Studies of Intermediates Created via Dissociative Electron Attachment through Heavy-Rydberg Ion-Pair State Formation in Rydberg Atom Collisions

by

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Master of Science

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Abstract

The lifetimes and decay energetics of intermediates have been studied by measuring the velocity and angular distributions of heavy-Rydberg ion pair states formed through electron transfer in thermal-energy collisions between Rydberg atoms and attaching targets. The analysis of the experimental results by using Monte Carlo simulations indicates that electron attachment to CF$_3$I and CH$_2$Br$_2$ forms very-short-lived intermediates whereas electron capture by CCl$_4$ produces a long-lived intermediate.
Acknowledgements

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Chapter 1

Introduction

Research Overview

Electron attachment processes have been a subject of substantial interest for many years. Understanding of electron–molecule collisions and the mechanisms responsible for negative ion-formation is important in diverse fields such as planetary atmosphere [1], biological toxicity [2] and photosynthesis [3], and plasma discharge process [4]. In particular an incoming, low-energy electron can be captured by a target molecule causing it to dissociate into fragments comprising a secondary neutral molecule and product ion [5, 6]. This reaction, called dissociative electron attachment (DEA), can be represented as

\[ e^- + XY \rightarrow XY^{*-} \rightarrow XY^- \rightarrow Y + X^- \]  \hspace{1cm} (1.1)

The attached electron is trapped temporarily in a resonant state forming a transient negative intermediate \( XY^{*-} \) that can either autodetach reverting to its original molecular ground state, often resulting in excitation of vibrational states of a target molecule, or dissociate into a fragment ion and neutral radical as in the equation (1.1). Not only does a free electron cause the dissociative attachment process to occur but also the weakly-bound essentially-free excited electron in a
Rydberg atom. This results in electron transfer in collisions between Rydberg atoms and target molecules. Schematically it can be written as

\[
K(n, \ell) + XY \rightarrow K^+ + XY^- \rightarrow K^+ + X^- \rightarrow K^+ + Y \rightarrow K^+ \cdots X^- + Y
\]  

(1.2)

where \(K(n, \ell)\) denotes a Rydberg atom. There is no alteration in the nature of the electron-molecule interaction when a free electron is replaced by a bound electron in a high-lying Rydberg state. Since the mean radius of a Rydberg orbital with a high principal quantum number \(n\) is large, scaling as \(n^2\) and the range of electron-molecule interactions is small, it is reasonable to assume that the electric field from the Rydberg core ion has a negligible effect on the attachment process. As a consequence, the target molecule cannot interact with both the ionic core and Rydberg electron simultaneously, resulting in the bound electron behaving essentially as a free electron.

One of the possible outcomes from Rydberg atom collisions with attaching target molecules is the formation of weakly-bound positive-negative ion-pair states \((K^+ \cdots X^-)\) as shown in reaction (1.3) [7-11]. The production and properties of such states have been of much recent interest as they comprise a novel long-range molecular system. Such systems also include Rydberg atom macrodimers [14-16] and long-range Rydberg molecules [17-20]. As \(n\) decreases toward intermediate values, \(-10-20\), the Rydberg electron cloud shrinks and therefore electron capture must occur at distances such in the range that the post-product interactions between the positive and negative ions become significant. Because the relative
kinetic energies of ion pairs formed in thermal energy collisions are small, they are unable to overcome their mutual Coulomb attraction and thus remain bound orbiting each other as a binary system. Since their properties parallel those of Rydberg atoms [12, 13], ion-pair states are also known as heavy-Rydberg states.

This work explores the lifetime and decay energetics of intermediates formed in dissociative electron capture by measurements of the velocity and angular distributions of heavy-Rydberg ion-pair states formed through Rydberg atom-molecule collisions and analyzing them with the aid of simulations based on a Monte Carlo collision code [21].
1.1 Rydberg atoms

Atoms with one or more electrons excited into states with high principal quantum number $n$, are referred as Rydberg atoms and possess exaggerated and unique properties. The weakly-bound high-$n$ electron can be considered as an electron revolving around the core ion in a large classical orbit. Due to their sizable atomic radiiuses and low binding energies, $13.6/n^2$ eV, Rydberg electrons are sensitive to external fields and measurements of the number of Rydberg atoms and their state distributions are straightforward because a small electric field is sufficient to ionize Rydberg atoms. Moreover, Rydberg states have decay lifetimes in the order of microseconds up to milliseconds allowing their study over extended time periods. All of these features make Rydberg atoms an ideal choice to perform electron-molecule collision experiments.

Significant Rydberg properties and their dependence on principal quantum number $n$ are illustrated in Table 1.1. Even at low quantum principal number $n$, as seen from the orbital radius, the range of the interaction between an electron and a molecule is typically much shorter than the mean orbital radius of Rydberg atom. Thus in collision with a neutral molecule the atom behaves not as an atom but as a pair of independent scatterers. As a consequence, an attaching target sees the approaching Rydberg electron as, essentially, a free electron.
Table 1.1 Properties of Rydberg atoms and their quantum number dependence.

<table>
<thead>
<tr>
<th>Property</th>
<th>$n$ dependence</th>
<th>$K(14p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy</td>
<td>$n^{-2}$</td>
<td>0.090 eV</td>
</tr>
<tr>
<td>Energy difference between adjacent $n$ states</td>
<td>$n^{-3}$</td>
<td>0.012 eV</td>
</tr>
<tr>
<td>Orbital radius</td>
<td>$n^2$</td>
<td>225$a_0$</td>
</tr>
<tr>
<td>Geometric cross section</td>
<td>$n^4$</td>
<td>159043$a_0^2$</td>
</tr>
<tr>
<td>Radiative lifetime</td>
<td>$n^3$</td>
<td>7.24 μs</td>
</tr>
</tbody>
</table>

The units using throughout in this work are atomic units. The four fundamental quantities, electron mass $m$, charge $e$, reduced Planck constant $\hbar$ and the Coulomb constant $k$ are taken to be unity by definition. Table 1.2 expresses frequently encountered atomic units in more common units.

