collisional
destruction of the Rydberg atom and the rate constant for capture of free electrons with the same velocity distribution as the Rydberg electron, so long as $n$ is sufficiently high ($\gtrsim 10$). Additionally, inspection of the results shows that for sufficiently high $n$ the measured rate constant is essentially independent of $n$, and therefore the velocity distribution of the electron. It can therefore be concluded, upon inspection of Equation 2.8 that the cross section varies as $1/v$, i.e. as $1/E^{1/2}$, where $E$ is the kinetic energy of the free electron, consistent with the Wigner threshold law for s-wave electron attachment reactions.

### 2.4 Heavy-Rydberg States

As $n$ decreases, the size of the Rydberg electron cloud decreases, and the separation between the positive and negative ions formed through Rydberg electron transfer becomes smaller. With decreasing $n$, the probability that the ions have the necessary kinetic energy of relative motion to escape their mutual Coulomb attraction decreases and an increasing fraction of the product ion pairs remain electrostatically bound. These states, consisting of weakly bound ion pairs orbiting at large separation are commonly referred to as heavy-Rydberg states, because many of their properties closely parallel those of a Rydberg atom, with the Rydberg electron having been replaced with a negative ion [2]. This substitution radically changes the properties of the system, most significantly by drastically increasing the reduced mass of the system. The new reduced mass is calculated using the equation

$$\mu = \frac{M_R M_T}{M_R + M_T}$$  \hspace{1cm} (2.9)

where $M_R$ is the mass of the Rydberg core ion and $M_T$ is the mass of the negative ion formed from the target molecule. Taking this into account the new scaling law is
given by

\[ R_H = M R_\infty \] (2.10)

where

\[ M = \frac{\mu}{m_e} \] (2.11)

For atomic systems, because the mass of the nucleus is much larger than that of the electron, \( \mu \approx m_e \) and the disparity between \( R_\infty \) and \( R_M \) is small. However, with heavy Rydberg systems, the value of \( \mu \) varies with the target molecule. Additionally, \( \mu/m_e \) is much larger for heavy-Rydberg systems than for atomic systems, typically on the order of \( 10^4 \) or more [2].

### 2.5 Formation of Heavy-Rydberg States

Heavy-Rydberg ion-pair states have been formed through the use of multi-step laser-induced photoexcitation or through electron transfer between Rydberg atoms and electron-attaching targets. Photoexcitation of targets such as \( \text{H}_2, \text{Cl}_2, \text{O}_2, \text{F}_2, \) and \( \text{HF} \) has resulted in the creation of \( \text{H}^+ \cdots \text{H}^- [51, 52, 2, 53, 54, 55], \text{Cl}^+ \cdots \text{Cl}^- [56, 57], \text{O}^+ \cdots \text{O}^- [58], \text{F}^+ \cdots \text{F}^- [59], \) and \( \text{H}^+ \cdots \text{F}^- [60] \) ion-pair states respectively. However, since electric dipole selection rules only allow excitations in which \( \Delta J = 0 \pm 1 \) [48], heavy-Rydberg states with small values of angular momentum \( L \) are populated.

In 2001, Reinhold et al. demonstrated that \( \text{H}^+ \cdots \text{H}^- \) ion-pair states photoexcited in the presence of a small electric field will undergo Stark precession, allowing the state to attain larger values of \( L \) [52]. Electron transfer in thermal-energy collisions with Rydberg atoms, on the other hand, can produce ion-pair states with large values of \( L \) and a broad distribution of \( L_z \) values. A variety of bound ion-pair states have been formed in this manner, including \( \text{A}^+ \cdots \text{Cl}^- [61, 62, 63, 11, 64, 65, 66, 67], \)
A$^{+} \cdots$CN$^{-}$ [68, 69, 65], A$^{+} \cdots$I$^{-}$ [70, 71, 72, 73], A$^{+} \cdots$Br$^{-}$ [61], and A$^{+} \cdots$SF$_{6}^{-}$ [65, 72, 63, 62, 74, 75, 76, 77]. A Monte Carlo collision code is used to model such reactions by simulating both the initial collision of the Rydberg atom with the target molecule, the capture process, and the subsequent evolution of the resulting ion pair. The results of these simulations are compared with experimentally measured ion pair velocity and binding energy distributions to understand the collision processes.

2.6 Field Ionization and Dissociation

Because Rydberg atoms are very weakly bound, it is relatively easy to ionize them with electric fields [78, 79, 80]. When a constant electric field $F$ is applied in the $+z$ direction, the resulting electron potential becomes

$$V = -\frac{1}{r} + Fz \quad (2.12)$$

This creates a saddle point at $z_s = -1/\sqrt{F}$ where the potential energy is $V_s = -2\sqrt{F}$. Therefore, for a state with energy $E$, the energy needed for classical over-the-barrier escape, is equal to

$$F = \frac{E^2}{4} \quad (2.13)$$

or in terms of the principal quantum number:

$$F = \frac{1}{16n^4} \quad (2.14)$$

However, for states with $m \neq 0$, there exists a $1/(x^2 + y^2)$ centrifugal barrier keeping the electron away from the $z$-axis, raising the threshold field. The fractional increase in the threshold field with $m$ is

$$\frac{\Delta E}{E} = \frac{|m|\sqrt{E}}{\sqrt{2n}} = \frac{|m|}{2n} \quad [78] \quad (2.15)$$
This calculation, however, ignores the Stark effect. For the extreme red-shifted Stark state, the energy is given approximately by

\[ E = -\frac{1}{2n^2} - \frac{3n^2F}{2} \]  

Using this energy, the critical field required to ionize this state becomes

\[ F_c = \frac{1}{9n^4} \]  

or in terms of binding energy

\[ F_c = \left(\frac{4}{9}\right) E_B^2 \]  

For blue-shifted Stark states \((m \neq 0)\), the Rydberg electron probability density is very low in the vicinity of the saddle point, where the electron can most readily
escape. As a result, blue-shifted Stark states remain stable in fields exceeding the classical ionization threshold [81]. Though it is much less simple to determine the threshold fields for the extreme blue-shifted states, these rarely exceed that of the extreme red-shifted state by more than by a factor of two [1].

Because of the weak binding energies of heavy-Rydberg ion-pair states, it is possible to dissociate them into their constituent ions through the application of relatively small electric fields. As with Rydberg atoms, the electric field creates a saddle point in the ion pair potential and classical over-the-barrier escape is again possible. The threshold field needed for classical dissociation scales as $E_B^2$ [60, 82].
Chapter 3

Experimental Apparatus and Procedures

In the present apparatus, thermal-energy potassium atoms in a collimated beam are excited to a preselected Rydberg state through single-photon excitation using a frequency-doubled ring dye laser. Photoexcitation occurs at the center of an interaction cell which contains an ambient electron-attaching target gas, and the laser beam is perpendicular to the atomic beam axis. Following photoexcitation, the Rydberg atoms undergo collisions in this cell, resulting in the formation of neutral products consisting of transient or metastable positive-negative ion pairs that remain electrostatically bound. A fraction of the product ion pairs exit the interaction cell through a slit and enter an analysis region, where they are detected through dissociation induced by application of a ramped electric field. The resulting positive or negative particles are detected using a position sensitive detector (PSD) which records both their arrival times and positions. The experiment is conducted in pulsed mode and ion arrival time and position distributions are built up following multiple collision events. These distributions are analyzed using a semiclassical Monte Carlo collision code.

3.1 Vacuum System

Survival of potassium Rydberg atoms and of the products formed upon collision with the target gas requires a high vacuum environment. The experiment is conducted in
a vacuum system consisting of two stainless steel vacuum chambers: a main chamber containing the interaction cell and analysis region, and an oven chamber containing the potassium oven. The chambers are separated by a 0.5 mm diameter aperture. Both chambers are pumped using oil diffusion pumps, typically reaching a background pressure of $\sim 0.5-1.0 \times 10^{-6}$ torr. The target gas is introduced into the main chamber, its pressure being controlled by a microvalve.
3.2 Potassium Beam

An effusive alkali beam is produced by heating a 1 g ampoule of potassium in a stainless steel oven. Resistive cartridge heaters are used to bring the temperature of the oven body to \( \sim 300^\circ \text{C} \). The resulting potassium vapor escapes from the oven through a 0.5 mm diameter aperture which is always kept 20°C hotter than the oven body to prevent clogging. The beam is further collimated by a 0.5 mm diameter aperture in the wall separating the oven chamber from the main chamber. Combined, these apertures produce a beam with a divergence of \( \sim 0.7^\circ \) \cite{83}. Beam density is measured using a hot wire detector in the main chamber.

Because the probability of an atom effusing through an aperture is proportional to its velocity, the velocity distribution of the potassium atoms in the beam in the main chamber is given by

\[
f(v) \propto v^3 e^{-\left(\frac{mv^2}{2k_BT}\right)}
\]  

(3.1)

However, the probability that an atom in the beam is photoexcited by the laser is proportional to the time for which that atom is in the laser beam, which is inversely proportional to the atom’s velocity. Therefore, the velocity distribution of those potassium atoms that are excited to a Rydberg state follows the familiar Maxwell-Boltzmann distribution.

\[
f(v) = 4\pi \left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2 e^{-\left(\frac{mv^2}{2k_BT}\right)}
\]  

(3.2)

and the most probable velocity of the Rydberg atoms in the beam for \( T = 300^\circ \text{C} \) is \( \sim 5 \times 10^4 \ \text{cm s}^{-1} \).
Figure 3.2: Speed distribution of potassium Rydberg atoms in the atom beam for an oven temperature $T = 300^\circ C$

### 3.3 Laser System

Ground-state potassium atoms are excited to $^2P_{3/2}$ states with preselected $n$ values through single-photon excitation. The wavelengths needed to excite atoms to the values of $n$ used in this work range from 290 nm to 294 nm. This light is generated by doubling the output of a Coherent CR699-21 ring dye laser, which is pumped by a Coherent Verdi V8® solid-state laser operating at 532 nm. Through the fluorescence of Rhodamine 6G dye, the CR699-21 laser produces an output beam with a power of $\sim 1 \text{ W}$ and a tunable wavelength ranging from 565 nm to 600 nm. This wavelength is measured through the use of a traveling Michelson interferometer, which compares its wavelength to that of a polarization-stabilized HeNe laser. The dye laser output beam is directed into a Spectra-Physics Wavetrain® frequency doubler. A nonlinear beta-Barium-Borate (BBO) crystal inside the doubler’s resonant cavity is used to produce a second harmonic output beam at twice the frequency of the input beam.
The continuous-wave output of the doubler is fed into an acousto-optic modulator (AOM) which chops the beam into pulses of 10 $\mu$s width at a frequency of 1 kHz. The chopped beam is directed into the chamber through a lens and a quartz window set at Brewster’s angle.

Without external stabilization, the dye laser output drifts by as much as 100 MHz/hr. This much drift is unacceptable, so the frequency is therefore externally stabilized using a Fabry-Perot etalon and the output of a frequency-stabilized helium-neon (HeNe) laser. The two laser beams are projected collinearly through the etalon, which is scanned by a piezo-electric transducer (PZT). The PZT detects the transmission peaks of the two beams. Drift in the dye laser’s frequency will cause a shift in the relative positions of the two series of transmission peaks. In response, the system generates an error signal to restore the relative positions to the desired value. Through the use of this system, the drift in the frequency of the dye laser output is reduced to $\sim 2$ MHz/day.

### 3.4 Interaction Cell and Analysis Region

To minimize Doppler broadening in the Rydberg excitation peak, the alkali beam and the laser beam are aligned normal to each other. Photoexcitation occurs at the center of a 10 mm diameter by 3 mm high interaction cell mounted in a polyether ether ketone (PEEK) housing. This cell is bordered above and below by metal electrodes. These electrodes produce a constant transverse electric field of 45 V cm$^{-1}$. One purpose for this field is to prevent stray ions produced through collisional ionization and blackbody photoionization from escaping the interaction cell and creating an unwanted experimental background. Another reason for this field is to drive electrons produced via blackbody photoionization of Rydberg atoms upward toward a
microchannel plate detector. The signal from this detector is used to aid in tuning
the laser to the proper frequency to produce the desired Rydberg state.

During each laser pulse, a portion of the potassium beam is photoexcited to the
preselected \( np \) state. These Rydberg atoms then collide with the target gas in the
chamber, forming (neutral) stable or metastable ion-pair states. The lifetime of the
Rydberg atoms is dependent upon the rate of electron attachment to the target
molecules. This rate is equal to \( \rho k_e \), where \( \rho \) is the target gas density and \( k_e \) is the
electron attachment rate constant. The target gases used in this work have electron
attachment rate constants of \( \sim 10^{-7} \text{ cm}^3 \text{ s}^{-1} \), and the experiment is conducted at a
target gas pressure of \( 3 \times 10^{-5} \text{ torr} \), which at room temperature results in a density
of \( \sim 1 \times 10^{12} \text{ cm}^{-3} \). Therefore, reaction rates \( \rho k_e \) of \( \sim 4 \times 10^5 \text{ s}^{-1} \) can be expected.
The effective lifetime of the Rydberg atom is given by the following equation:

\[
\tau_{eff} = \left( \rho k_e + \frac{1}{\tau_R} \right)^{-1}
\]

where \( \tau_R \) is the lifetime of the Rydberg atom, which is governed by radiative decay
and by blackbody radiation-induced transitions. These values are \( \sim 7 \mu s \) and \( \sim 4 \mu s \) for \( n = 14 \) and \( n = 12 \) respectively. The presence of the target gas reduces these
lifetimes to \( 1.8 \mu s \) and \( 1.5 \mu s \) respectively. Therefore, the average Rydberg atom
travels \( \lesssim 1 \text{ mm} \) before forming an ion-pair state, and it is reasonable to assume that
every ion-pair state is formed at the center of the interaction cell.

A fraction of the produced ion-pair states pass through a 1 mm high slit in the
outer wall of the interaction cell to enter the analysis region. The center of the slit is
set \( 45^\circ \) off the initial trajectory of the collimated potassium beam, and it subtends a
solid angle of \( \sim 0.002\pi \text{ sr} \) at the center of the cell. This off-axis geometry prevents
any surviving unscattered Rydberg atoms from entering the analysis region.
3.5 Analysis Region

After exiting the interaction cell through the slit, ion pairs enter an analysis region formed by circular grids made from fine (70 lines/inch, 90% transparency) copper mesh with their centers located 20 mm from the center of the interaction region. After a preselected time following the end of the laser pulse, a strong ramped electric field is applied across the analysis region that rises from 0 to $\sim 7.5$ kV cm$^{-1}$ in $\sim 5$ µs. The maximum rate of rise of the ramp is limited by electrical pickup concerns. Application of an electric field creates a saddle point in the potential energy curve of the ion-pair state over which, if the field is sufficiently strong, ions can escape allowing the ion-pair state to dissociate. The product positive or negative ions are then accelerated to impact a position-sensitive microchannel plate detector (PSD). The PSD consists of two microchannel plates connected in series with a resistive anode. The active area of the PSD is approximately circular and roughly 25 mm in diameter. The PSD records both the arrival time of each ion, which can be related to the electric field strength at the time at which it is dissociated, as well as the position of its impact on the detector surface. Periodic tests were conducted to ensure that the voltage applied across the PSD was sufficient to saturate the observed ion count rates. The ion trajectories from the analysis region to the PSD were simulated using SIMION 3D v.8.0, a program that allows analysis of three-dimensional electrostatic lens systems.

Because the angular momentum, $L$, and the projection of the angular momentum along the $z$ (field) axis, $L_z$, of the bound ion pairs can take a wide range of values, it is not possible to uniquely determine the field needed to dissociate an ion-pair state of a specific binding energy. However, earlier work suggests that a “typical” value for the binding energy of states that undergo dissociation in a given field $F$ can be
estimated as

\[ E_B(\text{meV}) = 14[F(\text{kV cm}^{-1})]^{1/2} \] [82]

\[ (3.4) \]

### 3.6 Monte Carlo Simulation

To perform analysis on the collected experimental data, a Monte Carlo code was developed to model the initial conditions of the reactants, the behavior of the transient intermediate, and the motions of the final products [70]. The nearly free electron model for high-\(n\) Rydberg atoms allows for the collision between the Rydberg atom and the target gas molecule to be treated as a binary reaction between the Rydberg electron and the target gas molecule. As a result, the collision and the post-collision kinematics can be accurately modeled through semiclassical analysis. Because low-energy electron attachment can be treated as primarily an s-wave process, the free-electron capture cross section \(\sigma(v)\) is inversely proportional to the electron velocity [84]. Therefore, the electron attachment rate constant, \(k = v\sigma(v)\) is independent of \(v\). Consequently, the probability of electron transfer can be taken to be proportional to the electron probability density \(|\Psi|^2\). To compensate for the large quantum defect of K(\(np\)) states, (\(\delta \approx 1.7\)) the experimental data for a particular K(\(np\)) state are compared to model calculations performed using the K(n-2)p hydrogenic state.

The initial velocities of the reactants are chosen at random from their appropriate distributions. The initial velocities of the Rydberg atoms are taken from the velocity distribution discussed in detail in Section 3.2. The target gas molecules’ velocities are chosen from an isotropic Maxwell speed distribution, with each component chosen at random from the following Gaussian distribution:

\[ f_t(v) = \frac{1}{\sqrt{\pi\alpha}} e^{-\frac{v^2}{\alpha^2}} \]

\[ (3.5) \]
where $\alpha = \sqrt{\frac{2k_B T}{m}}$ is the most probable velocity and $m$ is the molecular mass.

Dissociative electron attachment is simulated by selecting an intermediate lifetime from the following distribution

$$P(t) \propto e^{-\frac{t}{\tau}}$$  \hspace{1cm} (3.6)

where $\tau$ is the mean lifetime, which in the species utilized in this work never exceeds 10 ps. The translational energy released during dissociation is then modeled using several different distributions (delta function, exponential decay, Gaussian, etc.) The exact form of the distribution to be expected depends on the lifetime of the intermediate and how efficiently the excess energy of the reaction can be distributed among the vibrational modes of the intermediate prior to dissociation. The relative total (kinetic plus potential) energy of the ion pair is then calculated. If the value is positive, the ions will overcome their mutual Coulomb attraction and separate. If the total energy is negative, a bound ion-pair state is formed, and its subsequent motion is followed. Ion-pair states that exit the gas cell through the slit are identified and their spatial distributions within the analysis region are calculated as a function of time for comparison to experimental data. Non-dissociative electron capture can be modeled with this code as well by treating the molecular ion as an intermediate with an infinite lifetime.
Chapter 4

Results and Analysis

In this work, several electron-attaching gases were used as targets: trifluoriodomethane (CF$_3$I), dibromomethane (CH$_2$Br$_2$), carbon tetrachloride (CCl$_4$), 1,1,1-trichlorotrifluoroethane (1,1,1−C$_2$Cl$_3$F$_3$), iron pentacarbonyl (Fe(CO)$_5$), bromotrichloromethane (CCl$_3$Br), cyanogen bromide (BrCN), sulfur hexafluoride (SF$_6$), and nitromethane (CH$_3$NO$_2$). These targets were selected because they illustrate the variety of different behaviors that can accompany electron attachment. Following electron transfer, the behavior of the product ion-pair states, specifically their angular distributions and lifetimes can vary significantly depending on many factors, including the excess energy of the reaction (which depends significantly on the electron affinity of the resultant negative ion as well as the energy needed to break its bond to the parent molecule,) the lifetime of the excited intermediate, the presence and nature of available decay channels, and the electron attachment process itself. Through use of the present experimental apparatus and the analysis tools described in the previous chapter, it is possible to uniquely characterize the specific reaction mechanisms operative for each target species as well as determine the parameters that govern each reaction, including the energetics, the lifetimes of the transient intermediates, and the branching ratios for different reaction pathways.

This chapter is divided into three sections. The first section describes results obtained using CF$_3$I, CCl$_4$, and SF$_6$, which provide well-studied examples of the different behaviors that might be expected for reference. In the second section, ion
pair formation is used to examine electron transfer to new target species (CH$_2$Br$_2$, 1,1,1 − C$_2$Cl$_3$F$_3$, Fe(CO)$_5$, CCl$_3$Br, and BrCN) that display a range of different behaviors. In the third section, the study of electron transfer to CH$_3$NO$_2$, a molecule capable of forming dipole-bound negative ions, is reviewed.