Table 1.2 Fundamental units

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Atomic units</th>
<th>SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron mass</td>
<td>1</td>
<td>9.109x10^{-31} kg</td>
</tr>
<tr>
<td>Charge</td>
<td>1</td>
<td>1.602x10^{-19} C</td>
</tr>
<tr>
<td>Energy</td>
<td>1</td>
<td>4.360x10^{-18} J</td>
</tr>
<tr>
<td>Length</td>
<td>1</td>
<td>5.292x10^{-11} m</td>
</tr>
<tr>
<td>Speed of light</td>
<td>137</td>
<td>2.998x10^8 m/s</td>
</tr>
<tr>
<td>Proton mass</td>
<td>1836</td>
<td>1.672x10^{-27} kg</td>
</tr>
</tbody>
</table>
In order to understand the internal structure of a Rydberg atom, it is necessary to initially review the simplest model of the atom, the Bohr model of the hydrogen atom. This builds on three postulates. First, hydrogen atom consists of a proton as a nucleus and an electron travelling in a uniform classical circular orbit bound by Coulomb attraction. Second, the angular momentum, \( L \), of the electron is an integral multiple of \( \hbar \), \( L = mvr = n\hbar \) where \( n \) is any positive value. Third, an electron does not radiate continuously in a classical manner, but gives off radiation as it makes transitions between states with well-defined energies.

Based on these assumptions, the binding energy of a Bohr electron can be derived and given by

\[
E = \frac{mv^2}{2} - \frac{kZe^2}{r} = -\frac{k^2z^2e^4m}{2n^2\hbar^2}
\]

or \( E = -\frac{1}{2n^2} \) in atomic unit

The Rydberg states of potassium Rydberg atoms can be discussed using a similar classical picture. Both hydrogen and potassium Rydberg atoms have total nuclear charge of +1 although the potassium ionic core contains nineteen protons and eighteen electrons. Figure 1.1 illustrates the classical picture for hydrogen and potassium Rydberg atoms. Note that in figure 1.1a the valence electron of the hydrogen atom is shown in two different orbits with different orbital angular momenta. For a high orbital angular momentum \( \ell \), as indicated by the dash line, the Rydberg electron rotates in a near circular orbit and remains distant from the ionic core. This is not the case for a low orbital angular momentum \( \ell \). As \( \ell \) decreases, the
circular orbit becomes increasingly elliptical. For potassium the Rydberg electron penetrates through the inner electron cloud associated with the core ion and feels more of the nuclear charge. Since the electron potential for a potassium Rydberg atom contains a small departure from $1/r$ behavior, primarily by dipole polarization of the core, its elliptical orbit precesses about the force center as illustrated in figure 1.1b [22]. As a result, differences between hydrogen and potassium potentials emerge at short ranges reflected in figure 1.2 [23]. Note that for low-$\ell$ states as the Rydberg electrons move away from their ionic cores, they slow down, so they spend more time near their outer classical turning points.

![Classical trajectories of a Rydberg electron for (a) hydrogen and (b) potassium. In figure 1.1a, electron trajectories are shown for the states with high and low orbital angular momenta. An arrow in figure 1.1b indicates the direction of the orbital precession.](image)

**Figure 1.1** Classical trajectories of a Rydberg electron for (a) hydrogen and (b) potassium. In figure 1.1a, electron trajectories are shown for the states with high and low orbital angular momenta. An arrow in figure 1.1b indicates the direction of the orbital precession.
Figure 1.2 Schematic comparisons between the effective one-electron potential of a potassium atom (⋯) and the Coulomb potential of a hydrogen atom (−). At small r, the differences can be noticed.

Figure 1.2 shows the $1/r$ Coulomb potential of a hydrogen atom and the effective potential seen by a Rydberg electron in a potassium atom. At small radial distances, the potential well of potassium atom becomes a little deeper since the Rydberg electron penetrates through the electron cloud localized around the nucleus and interacts more strongly with the ionic core. Moreover its kinetic energy increases while its de Broglie wavelength of radial oscillations decreases ($p \sim \frac{\hbar}{\lambda}$). The electron wave function is then pulled closer to the origin resulting in larger binding energies for low-$\ell$ states. As a result, the energy levels of the Rydberg electron are written as

$$E = -\frac{1}{2(n-\delta_{\ell})^2}$$ (1.5)

where $\delta_{\ell}$ denotes the quantum defect. This equation expresses the deviations of alkali Rydberg atoms from pure hydrogenic behavior. Table 1.3 shows the
dependence of the quantum defects $\delta_\ell$ on the orbital angular quantum number $\ell$. As seen in table 1.3 [24], since the screening effect of the inner electrons is less for low-$\ell$ states than for high-$\ell$ states, the values of the quantum defects are maximized for $s$-states ($\ell = 0$) and decrease for higher $\ell$ states.

Table 1.3 Quantum defects for potassium Rydberg states for selected values of $n$ and $\ell$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\delta_{\ell=0}$</th>
<th>$\delta_{\ell=1}$</th>
<th>$\delta_{\ell=2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.182</td>
<td>1.715</td>
<td>0.266</td>
</tr>
<tr>
<td>14</td>
<td>2.181</td>
<td>1.713</td>
<td>0.272</td>
</tr>
<tr>
<td>20</td>
<td>2.181</td>
<td>1.712</td>
<td>0.274</td>
</tr>
<tr>
<td>55</td>
<td>2.178</td>
<td></td>
<td>0.276</td>
</tr>
</tbody>
</table>

1.1.1 Radiative lifetime

The radiative lifetime $\tau$ of the $n\ell$ Rydberg states is the inverse of the radiative decay rate which involves the electric dipole matrix elements between the initial and final states and the transition frequency. Since background black body radiation can induce transitions between high-lying Rydberg states, the effective radiative lifetime can be written as

$$\frac{1}{\tau_{total}} = \frac{1}{\tau} + \frac{1}{\tau_{BB}}$$

(1.6)

where $\tau_{total}$ and $\tau_{BB}$ denote the effective, or, measured and Black body radiative lifetimes respectively. Table 1.4 lists lifetime parameters for alkali atoms which can
be expressed simply as $\tau_{total} = \tau_0(n^*)^\alpha$ where $\alpha$ is close to value of 3 and $n^*$ is the effective principal quantum number, $\sim (n - \delta_\ell)$ [25].