4.1 Model Reactions: CF$_3$I, CCl$_4$, and SF$_6$

4.1.1 CF$_3$I

Trifluoriodomethane (CF$_3$I) dissociatively attaches thermal energy electrons, resulting in the formation of I$^−$ and neutral CF$_3$ molecules [85] with an attachment rate constant of $\sim 2 \times 10^{-7}$ cm$^3$ s$^{-1}$ [86]. Collisions with a potassium Rydberg atom, therefore, lead to reactions of the form:

$$K(np) + CF_3I \rightarrow K^+ + CF_3I^− \rightarrow K^+ + I^- + CF_3$$

(4.1a)

$$\rightarrow K^+ \cdots I^- + CF_3$$

(4.1b)

The energy, $\varepsilon$, released through attachment is determined by the following:

$$\varepsilon = EA(I) - D_0(CF_3 - I) + E_{int} + E_k(e^-)$$

[85]

(4.2)

where EA(I) is the electron affinity of iodine (3.06 eV) [87], $D_0(CF_3 - I)$ is the dissociation energy of the CF$_3$−I bond (2.31 eV) [88], $E_k(e^-)$ is the kinetic energy of the transferred electron, which is small for $n \gtrsim 10$ [5], and $E_{int}$ is the usable internal vibrational energy in the parent molecule, which is small at room temperature. Use of these values suggests an excess energy of $\varepsilon \sim 0.75$ eV. This energy can be manifest as translational energy of the dissociation fragments, as rovibrational excitation of the neutral fragment, or as a combination of both.
Previous work has concluded, through time-of-flight analysis and measurement of the longitudinal velocities of free ions detected following attachment of thermal-energy electrons to CF$_3$I, that nearly all of this excess energy of the reaction appears as translational energy of the dissociation fragments [85, 71, 70]. Therefore, it can be concluded that the lifetime of the transient intermediate is very short, affording no opportunity for energy to be redistributed to the internal modes of the molecular ion. This is typically the result of the electron being captured into an anti-bonding molecular orbital, resulting in immediate dissociation. The translational energy release distribution resulting from such direct dissociation can be approximated by a narrow peak, centered on the excess energy. In contrast, longer intermediate lifetimes allow the excess energy of the reaction to be redistributed among the internal modes of the intermediate, resulting in a broader translational energy release distribution. In the limit of long intermediate lifetime, unimolecular decay theory predicts that the translational energy release distribution will be Boltzmann-like ($f(\epsilon) \propto e^{-\epsilon/\epsilon}$) [89].

Figure 4.1 shows calculated time dependences of the position distributions for K$^+$···I$^-$ ion pairs produced in K(14$p$)-CF$_3$I collisions. Figure 4.1a shows the distribution of ion pair positions calculated assuming that all the excess energy of reaction, $\sim 0.7$ eV, appears as translational energy in the fragments, with conservation of momentum dictating that the I$^-$ ion receives 35% of the energy. The calculation shows that the ion pairs move away from their point of formation over a broad range of scattering angles, $\theta$. Figure 4.1b shows the effect of broadening the translational energy release distribution while maintaining the same mean, using a Gaussian centered at 0.7 eV with a FWHM of 0.2 eV. Inspection shows the calculated spatial distribution of ion pairs is largely insensitive to this broadening.

Figures 4.1c-f display the calculated position distributions of K$^+$···I$^-$ ion pairs
Figure 4.1: Calculated time dependences of the position distributions for $K^+ \cdots I^-$ ion pairs formed in $K(14p)$-CF$_3$I collisions for a laser pulse width of 1 $\mu$s and the delay times, $t_D$, indicated. The assumed translational energy release distributions are indicated in the lower panel and comprise (a) a $\delta$-function at $\varepsilon = 0.7$ eV, (b) a Gaussian distribution of 0.2 eV FWHM centered on $\varepsilon = 0.7$ eV, (c) a linearly increasing distribution that peaks at 0.7 eV, (d) a distribution that is flat from 0 to 0.7 eV, (e) a distribution that decreases linearly to zero at 0.7 eV, and (f) a Boltzmann-like distribution with $\varepsilon = 0.3$ eV. In this figure, the color scale in each panel is adjusted to the maximum value in that panel. The arrows indicate the directions of the potassium and laser beams and the bottom left corner in each panel is at the center of the gas cell. Each panel covers an area of 3 cm $\times$ 3 cm.
that would be produced by various translational energy release distributions in which an increasing portion of the excess energy of reaction manifests as internal excitation of the intermediate negative ion, indicating an increasing lifetime of the intermediate. Proceeding from c to f, the mean translational energy released decreases, with Figure 4.1 showing the distribution obtained assuming a Boltzman-like translational energy release distribution, the statistical long lifetime limit. It can be observed that as the mean translational energy decreases, the average velocity of the \( K^+ \cdots I^- \) ion pairs decreases and the angular distributions become more strongly forward peaked with respect to the initial trajectory of the potassium Rydberg atoms.

These trends can be explained kinematically. In the case of a narrow translational energy release distribution centered near the calculated excess energy of reaction, the mean velocity of the iodine anion upon dissociation of the intermediate will be \( \sim 600 \) m/s in the rest frame of the intermediate. This is much larger than the velocity of the original \( \text{CF}_3\text{I} \) molecule (\( \sim 200 \) m/s), so it can be concluded that the range of velocities of the iodine ion in the lab frame will be narrow. As can be seen in Figure 3.2, the peak velocity of the Rydberg atom beam is \( \sim 500 \) m/s, similar to that of the iodine ions. For the Rydberg core ion and the iodine ion to remain bound, their kinetic energy of relative motion, \( T_{rel} \), must be smaller than the potential energy of their mutual Coulomb attraction, so ion pairs with low \( T_{rel} \) are more likely to remain bound. On average, \( T_{rel} \) is minimized when both ions are moving in the same direction, i.e. when the \( I^- \) ion is formed moving in the original direction of the Rydberg atom. This explains why the distribution of bound ion pairs is strongly forward peaked. As can be seen in Figure 4.2, as the scattering angle, \( \theta \), increases, the binding energies of the ion pairs trend toward lower values. This is consistent with previous work, which measured a maximum in the production of free \( I^- \) ions
Figure 4.2: Dependence of the angular distribution of $K^+ \cdots I^-$ ion pairs formed in $K(14p)$-CF$_3$I collisions on ion pair binding energy. The range of binding energies corresponding to each curve are as indicated. The results assume a $\delta$-function translational energy release distribution with $\varepsilon = 0.7$ eV.
when the angle of relative motion of the ions, $\phi$, was $180^\circ$ [90].

As the mean translational energy released upon dissociation of the intermediate is reduced, the velocity distribution of bound ion pairs peaks at lower values and becomes more strongly forward peaked. This is explained by the increasing disparity between the velocities of the $\text{I}^-$ ions and the velocities of the Rydberg atoms. In the limit of a Boltzmann-like distribution with a mean energy $\epsilon = 0.3$ eV, the final $\text{I}^-$ velocity distribution peaks at $\sim 300$ m/s, significantly lower than the peak velocity of the Rydberg atom. As a result, the velocity of bound ion pairs is significantly slower than observed with a $\delta$-function distribution. Furthermore, because the larger relative velocity of these ion pairs implies larger kinetic energy of relative motion, the product ion pairs that remain bound have a significantly smaller range of angles of relative motion, $\phi$, resulting in more strongly forward peaking than is observed with a $\delta$-function distribution.

Figure 4.3 showcases our attempt to gauge the sensitivity of the ion pair spatial distribution to the lifetime of the $\text{CF}_3\text{I}^-\ast$ intermediate. Shown are the ion pair distributions as calculated using the extreme possibilities for the translational energy release distribution: a $\delta$-function and a Boltzmann-like distribution. The calculations are insensitive for intermediate lifetimes on the order of tens of picoseconds. Only when the lifetime becomes a significant fraction of the Kepler orbital periods of the $\text{K}^+ \cdots \text{Cl}^-$ ion pairs do we observe significant broadening. Therefore, analysis of arrival position distributions does not provide a sensitive direct measure of the lifetime of shorter-lived intermediates.

Figure 4.4 shows the arrival position distributions recorded at the PSD following $\text{K}(14p)\text{-CF}_3\text{I}$ collisions for several different delay times together with the results of model calculations. The simulations assume a laser pulse width of $\sim 10$ $\mu$s, as used
Figure 4.3: Calculated arrival position distributions for $K^+ \cdots I^-$ ion pairs formed in $K(14p)$-CF$_3$I collisions and the CF$_3$I$^-$ intermediate lifetimes indicated. The results are for a delay time $t_D = 30$ $\mu$s and assume (a) a $\delta$-function translational energy release distribution or (b) a Boltzmann-like distribution with $\bar{\epsilon} = 0.3$ eV. The other conditions are as in Figure 4.1.
Figure 4.4: Arrival position distributions at the PSD for K^+ \cdots \text{I}^- ion pairs with binding energies \lesssim 30 \text{ meV} formed in K(14p)-CF_3I collisions. The laser pulse width is \sim 10 \mu s and the delay times, \( t_D \), indicated are measured from the end of the laser pulse. As illustrated at the bottom of the figure, the white lines denote the area viewed by the PSD and the scattering angles defined by the slit at the entrance to the analysis region. The experimental results are shown in the left hand panels. The corresponding simulations for (a) a \( \delta \)-function translational energy release distribution with \( \varepsilon = 0.7 \) eV, (b) a rectangular distribution flat from \( \varepsilon = 0 \) to 0.7 eV, and (c) a Boltzmann-like distribution with \( \overline{\varepsilon} = 0.3 \) eV are also included. The other conditions are as in Figure 4.1.
in the experiment. Given the short Rydberg lifetime (as compared to the laser pulse width), \( \sim 2 \mu s \), it is reasonable to assume that the production of Rydberg atoms is constant throughout the duration of the pulse. To model the experimental results, the calculated distributions were restricted to ion pairs with binding energies sufficiently low (< 30 meV) that they could be dissociated in the range of fields that could be generated in the analysis region. The measured arrival position distributions are in good agreement with those calculated when assuming that nearly all the excess energy of reaction appears in translation. Therefore, it can be concluded that the thermal-energy electron attachment to CF$_3$I results in near-immediate dissociation of the intermediate negative ion, corresponding to direct electron capture into an antibonding orbital.

4.1.2 CCl$_4$

Thermal-energy electron collisions with carbon tetrachloride (CCl$_4$) lead to dissociative electron attachment and production of Cl$^-$ ions [91]. Given the Cl electron affinity of \( \sim 3.6 \) eV and the CCl$_3$-Cl bond dissociation energy of 3.07 eV, the excess energy of the reaction is \( \sim 0.5 \) eV. Previous studies of Rydberg electron transfer reactions with CCl$_4$

\[
K(np) + \text{CCl}_4 \rightarrow \text{K}^+ + \text{CCl}_4^{-*} \rightarrow \text{K}^+ + \text{Cl}^- + \text{CCl}_3 \\
\text{K}^+ \cdots \text{Cl}^- + \text{CCl}_3
\]  

(4.3a)  

(4.3b)

have shown that the intermediate negative ion CCl$_4^{-*}$ is long-lived, with a lifetime of \( \sim 7.5 \) ps [66]. Additionally, it has been previously determined that the mean translational energy released is \( \sim 0.1 \) eV [67], indicating that this lifetime is sufficiently long to allow efficient redistribution of the excess energy of the reaction within the
intermediate prior to dissociation. As a result, the translational energy release distribution can be accurately approximated as Boltzmann-like \( f(\varepsilon) \propto e^{-\varepsilon/\varepsilon_0} \) where \( \varepsilon = 0.1 \) eV \([11, 65, 92]\). Model predictions assuming such a translational energy release distribution agree well with experiment.