**Table 1.4** Lifetime parameters for alkali atoms

<table>
<thead>
<tr>
<th>Rydberg atom</th>
<th>$s$</th>
<th>$p$</th>
<th>$d$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>1.38</td>
<td>8.35</td>
<td>0.96</td>
<td>1.13</td>
</tr>
<tr>
<td>Potassium</td>
<td>3.00</td>
<td>3.11</td>
<td>2.99</td>
<td>2.96</td>
</tr>
</tbody>
</table>

1.1.2 Stark effect in static fields

Due to the large separation between the Rydberg electron and core ion, the atomic electric dipole moment can be extremely high making Rydberg atoms sensitive to external fields. By treating hydrogen atom in a presence of electric field $F$ using parabolic coordinates and ignoring very small electric dipole couplings between adjacent $n$ manifolds, the first order Stark energy level splitting can be expressed in terms of the parabolic quantum numbers $(n, n_1, n_2, m)$ as

$$E = -\frac{1}{2n^2} + \frac{3}{2}n(n_1 - n_2)F$$  \hspace{1cm} (1.7)$$

where $n_1$ and $n_2$ denote nonnegative integers which have the constraint of $n_1 + n_2 + m + 1 = n$. Note that for given values of the quantum numbers $n$ and $m$ there are $n - |m|$ Stark levels as illustrated in figure 1.3.
Figure 1.3 Stark splitting for the $|m| = 1$ states of the hydrogen atom. The curved line represents the classical field ionization limit $E = -2\sqrt{F}$ [25].

Sufficient electric field can ionize the electron from a Rydberg atom as shown by the broken lines of figure 1.3. The potential that the electron experiences is

$$V = -\frac{1}{r} + Fz$$  \hspace{1cm} (1.8)

which has a saddle point in the z direction located at $z = -\frac{1}{\sqrt{F}}$ where $V = -2\sqrt{F}$.

For a state with $m = 0$, the classical threshold field for ionization is given by

$$F = \frac{E^2}{4}$$  \hspace{1cm} (1.9)

and is shown by the curved line in figure 1.3. Without considering Stark shifts, the ionization field in terms of the quantum number $n$ for a hydrogen atom, is
\[ F = \frac{1}{16n^4} \]  

which is only valid for \( m = 0 \) states. In the case of \( m \neq 0 \) states, the expression for the fractional change of threshold field is approximately [26]

\[ \frac{\Delta F}{F} = \frac{|m| \sqrt{E}}{\sqrt{2}} = \frac{|m|}{2n} \]  

Notice in figure 1.3 that field ionization for the red-shifted Stark states occurs close to the classical limit (equation (1.9)) while the blue-shifted Stark states ionize at much higher fields. This can be explained using the potential well in figure 1.4 [23]. The applied electric field modifies the Coulomb potential. The blue shifted stark states are localized in a region far from the saddle point and thus have only a small probability density in this region dramatically reducing the ionization rate requiring higher field strength for ionization of the blue stark states. Classically ionization of blue shifted Stark states is suppressed because electrons in attempting to escape are back scattered off the nucleus.
Figure 1.4 Potential for a Hydrogen atom in the presence of electric field. The blue Stark states are localized on the high potential side whereas the red stark states are localized on the low potential side in the vicinity of the saddle point.

For the extreme red stark state, $n_2 - n_1 = n - 1 \approx n$. The energy level from equation (1.7) is turned into

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

(1.12)

Substituting the result in equation (1.9) to obtain the threshold field for the extreme red stark state yields

$$F = \frac{1}{9n^4}$$

(1.13)
Note that the numerical factor of 1/9 instead of 1/16 is due to the Stark shift of the level. For the blue states it is not possible to estimate simply the threshold field. However, blue and red states of the same \( n \) and \( m=0 \) often have the threshold fields differing by a factor of 2.

The pure Coulomb potential in hydrogen can provide no coupling between Stark states from adjacent \( n \)-manifolds, at least non-relativistically. As the electric field increases, the \( n \) and \( n+1 \) Stark levels actually cross at a field called the Inglis-Teller limit (see figure 1.3), which is given by

\[
F = \frac{1}{3n^5}
\]  

The ionization characteristics for alkali atoms depend strongly on \( \ell \). Recalling the quantum defect of \( n \) states of alkali atoms, the binding energies of high \( \ell \) states are about the same as for hydrogen \( 1/2n^2 \) whereas for low \( \ell \) such as \( s \) and \( p \) states their binding energies are larger. In an applied field for high \( \ell \) states behave much as for hydrogen but not \( s \) and \( p \) states. Unlike hydrogen, there are strong dipole couplings between adjacent manifolds, resulting in the appearance of avoided crossings between states in adjacent stark manifolds whose magnitudes are dependent on the coupling matrix element. Figure 1.5 shows the \( |m| = 0,1,2 \) Stark structure for potassium atoms [27]. The \( s \) and \( p \) states of potassium have large quantum defects \( (\delta_s = 2.181, \delta_p = 1.712) \) and, as the field increases, they initially encounter neighboring Stark manifolds of different \( n \). In contrast, the \( d \) states have a small quantum defect \( (\delta_d = 0.272) \), and the Stark states that they meet first have the same \( n \) value. Given that coupling is strongest between states belonging to the same
$n$ manifold, avoided crossings happen. As the $d$ state approaches its neighboring manifold, strong mix leads to the appearance of broad avoided crossings. The $s$ and $p$ states interact less strongly to their neighboring Stark states, resulting in a series of narrow avoided crossings and, consequently, the adiabatically connected states preserve much more of their initial character.

![Calculated Stark structure](image)

**Figure 1.5** Calculated Stark structure for $|m| = 0, 1, 2$ levels of potassium

### 1.1.3 Stark effect in time-varying fields

The behavior of Stark states at avoided crossings is related to the slew rate of the field. If the time scale of the applied pulsed electric field through the crossing region is longer than $\frac{1}{\omega_0}$, where $\omega_0$ defines the magnitude of the level separation
between those states, the passage will be adiabatic and the avoided crossing occurs as implied by the solid arrow of figure 1.6. However, if the rising time of the pulsed field is shorter than \( \frac{1}{\omega_0} \), then, the passage will be diabatic and there is an actual crossing as shown by the broken arrow of figure 1.6.

For hydrogen atoms, the spin-orbit effects produce very small couplings between adjacent \( n \) manifolds. As a result curve crossings are traversed diabatically.

**Figure 1.6** Stark level structure in the vicinity of an avoided crossing and adiabatic and diabatic passage indicated by the solid and broken lines, respectively [25].
1.2 Collisions between Rydberg atoms and molecules

The collisions of Rydberg atoms with molecules can result in many types of reactions as follows.

1.2.1 \( n, \ell \)-changing and collisional ionization

\[
K(n, \ell) + XY(\beta) \rightarrow K(n', \ell) + XY(\beta')
\]  \hspace{1cm} (1.15)

where XY can be a diatomic or a polyatomic molecule in its electronic ground state, and \( \beta \) and \( \beta' \) denote the set of rovibrational quantum numbers before and after the inelastic collision respectively. If the translational kinetic energy of the collisional pair is small, \( \ell \) changing predominates. Substantial changes in \( n \) can result from the resonant transfer of the internal energy between the target and the Rydberg atom [28]. The Rydberg electron gains either rotational energy or vibrational energy from the target and is excited to higher level states or even ionized via the reaction

\[
K(n, \ell) + XY(\beta) \rightarrow K^+ + XY(\beta') + e^-
\]  \hspace{1cm} (1.16)

1.2.2 Associative ionization

\[
K(n, \ell) + K \rightarrow K_2^{++} + e^-
\]  \hspace{1cm} (1.17)

In order for this reaction to proceed, the binding energy of the \( K_2^{++} \) ion must be positive, in other words, the ground state energy of the \( K_2^+ \) ion must be lower than that of the system \( K^+ + K \) at an infinite distance apart, allowing formation of a stable molecular ion requiring \( K \) have a positive proton affinity [29].
In the absence of collisions with other molecules, one way to stabilize the \( \text{K}_2^+ \) product is to convert internal energy to kinetic energy of the Rydberg electron. However, this is only possible when the Rydberg electron orbits near ionic core. This constrains the quantum number \( n \) of Rydberg states to the intermediate range \( 10 \leq n \leq 20 \). For the Rydberg atoms in higher states, the electron densities in the vicinity of the ionic core are small and electrons tend to stay far away from the positively-charged \( \text{K}_2^+ \) collision complex.

### 1.2.3 Electron capture

- **Non-dissociative electron attachment**

\[
\text{K}(n, \ell) + XY \rightarrow XY^- + K^+ \rightarrow K^+ + XY^-
\]  

(1.18)

where \( XY^- \) denotes a long-lived metastable negative ion. Electron attachment to polyatomic molecules with a positive electron affinity can form excited intermediates with very long lifetimes, \( > 10^{-6}\text{s} \) as illustrated in figure 1.8b. During the formation of the intermediate the excess energy derived from the reaction excites only a few vibrational modes and these excited modes are later coupled to a larger number of inactive modes within the molecule. As a result, the excess energy can be redistributed among a large number of inactive vibrational states, leading to the creation of a long-lived intermediate. This process of stabilization of the excited intermediate is called intramolecular vibrational energy redistribution (IVR) [30].
• **Electron autodetachment**

\[ K(n, \ell) + XY \rightarrow XY^{-*} + K^+ \rightarrow K^+ + XY + e^- \]  \hspace{1cm} (1.19)

If rapid IVR does not occur the electron can simply tunnel out of the centrifugal potential barrier in which it is temporarily bound, leading to electron autodetachment as in the reaction (1.19).

• **Dissociative electron attachment:**

\[ K(n, \ell) + XY \rightarrow XY^{-*} + K^+ \rightarrow K^+ + X^- + Y \]  \hspace{1cm} (1.20)

Reaction (1.20) shows decay of the negative intermediate \( XY^{-*} \) (negative-ion resonance) via dissociation into neutral and ion fragments. A Franck-Condon transition is defined as a vertical electronic transition that occurs without changes in positions of nuclei in a molecule because the time scale for an electronic transition is much shorter than that of nuclear motions of a molecule. During an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more strongly.

Intermediate lifetimes against dissociation are related to the efficiency of excess energy redistribution among the rovibrational modes of the transient molecular negative ion as well as to the orbital configuration of its excited electronic states. The values of intermediate lifetimes can be in the range of one to many thousands of molecular vibrational periods, i.e. in the range of picoseconds to milliseconds.
1.3 Molecular Negative-Ion Resonant states

The four mechanisms leading to the formation of an excited transient intermediate are shape resonances, core-excited shape resonances, nuclear-excited Feshbach resonances, and electron-excited Feshbach resonances [31].

In shape resonances as seen in figure 1.7, the incident high-energy electron is captured by the potential well associated with the interaction between the electron and the neutral molecule in its electronic ground state. This potential arising from the combination of the attractive polarization and repulsive centrifugal effects forms a transient barrier trapping the electron. As a result, the excited intermediate potential curve lies above that of the neutral molecule and has a negative electron affinity \((EA)\). Shape resonances usually decay to states of the parent molecules through autodetachment process with lifetimes in the scale of \(10^{-15}\) s to \(\geq 10^{-10}\) s, or, if energetically possible, they can dissociate into the fragments of an anion and a product molecule. The formation of core-excited shape resonances is similar to that for normal shape resonances except that the target molecule is in an excited electronic state instead of the ground state.
Figure 1.7 Schematic diagram for shape resonances of a diatomic molecule XY. The neutral curve is represented in black, and the molecular anion in red.

The potential curves associated with nuclear-excited Feshbach resonant states are shown in figure 1.8. In this case, the intermediate potential curves lie below those of the parent ground states especially at large internuclear separation, and their formation involves transitions between vibrational levels. These resonant states have positive molecular electron affinity (EA) and may decay through either autodetachment or dissociative attachment or may be stabilized through IVR or radiative processes. The intermediate lifetimes can vary from $\sim 10^{-15}$ to $>10^{-2}$ s depending on their decay channels.

The last type of mechanisms called electron-excited Feshbach resonances are formed as in the same manner of nuclear-excited Feshbach resonance, but with target molecules in the excited electronic states rather than the ground states.
Figure 1.8 Nuclear-excited Feshbach resonances.

(a) The potential for an excited intermediate that fragments immediately after electron capture. Examples of species that share this anion potential are CF$_3$I [32] and CH$_2$Br$_2$.

(b) The potential energy curve of long-lived intermediates such as CCl$_4$ [33] and SF$_6$ [34] is shown.
1.4 Heavy-Rydberg atom states

One remarkable result from thermal-energy collisions between Rydberg atoms with intermediate principal quantum number and neutral molecules is the formation of weakly-bound ion-pair states, termed “heavy-Rydberg states”. Such molecular states consist of positive and negative charged particles which orbit each other bound by their mutual Coulomb attraction, forming a two-body system. Such states are similar in many aspects to conventional Rydberg atoms, their valence electrons being replaced by molecular negative ions. The more massive negative ions increase the reduced mass of the system dramatically and, heavy-Rydberg atoms process more exaggerated properties than even Rydberg atoms.