To illustrate this, Figure 4.5 compares the measured K\(^+\cdots\)Cl\(^-\) ion pair position distributions with calculated results produced using \( \delta \)-function, rectangular, and Boltzmann-like translational energy release distributions. Because of the small mass of the Cl\(^-\) ion, it receives most of the translational energy released upon dissociation of the intermediate, so even with a Boltzmann-like translational energy release distribution the product Cl\(^-\) ions have sizable velocities and good velocity matching will typically only be achieved with Rydberg atoms on the high end of their thermal velocity distribution. Since near colinear trajectories of the ions are necessary to minimize \( T_{rel} \), it can be inferred that the bound ion-pair distribution will be strongly forward peaked. Comparison of theory with experiment shows good agreement between the experimental results and model distributions calculated assuming a Boltzmann-like translational energy release distribution, pointing to formation of intermediate ions with long lifetimes compared to the vibrational periods of its internal modes.

**4.1.3 SF\(_6\)**

Sulfur hexafluoride (SF\(_6\)) has a large electron affinity \( (\sim 1 \) eV \([93]\)), so capturing an electron releases a significant amount of energy. However, unlike the previous two species, SF\(_6\) does not undergo dissociative electron attachment when capturing thermal-energy electrons. Instead, the excited SF\(_6^*-\) ion undergoes intramolecular vibrational relaxation (IVR), in which the excess energy of reaction is distributed among the vibrational modes of the molecular ion. This redistribution of energy suppresses
Figure 4.5: (a) Calculated arrival position distributions for $K^+ \cdots Cl^-$ ion pairs formed in $K(14p)$-CCl$_4$ collisions for a laser pulse width of 1 µs and a delay time of 20 µs. The assumed translational energy release distributions comprise (i) a δ-function at $\varepsilon = 0.5$ eV, (ii) a rectangular distribution flat from 0 to 0.5 eV, (iii) a Boltzmann-like distribution with $\bar{\varepsilon} = 0.1$ eV. The intermediate lifetime is taken to be zero. (b) Comparison of theory to experiment. The laser pulse duration is 20 µs and the delay times $t_D$ are as indicated. The experimental results are shown in the left hand panels. The right hand panels show simulations for (iv) the rectangular and (v) the Boltzmann-like distributions used in (a). (For the δ-function distribution the product ion pairs have passed beyond the region viewed by the PSD by $t_D = 30$ µs.) All other conditions are as in Figure 4.4.
autodetachment because of the small likelihood of the energy being reconcentrated in a mode from which dissociation can occur. As a result, autodetachment lifetime can extend from several tens of microseconds when capturing suprathermal electrons to over 1 ms when capturing thermal and subthermal electrons [77].

Earlier studies of ion-pair states formed through collisions of Rydberg atoms with SF$_6$ molecules through the reaction

$$K(np) + SF_6 \rightarrow K^+ + SF_6^- \rightarrow K^+ \cdots SF_6^-$$  \hspace{1cm} (4.4)

have revealed that these states have lifetimes ranging from $\sim 1-20$ $\mu$s, and that they decay through one of two mechanisms: internal-to-translational energy conversion allowing the ions to separate as ions, and near-resonant charge transfer resulting in the two ions separating as neutrals [94, 63, 65]. However, the timescales of these earlier measurements, $\sim 1-10$ $\mu$s, were significantly smaller than those studied in this work and were therefore more sensitive to the decay of short-lived K$^+ \cdots$SF$_6^-$ states. Previous work has also observed a trend in which ion-pair lifetimes increase with decreasing ion pair binding energy [65, 92].

Figure 4.6 presents measured and calculated position distributions for K$^+ \cdots$SF$_6^-$ ion-pair states formed in K(12p)-SF$_6$ collisions, with binding energies in the range from $\sim 3$ to 40 meV for several different delay times. The measured and calculated distributions are rendered using two different normalizations: normalization to the peak signal in each distribution on the left-hand side to emphasize the shapes of the distributions, and normalization to the peak signal in each series on the right-hand side to emphasize decay of the total signal with time. Inspection of the data shows that the arrival position distribution is, like the distributions seen using the previous two species, strongly forward peaked. Additionally, because of the large mass of the SF$_6^-$ ion, the ion pairs formed have velocities significantly smaller than those seen
Figure 4.6: Position distributions for K$^+ \cdots$SF$_6^-$ ion pairs formed in K(12p)-SF$_6$ collisions. The ion pairs have “typical” binding energies of $\sim 3 - 40$ meV and the data were recorded following the time delays, $t_D$ indicated. The white lines denote the area viewed by the PSD and the lower left corner in each panel corresponds to the center of the gas cell. The distributions shown in the left-hand two columns are normalized to the peak signal seen in each distribution, while those in the right-hand two columns are normalized to the peak signal observed within each series. The results in columns (a) and (c) are experimental data. The results of model calculations that assume the K$^+ \cdots$SF$_6^-$ lifetimes shown in the inset in Fig. 4.7 are presented in (b) and (d).
with the other two species. Finally, the fact that a significant signal is detected at delay times as large as 100 μs demonstrates that Rydberg electron transfer can lead to the production of longer-lived ion-pair states than previous studies would suggest. In order to determine the relationship between binding energy and lifetime, calculations were performed using different binding energy ranges and assumed lifetimes and compared to the experimental data. The best fits between these calculations and the experimental data are shown in Figure 4.7 and were obtained using the lifetimes shown in the inset. It is clear that the ion pair lifetime increases with decreasing binding energy, the same trend as observed in previous work [65]. The best fit calculations show that the lifetimes of the ion pair states can vary from ∼ 140 to 40 μs over the binding energy range encompassed by the measured distributions.

In order to determine which of the two possible decay mechanisms (internal energy conversion or charge transfer) was chiefly responsible for the destruction of the ion-pair states, measurements were conducted in which a small dc field (∼ 45 V cm⁻¹) was applied across the analysis region rather than a pulse, in order to look for the free K⁺ ion signal that would result from dissociation of bound ion pairs through conversion of the internal energy of the SF₆⁻ ion into translational energy. However, no such signal was found. Therefore, it can be concluded that the majority of the free particles produced through ion-pair decay are neutrals, indicating that near-resonant charge transfer is the chief cause of the loss of these long-lived ion-pair states. This is consistent with the fact that the more tightly bound ion-pair states are in closer proximity to each other, which facilitates near-resonant charge transfer, resulting in shorter lifetimes.
Figure 4.7: K$^+$ ion signal resulting from dissociation of K$^+$···SF$_6^-$ ion pairs formed in K(12p)-SF$_6$ collisions as a function of delay time $t_D$ for the “typical” binding energy ranges indicated. The data sets are normalized to unity at a delay of 40 µs. The solid symbols show experimental data, the lines show the best fits to the experimental data obtained using the present model and which correspond to the lifetimes indicated. The inset shows these lifetimes expressed as a function of average binding energy together with the straight line fit which is used in computing the model predictions present in Fig. 4.6.
4.2 Species that highlight different behaviors

4.2.1 CH$_2$Br$_2$

Like the other brominated methanes, dibromomethane (CH$_2$Br$_2$) has a large rate constant for dissociative thermal-energy electron capture, resulting in the formation of Br$^-$ ions. Thus, collisions with Rydberg atoms lead to electron transfer reactions of the type

$$K(np) + CH_2Br_2 \rightarrow K^+ + CH_2Br^- \rightarrow K^+ + Br^- + CH_2Br$$

$$\rightarrow K^+ \cdot Br^- + CH_2Br$$ (4.5a)

The electron affinity of Br is $\sim$ 3.36 eV and the CH$_2$Br-Br bond dissociation energy is $\sim$ 3.06 eV [95], so the excess energy of reaction is about $\sim$ 0.3 eV. If the intermediate undergoes immediate dissociation, the velocity of the Br$^-$ ion in the rest frame of the intermediate, will be comparable to the mean initial velocity of the Rydberg atoms, leading to similar velocity distributions as for CF$_3$I.

Inspection of Figure 4.8 reveals reasonable agreement between the measured position distributions of K$^+ \cdot Br^-$ ion pairs and the distributions calculated assuming that all excess energy appears in translation. Therefore, it can be concluded that, as for CF$_3$I, the CH$_2$Br$_2^-$ intermediate is very short-lived.

4.2.2 1,1,1-C$_2$Cl$_3$F$_3$

Collisions between Rydberg atoms and 1,1,1-C$_2$Cl$_3$F$_3$ molecules result in the formation of K$^+ \cdot Cl^-$ ion-pair states through dissociative electron transfer reactions of
Figure 4.8: Arrival position distributions at the PSD for K⁺ ⋯ Br⁻ ion pairs formed in K(14p)-CH₂Br₂ collisions and the delay times indicated. The experimental results are shown in the left hand panels. The right hand panels show simulations for (a) a δ-function translational energy release distribution with \( \varepsilon = 0.3 \) eV, (b) a rectangular distribution flat from \( \varepsilon = 0 \) to 0.3 eV, and (c) a Boltzmann-like distribution with \( \varepsilon = 0.1 \) eV. The intermediate lifetime is taken to be zero. The other conditions are as in 4.4.
the type

\[
K(np) + C_2Cl_3F_3 \rightarrow K^+ + C_2Cl_3F_3^- \rightarrow K^+ + Cl^- + C_2Cl_2F_3 
\]

\[
\rightarrow K^+ \cdots Cl^- + C_2Cl_2F_3 
\]

(4.6a)  (4.6b)

Given the electron affinity of Cl of $\sim 3.6$ eV and the reported values for the $C_2Cl_2F_2$-Cl bond dissociation energy of 3.08 eV and 3.19 eV [96], an excess energy of reaction of $\sim 0.5$ eV is expected.

Figure 4.9: (a) Measured arrival position distribution for $K^+ \cdots Cl^-$ ion pairs formed in K(12p)-C_2Cl_2F_3 collisions and the time delays $t_D$ indicated. The distributions in this time-dependent series are normalized to the peak value within the series. The figure also includes arrival positions derived assuming (b) a Gaussian distribution of 0.1 eV FWHM and $\bar{e} = 0.5$ eV, (c) the same distribution as in (b) but with $\bar{e} = 0.35$ eV, (d) a triangular distribution that increases linearly from 0 at $\varepsilon = 0$ to a maximum at $\varepsilon = 0.35$ eV, (e) a triangular distribution that decreases linearly from a maximum at $\varepsilon = 0$ to 0 at $\varepsilon = 0.35$ eV, (f) a rectangular distribution that extends from 0 to 0.35 eV, and (g) a Boltzmann-like distribution with $\bar{e} = 0.05$ eV.