As mentioned earlier, Rydberg atoms can undergo collisions with attaching targets forming bound ion pairs via the reactions [7-11],

\[ K(n,\ell) + XY \rightarrow K^+ + XY^- \rightarrow K^+ \cdots XY^- \rightarrow K^+ \cdots X^- + Y \]  

(1.21)

where \( XY^- \) and \( XY^- \) represent short-lived and long-lived intermediate. Due to the large distribution of impact parameters electron capture can occur over a range of distances from the Rydberg core ion. The resulting ion pairs have large values of angular momentum \( L \) and wide ranges of their projections, \( L_Z \), as demonstrated in figure 1.9.

Moreover, ion pairs can be created by multistep laser-induced photoexcitation. Such a method has been used with diatomic molecules such as \( \text{H}_2 \),
Cl₂, and HF, leading to the production of H⁺⋯H⁻, Cl⁺⋯Cl⁻, H⁺⋯F⁻ ion-pair states [12, 13, 35-37]. Photoexcitation, however, leads to creation of ion pair states with small values of angular momentum L.

The properties of heavy-Rydberg ion par states are, governed by their mutual electrostatic interaction, \( V = -1/r \). Their binding energy obeys a generalized Rydberg formula

\[
E_B = -\frac{R_{pair}}{n_H^2}
\]

(1.22)

where \( n_H \) is the effective principal quantum number and \( R_{pair} \) is the effective Rydberg constant for ion pair given by

\[
R_{pair} = \frac{M(e^2/4\pi \varepsilon_0)^2}{2\hbar^2} = \frac{M}{m_e R_\infty}
\]

(1.23)

where \( M \) and \( m_e \) are the reduced mass of the ion pair and the mass of the electron respectively. For a Rydberg atom, \( M \approx m_e \), \( R_{pair} \) is nearly equivalent to \( R_\infty \), the fundamental Rydberg constant. However, for heavy-Rydberg systems \( R_{pair} \) is much larger than that for Rydberg atoms. For instance, the lightest ion-pair system H⁺⋯H⁻ has a reduced mass equal to a half of the mass of the hydrogen atom, resulting in \( R_{pair} \sim 900 \times R_\infty \). For a K⁺⋯I⁻ ion pair, its reduced mass is around 30 times the proton mass. Therefore, the ion-pair Rydberg constant \( R_{pair} \) is about 5.5\times10^4 times \( R_\infty \). Since the only major difference between molecular and atomic Rydberg systems is the larger reduced mass of the former, it is to be expected that heavy-Rydberg systems will share the same physical scaling laws as electronic
Rydberg systems and can be described by a single mass-scaling parameter that characterizes all properties of heavy Rydberg states.

### 1.4.1 Mass-scaling Properties of heavy-Rydberg states

For ion-pair states $A^+ \cdots B^-$, with reduced mass, $\mu \equiv \frac{M}{m_e}$, where $M = \frac{M_A M_B}{M_A + M_B}$, very useful mass-scaling relations for heavy-Rydberg atoms are derived as shown in the fourth column of Table 1.5 by substituting the electron mass $m_e$ in the atomic expressions with the ion-pair reduced mass $M$. For an electronic Rydberg system, all of the expressions are equal to unity as represented in atomic units. Note that the fundamental velocity remains unchanged because it does not involve $m_e$.

**Table 1.5** Fundamental parameters for Heavy-Rydberg ion-pair state

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Atomic expression</th>
<th>Ion-pair value in atomic units</th>
<th>Ion-pair value in SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$m_e$</td>
<td>$\mu$</td>
<td>$9.1094 \times 10^{-31} \mu \text{kg}$</td>
</tr>
<tr>
<td>Time</td>
<td>$\frac{(4\pi\varepsilon_0)^2 \hbar^3}{m_e e^4}$</td>
<td>$\frac{1}{\mu}$</td>
<td>$2.4189 \frac{\mu}{\mu} \times 10^{-17} \text{s}$</td>
</tr>
<tr>
<td>Length</td>
<td>$\frac{(4\pi\varepsilon_0)^2 \hbar^2}{m_e e^2}$</td>
<td>$\frac{1}{\mu}$</td>
<td>$5.2918 \frac{\mu}{\mu} \times 10^{-11} \text{m}$</td>
</tr>
<tr>
<td>Velocity</td>
<td>$\frac{e^2}{(4\pi\varepsilon_0) \hbar}$</td>
<td>$1$</td>
<td>$2.1877 \times 10^6 \text{m/s}$</td>
</tr>
<tr>
<td>Energy</td>
<td>$\frac{m_e e^4}{(4\pi\varepsilon_0)^2 \hbar^2}$</td>
<td>$\mu$</td>
<td>$4.3597 \times 10^{-18} \mu \text{J}$</td>
</tr>
<tr>
<td>Potential</td>
<td>$\frac{m_e e^3}{(4\pi\varepsilon_0)^2 \hbar^2}$</td>
<td>$\mu$</td>
<td>$27.2 \mu \text{V}$</td>
</tr>
<tr>
<td>Dimension</td>
<td>Atomic expression</td>
<td>Ion-pair value in atomic units</td>
<td>Ion-pair value in SI units</td>
</tr>
<tr>
<td>-----------------</td>
<td>-------------------</td>
<td>--------------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Electric field</td>
<td>$\frac{m_e^2e^5}{(4\pi\varepsilon_0)^3\hbar^3}$</td>
<td>$\mu^2$</td>
<td>$5.1422\times10^{11}\mu^2\text{V/m}$</td>
</tr>
<tr>
<td>Magnetic field</td>
<td>$\frac{m_e^2e^3}{(4\pi\varepsilon_0)^2\hbar^3}$</td>
<td>$\mu^2$</td>
<td>$2.3505\times10^{5}\mu^2\text{T}$</td>
</tr>
</tbody>
</table>

Typical physical quantities in atomic units for atomic and molecular Rydberg systems are exhibited in the second and third columns of table 1.6 expressed as functions of their principal quantum numbers and binding energies. It can also be seen that the replacement of the electron mass by $M$ does not alter the scaling properties of ion pairs but only changes their physical magnitudes.