Figure 4.9 shows the measured arrival position distributions for $K^+ \cdots Cl^-$ ion pairs as well as distributions predicted using a narrow Gaussian translational energy
release distribution of FWHM 0.1 eV centered on the mean value $\bar{\varepsilon} = 0.5$ eV. Use of this value of $\bar{\varepsilon}$ results in ion pair velocities larger than those observed, but when a similar distribution centered at $\bar{\varepsilon} = 0.35$ eV, a value slightly less than what the thermochemical data predicts, is used, the result is in better agreement with the observed distribution. This agreement suggests that most of the intermediate negative ions are short-lived. However, careful inspection of the measured distribution reveals the presence of a low-velocity component that is not predicted using a simple Gaussian distribution, suggesting it is possible that the electron capture can also lead to the formation of intermediates with lifetimes sufficient to allow at least partial redistribution of the excess energy of reaction prior to dissociation. This question is examined further in Figure 4.9, which also includes distributions calculated using a variety of different trial translational energy release distributions that allow for various degrees of redistribution of the excess energy. The best agreement with the measured long-lived component is reached through the use of a triangular distribution that peaks at $\varepsilon = 0$ and decreases linearly to 0 at $\varepsilon = 0.35$ eV.

A good overall fit to the total distribution can be achieved through a linear combination of this decreasing triangular distribution and the short-lived Gaussian distribution centered at $\bar{\varepsilon} = 0.35$ eV, with the relative weight of each component being varied to best fit the observed data. The quality of the fit can be gauged through both the position distributions, as seen in Figure 4.10 and through the total ion signal vs. delay time, as seen in Figure 4.11. While the data are not especially sensitive, to the calculated relative weight, they do suggest that anywhere from 70% to 90% of attachment events that produce detectable ion pairs produce short-lived intermediates that undergo direct dissociation. These findings are consistent with measurements of free Cl$^-$ ions created through collisions of C$_2$Cl$_3$F$_3$ with high-$n$ Rydberg atoms, where
Figure 4.10: (a) Measured arrival position distribution for K$^+ \cdots$Cl$^-$ ion pairs formed in K(12p)-C$_2$Cl$_2$F$_3$ collisions and the time delays $t_D$ indicated. (b)-(d) Predictions of model calculations which assume that capture results from a combination of direct dissociation (DD) resulting in the translational energy release distribution seen in Fig. 4.9(c) and from partial redistribution (PR) of this energy to internal motions resulting in the distribution seen in Fig. 4.9(e). The percentage contributions from each channel are (b) 100% DD, (c) 100% PR, (d) 50% DD - 50% PR, (e) 70% DD - 30% PR, (f) 85% DD - 15% PR.
Figure 4.11: •, total K$^+$···Cl$^-$ ion signal recorded at the PSD as a function of time delay. The lines show the results of model calculations that employ different relative contributions from the same two reaction channels as used in Fig. 4.10. The labels (b)-(f) correspond to the same relative contributions as in Fig. 4.10.
post-attachment electrostatic interactions can be neglected [61]. Theoretical analysis in this earlier work suggests that the excess charge on the intermediate should reside primarily on the Cl end of the molecular ion. If capture at this end results in direct dissociation, this would serve to explain the dominance of the high-velocity component in the ion-pair position distribution. Electron attachment to the F group is possible, but direct dissociation to form an F\(^-\) ion is not possible due to the larger bond dissociation energy [96]. Any electron captured on the F group must therefore transfer to the Cl group before dissociation, allowing for some energy redistribution.

4.2.3 CCl\(_3\)Br

Thermal electron attachment to CCl\(_3\)Br leads to dissociation channels that can produce both Cl\(^-\) and Br\(^-\) ions with the Br\(^-\) production being dominant [97, 98]. Collisions with low-\(n\) Rydberg atoms can therefore lead to ion pair formation via the following reactions.

\[
K(np) + \text{CCl}_3\text{Br} \rightarrow K^+ \cdots \text{CCl}_3\text{Br}^-* \rightarrow K^+ \cdots \text{Br}^- + \text{Cl}_3 \\
\rightarrow K^+ \cdots \text{Cl}^- + \text{CBrCl}_2
\]

The electron affinities of bromine and chlorine are 3.37 eV and 3.61 eV respectively [99]. Previous studies of Rydberg atom collisions at higher \(n\) have determined the energy necessary to dissociate the CCl\(_3\)-Br bond to be \(\sim 2.7\) eV [100], suggesting the excess energy of the Br\(^-\)-producing reaction to be \(\sim 0.7\) eV. Theoretical calculations yield an approximate value for the CCl\(_2\)Br-Cl bond dissociation energy of \(\sim 3.60\) eV [100], so the excess energy of the Cl\(^-\)-producing reaction is \(\lesssim 0.1\) eV. Free-electron studies have shown that the Br\(^-\) reaction is dominant at room temperature, though a large increase in Cl\(^-\) production was noted with increasing temperature. This was
attributed to a small $\sim 50$ meV activation energy to the Cl$^-$ formation channel [33].

Figure 4.12: (a) Measured arrival position distribution for ion pairs formed in K(12p)-CCl$_3$Br collisions via reactions 4.7a and 4.7b. The figure includes separate model predictions for the formation of ((b) and (c)) K$^+$···Br$^-$ ion pairs and (d)-(g) K$^+$···Cl$^-$ ion pairs. These distributions assume (b) a Gaussian distribution of 0.015 eV FWHM centered on $\varepsilon = 0.7$ eV, (c) a Boltzmann-like distribution with $\overline{\varepsilon} = 0.15$ eV, (d) a Gaussian distribution of 0.075 eV FWHM centered on $\varepsilon = 0.3$ eV, (e) a Gaussian distribution of 0.075 eV FWHM centered on 0.075 eV, (f) a rectangular distribution with $\overline{\varepsilon} = 0.075$ eV, and (g) a Boltzmann-like distribution with $\overline{\varepsilon} = 0.03$ eV. (h) Predictions of model calculations which assume that 70% (30%) of attachment events lead to K$^+$···Br$^-$ (K$^+$···Cl$^-$) formation via a long-lived (short-lived) intermediate state.

Since the current apparatus produces distributions through the collection of positive ions, it is impossible to separately identify the two reaction channels. However, as Figure 4.12 shows, it is possible to separately calculate distributions for the two reaction channels, assuming various intermediate lifetimes, and producing a linear combination of these distributions to best fit the experimental data. Previous work has determined that K$^+$···Br$^-$ is the dominant reaction channel at room temperature. Calculated position distributions for ion pairs produced via this reaction channel with a Gaussian translational energy release distribution centered at $\varepsilon = 0.7$ eV, implying
a short-lived intermediate that undergoes direct dissociation, are in poor agreement with the experimental data, with the ion pairs having larger velocities than what the experimental data suggest. Therefore it can be concluded that intermediates that dissociate to produce Br$^-$ ions must be long-lived. This is corroborated by the much better agreement that is achieved by using a Boltzmann-like distribution with $\bar{e} = 0.15$ eV, which shows much better agreement with the experimental data.

Previous work has shown that agreement with experimental and calculated distributions of K$^+$···Cl$^-$ ion pairs could be achieved using a Gaussian translational energy release distribution centered on $\bar{e} = 0.075$ eV or using a rectangular translational energy release distribution with a mean energy $\bar{e} = 0.075$ eV, but agreement was poor when attempting to fit the experimental data with any distribution calculated using a Boltzmann-like translational energy release distribution [100, 97]. These results indicate that intermediates that dissociate to form Cl$^-$ ions are insufficiently long-lived to allow for full statistical distribution of the excess energy of reaction. Figure 4.12 shows that the collected arrival position distributions with this apparatus are consistent with earlier findings. As a result of the small excess energy of reaction of the Cl$^-$-producing reaction channel, the apparatus cannot significantly differentiate the position distributions produced using Gaussian and rectangular distributions. However, these distributions are in significantly better agreement with the experimental data than the distribution produced using a Boltzmann-like translational energy release distribution. Therefore, it can be concluded that when CCl$_3$Br dissociates to produce to Cl$^-$ ions, the intermediate has a shorter lifetime than when the dissociation produces Br$^-$ ions.

Previous theory has suggested that a large portion of the charge is located on the Cl site of the intermediate and the electron is captured into an antibonding orbital.
However, the low excess energy of reaction coupled with a 50 meV potential barrier reduces the probability of rapid dissociation to form Cl$^-$ ions, allowing for energy to be redistributed among the vibrational modes of the intermediate, and permitting the formation of Br$^-$ ions [33]. Various linear combinations of K$^+ \cdots$Cl$^-$ ion pairs produced by short-lived intermediates and K$^+ \cdots$Br$^-$ ion pairs produced by long-lived intermediates have been calculated to achieve a best fit to the experimental data in the hopes of determining the branching ratio of the two reaction channels. Good overall fit to the experimental data can be achieved by assuming that $\sim 70\%$ of collisions lead to the production of K$^+ \cdots$Br$^-$ ion pairs through dissociation of a long-lived intermediate and $\sim 30\%$ lead to creation of K$^+ \cdots$Cl$^-$ through dissociation of short-lived intermediates.

4.2.4 Fe(CO)$_5$

Rydberg atom collisions with iron pentacarbonyl can result in thermal-energy electron transfer producing K$^+ \cdots$Fe(CO)$_4^-$ ion-pair states via the following reaction.

$$K(np) + Fe(CO)_5 \rightarrow K^+ + Fe(CO)_4^{-*} \rightarrow K^+ \cdots Fe(CO)_4^- + CO \quad (4.8)$$

The dissociation energy of the Fe(CO)$_4$-CO bond is not well known, with values of $1.8 \pm 0.5$ eV [101] and $2.4 \pm 0.3$ eV [102] having been reported. With an electron affinity Fe(CO)$_4$ of $\sim 2.4$ eV [102], the expected excess energy of reaction is $\sim 0.6$ eV, but the large uncertainty in the bond dissociation energy will result in large uncertainty in the excess energy of reaction.

Figure 4.13a presents the measured position distributions for K$^+ \cdots$Fe(CO)$_5^-$ ion-pair states formed in K(12p)-Fe(CO)$_5$ collisions. The Fe(CO)$_4^-$ ion is significantly larger ($\sim 168$ amu) than other ions featured in this work produced by dissociative
electron transfer. As a result, upon dissociation, the majority of the translational energy is imparted to the CO neutral. Therefore, the velocity of the Fe(CO)$_4^-$ fragment is largely unchanged, rendering the resulting ion pair position distribution largely insensitive to the choice of translational energy release distribution as can be seen in Figure 4.13c-e. Inspection of the measured position distribution and the calculated position distributions produced using a Boltzmann-like translational energy release distribution, shown in Figure 4.13c, reveals reasonable agreement. However, long-lived intermediates lead to negative ions with significant internal energy and, as was shown with SF$_6$, internal energy can result in ion-pair states dissociating via internal-to-translational energy conversion and near-resonant charge transfer. Figure 4.13b presents the calculated position distributions assuming a Boltzmann-like translational energy release distribution assuming ion-pair lifetimes equal to those of K$^+ \cdots$SF$_6$ ion-pair states. These results are in poor agreement with the measured results, with the predicted ion-pair signal diminishing significantly more quickly than the measured signal, leading to the conclusion that the lifetimes of the K$^+ \cdots$Fe(CO)$_5^-$ ion-pair states are significantly longer than those formed by Rydberg atom collisions with SF$_6$. Figure 4.13c shows the predicted ion pair position distributions using the same translational energy release distribution and the best fit ion pair lifetime of 50 µs.

A Boltzmann-like distribution is the form the translational energy release distribution takes in the limit of long lifetime of the transient intermediate negative ion. In this limit, it is expected for the excess energy of reaction released by the electron attachment to have undergone full statistical redistribution among the molecular ion’s vibrational modes prior to dissociation. Non-linear molecules have 3N-6 normal vibrational modes, where N is the number of atoms in the molecule [103]. Fe(CO)$_5$ has
27 normal vibrational modes. Therefore, assuming full statistical redistribution, for a mean translational energy release $\bar{\varepsilon} = 0.2$ eV, the total excess energy of reaction should be $E_E = 27 \times \bar{\varepsilon} \sim 5$ eV. This value is well outside the anticipated range for the excess energy of reaction. Therefore, it is unlikely the intermediate is sufficiently long-lived to allow full statistical redistribution of this energy. However, an intermediate sufficiently long-lived to allow partial distribution of the excess energy is still possible. Comparision of the measured position distributions with calculated position distributions produced assuming a rectangular translational energy release distribution centered at $\bar{\varepsilon} = 0.2$ eV and a 50 $\mu$s ion-pair lifetime, is shown in Figure 4.13d. An additional set of ion pair position distributions was calculated assuming a Gaussian translational energy release distribution centered at $\varepsilon = 0.2$ eV with a FWHM of 0.05 eV and a 50 $\mu$s ion-pair lifetime, as shown in Figure 4.13e. Though such a distribution assumes no internal redistribution of the excess energy of reaction, decay of the ion-pair state by internal energy conversion is still possible because at room temperature the target molecules still contain significant internal energy ($\sim 0.25$ eV) for dissociation, thereby reducing ion pair lifetimes. Based on the strong agreement of these position distributions with the measured ion pair position distributions, it can be concluded that thermal electron attachment to Fe(CO)$_5$ results in fairly rapid dissociation of the transient intermediate ion (on a timescale of a few vibrational periods). The agreement also points to an excess energy of reaction $\lesssim 0.4$ eV.

4.2.5 BrCN

Dissociative electron transfer to cyanogen bromide (BrCN) can lead to formation of bound $K^+ \cdots CN^-$ ion pairs via the reaction.

$$K(np) + BrCN \rightarrow K^+ + BrCN^* \rightarrow K^+ \cdots CN^- + Br$$ (4.9)
Figure 4.13: (a) Measured arrival position distributions for $K^+ \cdots \text{Fe(CO)}_4^-$ ion pairs produced in K(12p)-Fe(CO)$_5$ collisions. The figure includes model predictions obtained assuming Boltzmann-like distributions with $\varepsilon = 0.2$ eV and (b) ion-pair lifetimes equal to those of $K^+ \cdots \text{SF}_6^-$ ion pairs, (c) a fixed timeline $\tau = 50 \mu$s, (d) a rectangular distribution with $\varepsilon = 0.2$ eV and $\tau = 50 \mu$s, and (e) a Gaussian distribution of 0.05 eV FWHM centered on $\varepsilon = 0.2$ eV and $\tau = 50 \mu$s.
Being a pseudohalogen, the CN radical has a large electron affinity: $\sim 3.86$ eV [99]. Thermochemical and photodissociation measurements have determined the dissociation energy for the Br-CN bond to be $\sim 3.70$ eV [104]. Therefore, the energy released via electron capture is $\sim 0.2$ eV.

As with SF$_6$, previous work has shown that the lifetimes of ion-pair states formed by collisions between Rydberg atoms and BrCN molecules are dependent on their binding energies, though the nature of the dependence is different from that which is observed with K$^+ \cdots$SF$_6^-$ states. K$^+ \cdots$CN$^-$ states with binding energies of $\sim 9$ meV decayed after an average lifetime of 7 $\mu$s. States with binding energies of $\sim 20$ meV decayed after an average lifetime of 25 $\mu$s. No significant decay was observed for states with binding energies greater than 30 meV [65]. Decay via mutual neutralization is highly exothermic ($\sim 0.5$ eV), and such a nonresonant process would occur too seldom to explain this behavior. However, CN$^-$ has a significant dipole moment ($\mu \sim 0.6$ D) [105]. This allows for rotational energy in the CN$^-$ ion to be converted into translational energy through long-range, dipole-allowed $J \rightarrow J - 1$ rotational transitions in the CN$^-$ ion. The CN$^-$ rotational constant, $B$, is $\sim 0.23$ eV, so the conversion of $\sim 10$ meV of internal energy would result from a $J \sim 18 \rightarrow J \sim 17$ transition. The existence of rotationally excited CN$^-$ ions as a result of dissociative attachment of thermal energy electrons is not unreasonable. Threshold ion-pair production spectroscopy of HCN was shown to produce “rotationally hot” CN$^-$ ions, with the distribution of rotational excitation peaking at $J \sim 12$ [106].

Figure 4.14 shows the measured and calculated ion pair position distributions for K$^+ \cdots$CN$^-$ ion pairs produced in collisions between K(12p) Rydberg atoms and BrCN molecules. The calculated ion-pair position distributions were produced using binding energy distributions weighted to account for the lifetime dependence described previ-
Figure 4.14: (a) Measured arrival position distributions for $K^+ \cdots CN^-$ ion pairs produced in $K$(12p)-BrCN collisions. The figure includes model predictions obtained using the measured $K^+ \cdots CN^-$ ion pair lifetimes assuming (b) a Gaussian distribution of 0.05 eV FWHM centered on $\varepsilon = 0.2$ eV, (c) a Gaussian distribution of 0.05 eV FWHM centered on $\varepsilon = 0.1$ eV, (d) and (e) Boltzmann-like distributions with $\varepsilon = 0.05$ and 0.1 eV, respectively, and (f) a distribution that assumes an excess energy $E_E = 0.14$ eV and a CN$^-$ rotational temperature of 600 K.
ously. Figures 4.14b-c contain calculated distributions produced assuming Gaussian translational energy release distributions centered on $\varepsilon = 0.2$ eV and $\varepsilon = 0.1$ eV, respectively, typical of a short-lived intermediate and direct dissociation. However, neither set of distributions provides results in agreement with the experimental results, confirming that even if the translational energy release distribution is centered on a value other than the excess energy of reaction, a model involving the direct dissociation of a short-lived intermediate does not provide a good fit to the data.

Figure 4.14 also features calculated distributions produced using Boltzmann-like translational energy release distributions, i.e., assuming a sufficiently long-lived intermediate to allow for a full statistical redistribution of the excess energy of reaction, with Figures 4.14d-e containing calculated distributions produced using such translational energy distributions with mean energies $\bar{\varepsilon}$ of 0.05 and 0.1 eV, respectively. The agreement using such a model is also poor (though better than what is observed when Gaussian translational energy release distributions are used), but inspection of the energetics of the molecule reveals this is not unexpected. The excess energy of reaction is $\sim 0.2$ eV. A Boltzmann-like translational energy release distribution implies full statistical redistribution of this energy among the internal modes of the BrCN$^{-*}$ transient intermediate ion. However, the vibrational spacing of the C-N stretch mode is $\sim 0.27$ eV [107], larger than the energy available, so this mode is not significantly excited in the CN$^{-}$ ions formed upon dissociation of the transient intermediate ion. However, the vibrational spacing of the bending mode is only $\sim 0.04$ eV, so it can become highly vibrationally excited by the excess energy of reaction. Upon dissociation of the intermediate, this vibrational excitation manifests as rotation of the resulting CN$^{-}$ ion. Therefore, analysis of the position distributions of bound K$^{+} \cdots$ CN$^{-}$ ion-pair states can provide information about the rotational excitation of the CN$^{-}$ ion as
well as the lifetime of the intermediate.

Since the excess energy of reaction following dissociation of the intermediate negative ion can only be transported away through rotational excitation of the CN$^-$ ion, a Boltzmann-like translational energy release distribution does not serve as a realistic model for the energetics of the dissociation of the intermediate. A Boltzmann-like distribution peaks at $\varepsilon = 0$. This necessitates the preferential population of highly rotationally excited states over less rotationally excited states. CN$^-$ has a rotational constant $B \sim 0.23$ meV [108]. With rotational energy given by $\varepsilon = BJ(J + 1)$, a rotational energy distribution peaking at $\varepsilon \sim 0.2$ eV implies a peak rotational quantum number $J \sim 28$ and a rotational temperature of $T \sim 2300$ K, which is unreasonably high. Furthermore, a translational energy release distribution peaking at $\varepsilon = 0$ implies a rotational energy distribution peaking at the excess energy of reaction and then abruptly dropping to zero at higher energies. A mechanism that would produce such a distribution would be difficult to envision.

Based on the poor agreement of the previous two models and the energetics of the BrCN$^{-*}$ intermediate, it is reasonable to predict that good agreement with the measured position distribution can be achieved by assuming the production of CN$^-$ ions with a broad distribution of rotational excitation. It can be concluded that the distribution must be broad because calculated distributions produced using Gaussian translational energy distributions are in poor agreement with the measured distributions regardless of the energy on which the Gaussian function is centered. Figure 4.15 compares a measured position distribution of $K^+ \cdots CN^-$ ion-pair states with calculated position distributions produced using the translational energy release distributions illustrated in the insets. Figure 4.15(a) includes calculations undertaken using a translational energy release distribution chosen to mirror that expected if col-
Figure 4.15: (Expt) Measured arrival position distributions for $\text{K}^+ \cdots \text{CN}^-$ ion pairs produced in $\text{K}(14\text{p})$-$\text{BrCN}$ collisions for $t_D = 50 \ \mu\text{s}$. (a)-(c) Calculated position distributions for $\text{K}^+ \cdots \text{CN}^-$ ion-pair states produced using translational energy release distributions shown in the insets.
lisions predominantly lead to the population of low-lying rotational states and Figure 4.15(b) includes calculations undertaken using a distribution chosen to mirror that expected if collisions predominantly lead to the preferential population of highly excited rotational states, as would be observed with a Boltzmann-like translational energy release distribution. Figure 4.15(c) contains a calculated distribution produced when modeling a distribution of rotational states which peaks at \( J \sim 12 \), i.e., peaks at energies \( BJ(J + 1) \sim 35 \) meV, corresponding to a suprathermal distribution. This distribution is in good agreement with the measured distribution. Comparison of the measured distribution to similar calculated distributions in which the rotational temperature was adjusted revealed little sensitivity to the rotational temperature over the range 450-900K. However, these results confirm the production of a suprathermal “rotationally hot” distribution of \( \text{CN}^- \) ions upon dissociative electron attachment to \( \text{BrCN} \). Good agreement to the measured distributions in Figure 4.14a and the calculated distribution produced assuming a rotational temperature of \( \sim 600 \) K in Figure 4.14f further confirms this.