For a given principal quantum number, the binding energy of a heavy-Rydberg state is much higher and its orbital radius is much smaller than for a Rydberg state. As seen in Table 1.6, for the ground state of a hydrogen heavy-Rydberg state, theoretically, the binding energy is as high as 12.5 keV, whereas the ground state binding energy of ordinary Hydrogen atom is only 13.6 eV. However, ion-pair states with a small principal quantum numbers are not realized because of their physical sizes. Consider the $\text{H}^+ \cdots \text{H}^-$ case, the size of $\text{H}^-$ is $2.08 \times 10^{-10}\text{m}$. Hence, the possible lowest principal quantum numbers of the ion-pair states are given by $n_H^2a_0/\mu \approx 2.08 \times 10^{-10}\text{m}$ or $n \approx 60$. 
Table 1.6 Heavy-Rydberg ion-pair state properties

| Property                  | Rydberg atom | Heavy-Rydberg atom | Law scaled to $|E_B|$ |
|---------------------------|--------------|--------------------|---------------------|
| Binding energy            | $-\frac{1}{2n^2}$ | $-\frac{\mu}{2n_H^2}$ |                     |
| Level spacing             | $\frac{1}{n^3}$ | $\frac{\mu}{n_H^3}$ | $2 \sqrt{\frac{2|E_B|^3}{\mu}}$ |
| Kepler radius             | $n^2$        | $\frac{n_H^2}{\mu}$ |                     |
| Kepler orbital period     | $2\pi n^3$   | $\frac{2\pi n_H^3}{\mu}$ | $\pi \sqrt{\frac{\mu}{2|E_B|^3}}$ |
| Inglis-Teller limit       | $\frac{1}{3n^5}$ | $\frac{\mu^2}{3n_H^5}$ | $\frac{4}{3} \sqrt{\frac{2|E_B|^5}{\mu}}$ |
| Stark splitting           | $3Fn$        | $\frac{3Fn_H}{\mu}$ | $3F \sqrt{\frac{1}{2|E_B|^2\mu}}$ |
| Stark oscillation time    | $\frac{2\pi}{3Fn}$ | $\frac{2\pi\mu}{3Fn_H}$ | $\frac{2\pi}{3F} \sqrt{\frac{2|E_B|}{\mu}}$ |

Moreover, comparison between the principal quantum number of ion-pair states to those of Rydberg atoms shows that for a given energy binding $E$, the principal quantum number of the Rydberg state is far less than that of the heavy-Rydberg state. From the expression $n_H = (\frac{\mu}{2E})^{1/2}$, substituting $E = 136$ meV, leads to $n \sim 10$ for hydrogen Rydberg atoms and $n_H \sim 317$ for $H^+ \cdots H^-$ ion pairs. Despite the huge difference in their principal quantum numbers, the size of the ion pairs remains the same as seen from the expression for the Kepler radius in the table 1.6.
The motional time scales for ion pair states are much slower. According to Bohr's corresponding principle, the classical orbital frequency is approximately equal to the frequency for transitions between adjacent energy levels, resulting in the Kepler orbital period \( T_n \approx 2\pi n^3 \). Again for a binding energy of 136 meV, a hydrogen Rydberg atom has \( T_n \) of 0.15 ps whereas for \( H^+ \cdots H^- \) ion pairs \( T_{n_H} \sim 5.2 \) ps, indicating that the ion pairs revolve around their center of mass \( \sim 35 \) times slower than is the case for a Rydberg atom.

In response to an applied electric field, the energy levels of Heavy-Rydberg systems are split into a manifold of Stark states with Stark level spacing and Inglis Teller-limit at much smaller values since they are scaled as \( 1/\mu^{1/2} \). Therefore, the sensitivity of heavy-Rydberg atom to electric fields is significantly magnified.

### 1.4.2 Dissociation field for ion-pair states

The dissociative behavior of ion-pair states in an electric field is the similar manner as for the ionization of atomic Rydberg atoms which was discussed in section 1.1. Classically, in the presence of an electric field ion pairs can be pulled apart if their binding energies \( E_B \) exceed the potential barrier at the saddle point which is given by \( V = -2\sqrt{F} \), producing dissociation field \( F = E_B^2/4 \). Note also that due to the large reduced mass \( \mu \) of heavy-Rydberg systems, dissociation through the tunneling is unimportant and can be ignored.
The effect of core-scattering interactions causes the low-$\ell$ ion pair states to precess rapidly. Theoretically, in fields with low slew rates, the very low-$\ell$ states undergo the adiabatic. The dissociation field for such states is reduced to the "adiabatic" dissociation threshold and can be written as

$$F_{ad} = \frac{\mu^2}{16n_H^5}$$

(1.24)

In contrast to low-$\ell$ states, high-$\ell$ states experience much less of the potential from the short-range core interaction. Applying a field with a sufficiently rapid slew rate, the level crossings are traversed diabatically. From the binding energy for ion-pair extreme red-shift states $E \sim -\mu/2n_H^2 - 3Fn_H^2/2\mu$, the dissociation threshold becomes [38]

$$F_{da} = \frac{\mu^2}{9n_H^4}$$

(1.25)

which is called the "diabatic" dissociation threshold. Typically, for extreme blue-shifted ion-pair states, the dissociation field is equivalent to $2F_{da} \sim 2\mu^2/9n_H^4$. As a consequence, for heavy-Rydberg states with a broad distribution of high angular momenta $L$ created from the thermal Rydberg atom-molecule collisions as seen in figure 1.9, the average dissociation field lies between those extremes is given an average by

$$F = \frac{\mu^2}{6n_H^4}$$

(1.26)
which is represented in common units for the experiment as

\[ E_B(\text{meV}) = 14\sqrt{F(\text{kV/cm})} \]  

(1.27)

Figure 1.9 Dependence the angular momentum \( L \) on effective principal quantum number \( n_H \) for \( K^+ \cdots I^- \) ion pairs formed in \( K(14p)/CF_3I \) collisions where \( L \) is in units of \( \hbar \). The calculation assumes a \( \delta \)-function translational energy release distribution with energy \( \varepsilon = 0.7 \text{ eV} \).
Chapter 2
Experimental setup