### 4.3 Dipole-Bound Negative Ions: \( \text{CH}_3\text{NO}_2 \)

When Rydberg atoms collide with molecules with dipole moments greater than \( \sim 2 \) Debye [109], Rydberg electron transfer can lead to the formation of a dipole-bound negative ion in which the extra electron is bound near the positive end of the polar molecule by a long range electrostatic interaction with the molecular dipole moment [110, 111, 73, 112, 69]. The orbital which the electron inhabits is very diffuse, with most of the electron density lying outside the parent molecule.

Unlike the case for Rydberg electron transfer to form valence-bound negative ions, the rate constant for Rydberg electron transfer to form dipole-bound negative ions
Figure 4.16: Formation of Dipole-Bound Negative Ions (Taken from [113])

Figure 4.17: Covalent potential curves corresponding to Xe\((nl)\)+M and ionic potential curve corresponding to Xe\(^+\)⋯M\(^−\) ion pairs as a function of the internuclear distance \(R\), for a zero impact parameter \(b\). At each crossing radius \(R_c\) the ionic-covalent coupling term \(H_{ic}(R_c)\) can make the system pass from one curve to the other with a probability \(p\). \(P\) is the resulting ion-pair formation probability (Taken from [111]).
is strongly dependent on the principal quantum number \( n \) of the Rydberg atom, peaking sharply over a narrow range of \( n \), \((n \sim 14 \text{ in the case of } \text{CH}_3\text{CN} [69])\). A curve-crossing model was proposed by Desfrancois and coworkers to explain this dependence. This model is illustrated in Figure 4.17 for the case of xenon Rydberg atoms. The figure includes the flat potential curves representing neutral xenon atoms excited to different \( nl \) Rydberg states plus a neutral polar molecule. These potential curves cross those associated with \( \text{Xe}^+ \)-dipole-bound \( \text{CH}_3\text{CN}^- \) ion pairs [111]. At these crossings, a fraction \( p \) of the neutrals can transfer to the ionic curve, experiencing additional crossings as they approach further. The fraction \((1 - p)\) remain on the covalent curve, but have a chance \( p \) of transfer to the ionic curve as they move apart. As a result the fraction \( p(1 - p) \) of the collision partners can transfer to the ionic channel creating a dipole-bound anion. The transition probability \( p \) is given by the Landau-Zener expression

\[
p = 1 - \exp \left( \frac{-2\pi H^2_{ic} R^2_c}{v_r} \right)
\]

(4.10)

where \( H_{ic}(R_c) \) is the Hamiltonian interaction term and \( v_r \) is the relative radial velocity of the reactants at \( R_c \). The rate constant of ion formation depends heavily on \( n \), peaking at some \( n = n_{\text{max}} \) for which the Rydberg electron probability density in the vicinity of the curve crossing is large. As \( n \) increases (or decreases), the curve crossings occur at larger (smaller) radii, reducing the overlap with the Rydberg wave function, and therefore reducing the transition probability [69].

The goal in this work was to collide Rydberg atoms of intermediate \( n \) with nitromethane, \( \text{CH}_3\text{NO}_2 \) and look for formation of ion-pair states via the following reaction

\[
\text{K}(np) + \text{CH}_3\text{NO}_2 \rightarrow \text{K}^+ \cdots \text{CH}_3\text{NO}_2^- \rightarrow \text{K}^+ \cdots \text{CH}_3\text{NO}_2^-
\]

(4.11)
to assess the role of dipole binding as a "doorway" for creation of ion-pair states.

CH$_3$NO$_2$ has a dipole moment of 3.46 Debye, which is sufficient to produce dipole-bound negative ions. CH$_3$NO$_2$ was attractive as a target because previous work has also demonstrated the presence of strong coupling between the dipole-bound ionic state and the standard valance-bound ionic state. As a result, it was expected that on the timescale of this experiment, this coupling might facilitate the production of long-lived K$^+ \cdots$CH$_3$NO$_2^-$ valence-bound ion-pair states [76]. The formation rate of free CH$_3$NO$_2^-$ ions through Rydberg electron transfer peaks sharply $n \sim 15$ [112], which is expected for dipole-bound negative ions. However, earlier work has shown the product CH$_3$NO$_2^-$ anions demonstrate behavior different from that of other dipole-bound negative ions. In particular, their field-induced detachment behavior is very different from that of other dipole-bound anions. Additionally, CH$_3$NO$_2^-$ ions have lifetimes on the order of several milliseconds while other dipole-bound anions have lifetimes in the range $\sim 50 - 100$ µs limited by blackbody radiation induced photodetachment. This was explained by a model exploiting the theoretically predicted strong coupling between the dipole-bound state and valence-bound states, allowing the dipole-bound state to act as a precursor to the formation of a long-lived valence-bound anion [112].

Figure 4.18a shows the measured arrival position distributions of K$^+$ ions detected at the PSD after application of a ramped field in the analysis region. These distributions are similar to the measured K$^+$ distributions produced through field-induced dissociation of stable K$^+ \cdots$SF$_6$ ion-pair states as shown in Figure 4.6a, but they suggest a larger ion-pair velocity. When the polarity of the apparatus voltages was reversed so that the PSD collects negative ions, the measured arrival position distributions of the detected particles, as shown in Figure 4.18b, strongly resembled the K$^+$ position distributions. This was not unexpected. If the collected signals are
Figure 4.18: a) $K^+$ arrival position distributions recorded following $K(12p)$-CH$_3$NO$_2$ collisions and the delay times $t_d$ indicated. b) electron arrival position distributions. c)-e) model predictions obtained by assuming that transient $K^+ \cdots$ CH$_3$NO$_2^-$ ion pairs are formed at a radius of 200 a.u. and that they have the lifetimes indicated. The data in each panel are normalized to the peak signal seen in each distribution.
Figure 4.19: a) Time dependence of the electric field ramp applied in the analysis region. b) Time dependence of the measured K$^+$ ion signal at the PSD during application of the field ramp following K(12p)-SF$_6$ collisions (solid line); results of model predictions using the lifetimes shown in Figure 4.18 (dashed line). c) Time dependence of the measured K$^+$ ion signal during the field ramp following K(12p)-CH$_3$NO$_2$ collisions (solid line); results of model predictions (dashed line). The inset shows the equilibrium structure for both CH$_3$NO$_2$ molecules and CH$_3$NO$_2^-$ anions.
produced through field-induced dissociation of electrostatically bound ion-pair states, then the position distributions of positive and negative particles collected should be roughly identical to each other. However, Figure 4.19, which shows the measured time dependence of the measured $K^+$ signal following $K(12p)$-SF$_6$ and $K(12p)$-CH$_3$NO$_2$ collisions, as well as the predicted time dependence of the signals during the electric field ramp reveals marked differences from the behavior predicted by the collision model if collisions form long-lived $K^+ \cdots CH_3NO_2^-$ ion-pair states. In particular, the time dependence of the ion signal observed is different from that seen with SF$_6$ and from that predicted assuming the creation of stable ion-pair states. Therefore, it was concluded the electron transfer does not lead to the production of stable, long-lived $K^+ \cdots CH_3NO_2^-$ ion-pair states.

Previous work has revealed that a large fraction of the free CH$_3$NO$_2^-$ ions produced in electron transfer reactions undergo detachment in electric fields of $\sim 30$ kV cm$^{-1}$. This is due to the fact that CH$_3$NO$_2$ has a negative vertical electron affinity, meaning it can not form a stable negative ion in its neutral equilibrium geometry. The binding energy of the electron depends on the angle between the O-N-O plane of the molecule and the C-N plane, as illustrated in the inset of Figure 4.19. The large adiabatic electron affinity of CH$_3$NO$_2$ ($\sim 0.26$ eV) requires the anion to be created in a highly vibrationally excited state. At the extremes of the vibration, the tilting angle of the molecule is small and the anion's geometry approaches the equilibrium geometry of the neutral molecule. As a result, at these extreme points of motion the electron is only weakly bound to the ion [114]. The radius of a Rydberg atom scales with $\sim 2n^2 = 2(n - \delta)^2$, which for a potassium atom excited to $n = 12$ is roughly 200 a.u.. Therefore, it is reasonable to conclude that CH$_3$NO$_2^-$ ions upon formation will be separated from the core ion by roughly this distance. However, electric fields of
∼ 30 kV cm\(^{-1}\) are present within 200 a.u. of a Rydberg core ion, so CH\(_3\)NO\(_2^-\) ions should quickly undergo field-induced detachment for separations where it was believed that long-lived K\(^+\)···CH\(_3\)NO\(_2^-\) ion-pair states might be formed by Rydberg electron transfer. Instead, the electron will detach, forming a Rydberg atom in a different \(nl\) state and a neutral molecule, allowing the formation of only transient ion pairs. Since the Rydberg atom and neutral molecule are still close the electron might reattach to the molecule, repeating formation of a transient ion pair state.

To better understand the nature of the particles responsible for the PSD signals, arrival time distributions were collected in which the polarity of the apparatus was set to collect either negatively or positively charged particles. For bound ion-pair states, field-induced dissociation should yield negative ions which would require significant time \(\gtrsim 0.7 \mu s\) following the activation of the field to reach the PSD. However, as can be seen in Figure 4.20, the time delay between application of the electric field ramp (at \(t = 0\)) and the onset of the collected negative charge signal is too small to attribute the signal to negative ions. The delay is consistent, however, with the flight time of electrons. Additionally, there is no evidence of a peak in the arrival time signal at the time at which CH\(_3\)NO\(_2^-\) ions are expected to arrive. Since small dc electric fields surrounding the analysis region prevent the ingress of charged particles, these electrons must be produced through field ionization of Rydberg atoms. Because the field produced in the analysis region is not strong enough to ionize the original \(n = 12\) Rydberg atoms, it can be concluded that the electrons are produced by field ionization of higher Rydberg atoms produced through interactions with CH\(_3\)NO\(_2\) molecules. In contrast, Figure 4.19b shows that the arrival time dependence of negatively charged particles produced following K(12p)-SF\(_6\) collisions does not have that early onset, demonstrating that the negatively charged particles are free SF\(_6^-\) ions produced by
Figure 4.20: a) Time dependence of the electric field ramp applied in the analysis region. b) Time dependence of the measured (electron) signal during the application of the field ramp following K(12p)-CH$_3$NO$_2$ collisions. The arrows indicate the times (fields) at which diabatic ionization of Rydberg states with the values of $n$ indicated is expected (see text). The heavy solid arrow shows the time at which CH$_3$NO$_2^-$ ions are expected to begin arriving.
field-induced dissociation of bound \( K^+ \cdots SF_6^- \) ion-pair states. However, the \( K^+ \) signal rates for both species are similar, suggesting that the rate constant associated with \( K(12p)\text{-CH}_3\text{NO}_2 \) collisions is large.