This work presents measurements of the velocity and angular distributions of product ion pairs which can be used as a tool to probe the lifetime and decay energetics of excited intermediates. As seen in figure 2.1a, potassium atoms in a collimated beam are photo-excited to selected Rydberg state by dye laser pulses near the center of a small gas cell filled with the target gas molecules. Their rapid collisional destruction leads to creation of ion-pair states. A fraction of these that travel in the xy plane defined by the laser and the atom beam exit the gas cell through a narrow slit and enter an analysis region where they are probed via dissociation induced by a pulsed electric field. The resulting ions are then accelerated to be detected by a position sensitive detector (PSD) that can record both their arrival times and positions as seen in figure 2.1b. Time-of-flight techniques are used to determine the ion-pair velocity distributions. The arrival position distributions as a function of the delay time, tD, between the formation of the ion pairs and their detection at the PSD, are then compared to the results of simulations with different assumed input parameters to explain the energetic properties of the negative intermediates. Detailed descriptions of the apparatus are provided in following sections.
Figure 2.1 Schematic top views of experimental apparatus. (a) Ion pairs created in the gas cell are scattered into the analysis region where they are detected by the PSD. (b) An experimental arrival position distribution for $\text{K}^+ \cdots \text{I}^-$ ion pairs formed in K(14p)-CF$_3$I collisions as measured at $t_D=30$ μs.

Figure 2.2 Side view of the experimental apparatus. The apertures drawn in the walls of the gas cell allow passage of the laser and atom beams.
2.1 Vacuum system

There are two differentially-pumped stainless steel chambers in the experiment; the oven chamber and the main chamber which contains the gas cell and the analysis region. At room temperature the gas cell contains the target gas pressure of $\sim 2 \times 10^{-5}$ torr controlled via a needle valve which connects to the target gas reservoir. This pressure is monitored and kept constant while experiments are performed.

The potassium atom beam is produced in the oven chamber and collimated with a 0.3 mm diameter circular aperture that isolates the higher pressure in the oven chamber from the main chamber. Both chambers use high vacuum diffusion pumps which need mechanical backing pumps. The gas pressures in the two vacuum chambers are measured by ionization gauges.

2.2 Atomic beam

Potassium vapor is produced by heating a small quantity of metallic potassium ($\approx 1$ gram) inside a stainless steel oven. The oven is kept at a temperature $T \approx 573$ K as measured by a thermocouple located on the wall of the oven.

Given atomic mass $m$, Boltzmann constant $k$, and oven temperature $T$, the velocity distribution of potassium atoms in the beam $f(v)$ for speeds ranging from $v$ to $v + dv$ is given by

$$f(v) \propto v^3 e^{-\frac{mv^2}{2kT}}$$  
(2.1)
For long duration (~ 10 – 20 μs) laser pulsed as employed here, the number of Rydberg states created by a photo-excitation of potassium atoms is dependent on the time they are exposed to the laser beam, requiring a factor $1/n$ be included into the expression above. Therefore, the velocity distribution of the Rydberg atoms excited can be written as

$$f_R(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$  \hfill (2.2)

The resulting velocity distribution is shown in figure 2.3.

![Velocity distribution of photoexcited Rydberg atoms](image)

**Figure 2.3** Velocity distribution of photoexcited Rydberg atoms

Considering the collisional cross section, $\sigma$, for potassium atoms which is given by $\sigma = 4\pi r^2 = 10.3 \times 10^{-15} \text{cm}^{-2}$, where $r$ is a mean potassium atomic radius and equal to 0.235 nm, the mean free path of the atoms inside of the oven is given by

$$\lambda = \frac{1}{\sqrt{2}n\sigma} = T/\sqrt{2}(9.656 \times 10^{18})P\sigma = 0.27 \text{ mm}$$  \hfill (2.3)
which is somewhat less than the 0.6 mm-diameter circular aperture $D$ in the oven nose which is maintained 20 K higher than the temperature of the oven body so as to prevent potassium atoms from condensing and clogging the aperture. Because $\lambda \ll D$ is not satisfied, the potassium beam flows effusively through the nose.

### 2.3 Laser system

The laser used in this work is an extracavity-doubled Coherent CR699-21 ring dye laser. A dye laser power of 1 Watt with a tuning wavelength ranging from 570~650 nm is obtained by using Rhodamine 6G dye and a coherent Verdi V8 solid state laser which provides the dye laser with 7.5 watt of 532 nm light. Three optical elements of the ring laser cavity, a birefringent filter with a passive bandwidth of 380 GHz, a thin etalon with a free-spectral-range (FSR) of ~ 200 GHz, and a thick etalon with a 10 GHz FSR are used for frequency control resulting in a single frequency output with a line width of 500 kHz. The resulting visible light from the cavity is focused into a Wavetrain frequency doubler where its frequency is doubled by a KDP (Potassium Dihydrogen Phosphate) crystal to obtain ultraviolet light that can be used for the direct excitation of potassium atoms from ground to Rydberg states. The ultraviolet laser output is chopped into pulses of duration ~ 10μs with a repetition frequency of ~ 1 kHz by using an acousto-optic modulator (AOM) and then focused using a lens at the center of the gas cell.

In order to stabilize the output frequency of the dye laser, a Helium-Neon (HeNe) laser and a Fabry-Perot etalon (the superlock system) are used. Both laser
beams are superposed and directed through the etalon which is scanned at a frequency of 50Hz using a piezoelectric transducer (PZT). The emerging light is then separated by a polarizing beam splitter. As the length of the cavity changes, two series of transmission peaks are detected and associated with each of the input lasers. Any deviation in frequency by the dye laser will result in a shift of its transmission peak relative to that of HeNe laser. Error signals are generated and return the dye laser to the desired frequency. Stabilization in this way limits the long-term frequency drift of the dye laser to less than 1 MHz/day.

A Michelson interferometer is used to measure the wavelength of the dye laser. Both the dye laser and a parallel, collinear HeNe laser are sent through the interferometer and detected by independent photodiodes, as shown in figure 2.4. As the retroreflector carriage travels along the track between the two folding mirrors, the fringes in the interference patterns for each laser beam are counted. The number of fringes $N$ for both laser beams is simply given by

$$N = \frac{4d}{\lambda}$$

(2.4)

where $d$ is the distance the carriage travels and $\lambda$ is the wavelength of the laser. Since the carriage moves the same distance $d$ for both laser beams and the wavelength of HeNe laser is already known, $\sim 632.991 \text{ nm}$, the dye wavelength can be determined by taking the ratio of the measured number of fringes which can be written as

$$\lambda_D = \left(\frac{N_H}{N_D}\right) \lambda_H$$

(2.5)
where \( \lambda_H \) and \( \lambda_D \) are the wavelengths of HeNe and the dye laser respectively and \( N_H \) and \( N_D \) are the number of fringes counted for each laser.