Theoretical work by Lebedev et al. on Rydberg atom quenching by highly polar molecules offers an explanation [115]. It was determined that inelastic scattering of Rydberg atoms with polar molecules via the reaction

\[
K(12p) + AB \rightarrow K^+ + AB^{-*} \rightarrow K(n' l') + AB
\]  

has a large rate constant. Since the binding energy of a dipole-bound electron to \( \text{CH}_3\text{NO}_2 \) is \( \sim 13 \text{ meV} \), the crossing between the covalent \( K(12p)\text{-CH}_3\text{NO}_2 \) and ionic \( K^+-\text{CH}_3\text{NO}_2^- \) terms occurs at a separation of \( \sim 200 \text{ a.u.} \), which is similar to the size of an \( n = 12 \) Rydberg atom. Theoretical calculations showed that for \( \text{CH}_3\text{NO}_2 \) resonant quenching is strongly peaked in the range \( n^* \sim 8 - 14 \) with a cross-section of \( \sim 3 \times 10^{12} \text{ cm}^2 \). The calculated reaction rate constant, \( k \sim 6 \times 10^{-7} \text{ cm}^3\text{s}^{-1} \), is consistent with the amplitude of the measured \( K^+ \) signal.

In order for there to be significant quantities of scattered Rydberg atoms entering the analysis region, which is significantly off-axis from the original Rydberg atom trajectory, the lifetime of the \( \text{CH}_3\text{NO}_2^- \) ion prior to dissociation has to be sufficiently large for the ion pair to undertake significant joint orbital motion. Figure 4.18c-e shows calculated position distributions assuming that the scattered Rydberg atoms result from a single scattering event, that ion-pair formation occurs at a radius of 200 a.u., and that the transient intermediate \( K^+ \cdots \text{CH}_3\text{NO}_2^- \) ion-pair states have the lifetimes indicated before their decay. Comparison with the measured distributions suggest ion-pair lifetimes \( \gtrsim 10 \text{ ps} \).

A significant decrease in the Rydberg atom signal was observed with increasing flight time. The rate of the decrease suggests an average Rydberg atom lifetime of
\( \sim 20 \mu s \). With Rydberg-atom radiative lifetime scaling as \( n^3 \), this lifetime is consistent with low-\( n \) states, \( n \lesssim 25 \). The arrival time distribution of electrons produced via field ionization of scattered Rydberg atom is shown in Figure 4.20 and includes the strength of the electric field at that time as measured using a high voltage probe. Since it is reasonable to assume the Rydberg quenching reaction results in Rydberg atoms with a large range of values of \( l \), there is a broad range of field strengths over which Rydberg atoms for a given value of \( n \) will be ionized. However, a sizable fraction of these states typically ionize at fields near the diabatic threshold, \( \sim 1/9n^4 \) [82]. These thresholds are indicated in the figure for different values of \( n \) (The field produced in the analysis region is insufficient to ionize Rydberg atoms for which \( n \lesssim 16 \).) Comparison of the shape of the arrival time distribution with the markers for various values of \( n \) shows that the majority of the signal consists of electrons produced through ionization of low \( n \) (\( \lesssim 25 \)) atoms, a fact which is consistent with the relatively short Rydberg atom lifetimes observed and theoretical predictions.
Chapter 5

Conclusions and Future Directions

In this work, it was further demonstrated that long-lived bound ion-pair states can be formed in collisions between Rydberg atoms and a wide variety of electron-attaching target molecules. It was also confirmed that through the use of a ramped electric field to dissociate these states, the distributions of velocity and binding energy of these states can be measured. Analysis of these distributions has shown that the nature of the formation, movement, and decay of these states depends markedly on the electron-attaching species employed and factors such as whether or not the parent transient negative ion formed through electron transfer dissociates, the lifetime of the transient negative ion prior to dissociation (which determines the likelihood of significant internal excitation prior to dissociation,) and the branching ratio into different dissociation channels (which determines the nature of the product ion-pair states.) The present results illustrate the utility of Rydberg atoms as a probe to investigate the attachment of low-energy electrons to molecules.

Collisions with CF$_3$I result in strongly scattered, fast-moving ion pairs consistent with the formation of a short-lived transient intermediate ion. The slow-moving, strongly-forward peaked ion pair distributions seen using CCl$_4$ indicate a long-lived transient intermediate ion. Measurements also showed that ion-pair states formed through non-dissociative electron attachment to SF$_6$ have lifetimes dependent upon their binding energies. Ion-pair states formed using CH$_2$Br$_2$ exhibit similar behavior to CF$_3$I, indicating that the transient negative ions formed also have very small
lifetimes. Measurements of the ion pair distributions resulting from electron transfer to 1,1,1-C\textsubscript{2}Cl\textsubscript{3}F\textsubscript{3} indicated the formation of both fast-moving and slow-moving ion pairs states, indicating the presence of two reaction channels, one in which the transient negative ion is short-lived, the other long-lived. The branching ratios for these channels are consistent with previous measurements. Electron attachment to CCl\textsubscript{3}Br leads to the formation of Br\textsuperscript{-} and Cl\textsuperscript{-} ions. Ion-pair states formed by both channels are observed, and the energetics for each reaction channel are in agreement with previous studies of this molecule. Despite the dissociation of Fe(CO)\textsubscript{5} yielding a slow-moving negative ion that tested the sensitivity of the apparatus, it could be reasonably determined that the intermediate is sufficiently long-lived to allow partial redistribution of the excess energy of reaction. Measurements of ion pair formation through electron transfer to BrCN confirm the formation of product CN\textsuperscript{-} ions with a broad suprathermal distribution of rotational energies. Remarkably, measurements of the velocity and binding energy distributions of the products formed following Rydberg electron transfer to the polar molecule CH\textsubscript{3}NO\textsubscript{2} revealed no evidence for formation of long-lived ion-pair states at all. Rather, transient ion-pair states are created which, upon decay, form scattered Rydberg atoms. The data are consistent with production of Rydberg atoms with a range of values of \( n \), the CH\textsubscript{3}NO\textsubscript{2} molecule facilitating quenching of the parent Rydberg states.

Several future paths of investigation in this field appear quite promising. Rydberg electron transfer to CCl\textsubscript{3}Br was shown to produce both Cl\textsuperscript{-} ions and Br\textsuperscript{-} ions. The measurements done for this work using this species were conducted by collecting distributions of positive K\textsuperscript{+} ions. Because the flight time of K\textsuperscript{+} ions from the analysis region to the PSD upon activation of the ramped field will be the same regardless of whether they are produced by dissociating K\textsuperscript{+}···Cl\textsuperscript{-} ion-pair states or K\textsuperscript{+}···Br\textsuperscript{-}
ion-pair states, it is not possible to discriminate which counts in the arrival time and position distributions originate from which ion pair. However, by reconfiguring the apparatus to collect negative ions, because of the difference in mass between the Cl$^-$ ion and the Br$^-$ ion, ion flight times to the detector can be used to effectively discriminate the position distributions associated with each ion species. More precise determinations about the branching ratio of the two reaction channels and of the energetics of each reaction channel could be achieved through such measurements. This same methodology could be applied to any electron-attaching molecule with multiple reaction channels that produce product ions with significantly different masses.

Molecules like CCl$_4$ and CCl$_3$Br upon attachment of thermal energy electrons will dissociate to form the radicals CCl$_3$ and CCl$_2$Br. These radicals are capable of undergoing secondary electron attachment and dissociating again. Measurement of electron attachment to these molecules using the FALP method has shown signs of electron loss due to such processes. Significant observation of these processes would require conducting measurements using target gas pressures significantly higher than those used for this work. However, insertion of the gas directly into an enclosed interaction cell, such as the one used in the current apparatus, rather than ambiently into the vacuum chamber, may produce the pressure needed to observe ion-pair states resulting from secondary electron attachment.

The ion-pair states formed in this work were formed using reactants with broad velocity distributions, resulting in broad ion pair velocity and binding energy distributions. More precise determination of the energetics of electron transfer reactions can be achieved by narrowing the velocity distribution of the Rydberg atoms and/or the target gas molecules. The Rydberg atom velocity distribution can be narrowed by exploiting the Doppler effect and directing the laser into the vacuum chamber at
an off-normal angle to the potassium atom beam. As a result, the frequency of the laser observed by the atoms in the beam will depend on the velocities of the atoms. Therefore, only atoms with a relatively narrow range of velocities will be excited. Additionally, the target gas can be introduced in the form of a directed beam moving either parallel or perpendicular to the Rydberg atoms. These measures will allow better definition of the initial collision conditions and more detailed analysis of the reaction dynamics.

Work has been conducted demonstrating the viability of producing strontium Rydberg atoms. The excitation probability was shown to be significantly larger than what has been observed for potassium, so the use of a strontium atom beam should result in a much larger yield of Rydberg atoms, and therefore, ion-pair states. As a result, it will be more feasible to employ the velocity and trajectory discrimination techniques described previously while still producing well resolved distributions for the position and arrival times of the ion-pair states. Additional discrimination methods could be employed such as filtering measured arrival time distributions by scattering angle of the ion-pair states. Furthermore, because alkaline-earth metals like strontium possess a second valence electron, it is possible to create a heavy-Rydberg ion-pair state in which the Sr$^+$ core ion is excited. Assessing the stability of such ion-pair states with an excited positive core ion should prove interesting.

Another interesting avenue of investigation will be to assess the dependence of the formation of bound ion-pair states on temperature. Target gas at a higher temperature will have molecules with greater rotational and vibrational excitation. One particular species for which measurements at higher target gas temperatures would be interesting is BrCN. Upon dissociation of the BrCN-- transient intermediate ion, the greater vibrational excitation will manifest as greater rotational excitation in the
CN$^-$ ion. Because the energy released in a dipole-allowed $J \rightarrow J - 1$ transition is a function of $J$, the temperature will influence the amount of rotational energy converted into translational energy during these transitions and, therefore, the fraction of ion-pair states that decay as a result of these transitions. As a result, the final velocity distribution and the distribution of rotational excitation of ion-pair states that remain bound could depend heavily on temperature.
Bibliography