![Figure 2.4 Optical component schematic of a Michelson interferometer.](image)

### 2.4 Interaction region

The interaction region is the gas cell where Rydberg atom collisions with target gas molecules occur. The collimated potassium beam from the oven chamber passes through the center of the gas cell that contains target gas molecules as shown in the figure 2.1a. Rydberg states are then created using the UV radiation provided by the extracavity-doubled Rh6G dye laser which is in the form of pulses of \( \sim 10 \) \( \mu \)s duration and pulse repetition frequency \( \sim 1 \) kHz obtained using an acousto-optic modulator. A small transverse electric field (\( \sim 45 \) \( \text{V cm}^{-1} \)) is applied to aid in tuning the laser to the desired state and accelerates ions produced by blackbody radiation-
induced photoionization (or collisions) inside the cell into the drift region. These ions are detected by a microchannel plate. This field also prevents free ions or unbound ion pairs produced in the gas cell from escaping into the analysis region.

In spite of the relatively long lifetimes of K(14p) states, \( \sim 6 \, \mu s \), collisions decrease their effective lifetimes, \( \tau_{\text{eff}} \), to \( \sim 2 \, \mu s \) given the mean Rydberg atom velocity of \( \sim 6 \times 10^4 \, \text{cm s}^{-1} \), ion pairs must be formed within \( \sim 1 \, \text{mm} \) of the center of the gas cell.

### 2.5 Analysis region

Bound ion pairs formed in the gas cell enter the analysis region through a slit which limits the scattering angles \( \theta \) (defined from the atomic beam) in the xy plane from \( 22.5 \) to \( 67.5^\circ \), and angles of \( \pm 4^\circ \) from the horizontal plane as illustrated in figure 2.1a. Use of an off-axis geometry provides opportunities to investigate the velocity and angular distributions of the ion-pairs spatially. It also distinguishes the trajectories of the ion pairs from those of any surviving Rydberg atoms, which simplifies data analysis by getting rid of spurious ion signals associated with field ionization of surviving Rydberg atoms. Since only a small fraction of the product bound ion pairs travel within the solid angle defined by the slit, data must be acquired over many laser pulses to determine the distribution of ion pair arrival positions.

As seen in the figure 2.5, the analysis region consists of several fine mesh grids and a one-inch diameter PSD. Ion pairs entering the analysis region are
dissociated by application of a voltage pulse of grid G2 creating an electric field that rises from $\sim 0$ to 5 kV/cm in 3 $\mu$s thereby dissociating ion pairs with binding energies less than $\sim 30$ meV. The resulting ions are extracted the positive potassium ions being accelerated toward the PSD while the negative ions travel toward the top ion collection plate. This field configuration also suppresses spurious signals due to secondary ions produced by negative ion collisions with the collection plate. The values of the voltages applied to the electrodes for the present study of $\text{K}(14p)/\text{CF}_3\text{I}$ collisions are listed in table 2.1.

**Figure 2.5** Schematic diagram of the analysis region. The voltage pulse for dissociation is applied to the grid G2.
Table 2.1 Voltage values for each mesh grid

<table>
<thead>
<tr>
<th>Grid</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Collection Plate</td>
<td>1600</td>
</tr>
<tr>
<td>G1</td>
<td>1700</td>
</tr>
<tr>
<td>G2</td>
<td>0-1500</td>
</tr>
<tr>
<td>G3</td>
<td>0</td>
</tr>
<tr>
<td>G4</td>
<td>-500</td>
</tr>
<tr>
<td>G5</td>
<td>-600</td>
</tr>
<tr>
<td>PSD</td>
<td>-700</td>
</tr>
</tbody>
</table>

2.6 Monte Carlo simulation model

A Monte Carlo calculation is used to model ion pair formation and its dependence on the properties of the excited intermediates. The model randomly selects reactant velocities from appropriate distributions and utilizes the electron probability density of hydrogenic wave functions with a principal quantum number \((n-2)\) to represent potassium Rydberg states to determine the distributions of interparticle separations at which electron attachment occurs. Electron attachment is assumed to be an s-wave process whereupon the attachment rate is approximately independent of electron velocity and can be assumed to be a constant.

After attachment, the mutual Coulomb attraction of the Rydberg core ion and excited intermediate forms ion pairs whose trajectories are computed by using Classical Mechanics. If the exited intermediate is short lived it will, after some time \(t\),
dissociate into a stable negative ion and a neutral molecule. This anion then interacts with the positive ionic core, leading to the formation of ion-pair states. The time evolution of the position of ion pairs travelling near the horizontal plane is determined and ion-pair position distributions at the PSD at any delay time, $\tau_p$, determined. The results are then compared to experimental data. The simulation steps are explained in more detail below.

Firstly, the Rydberg atom velocity is randomly selected from the velocity distribution of an effusive beam which is given by equation (2.2).

For the target molecules, a Gaussian distribution is employed with components

$$f_{T}(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2}e^{-\frac{mv_x^2}{2kT}}$$  \hspace{1cm} (2.6)

Target molecules move randomly in all direction with velocity spreads centered on the most likely value of $\bar{v} = \sqrt{kT/m}$. Both of the distributions are stored in lookup tables with equal probability bins.

The initial spatial distribution of the Rydberg atoms is taken to match the Gaussian distribution in laser beam defined as

$$f(r) \propto e^{-\left(\frac{r}{2w^2}\right)^2}$$  \hspace{1cm} (2.7)

where $w$ is the laser-focus width and $r$ is the radial position in the laser beam.
The target molecules are located initially at any random position inside a spherical volume spread from the radius of positive Rydberg core to the maximum radius of the Rydberg electron cloud. The radial probability density $|\psi(r)|^2$ for hydrogen is used to determine the distribution of atom-molecule separations at which attachment occurs. The hydrogenic radial wave function is represented as

$$\psi(r)_{n',\ell} = \sqrt{\frac{(2\pi)^3}{a_0^n}} \frac{(n-\ell-1)!}{2n(n+\ell)!} e^{-\frac{\rho}{2}p^{\ell}} L_{n'-\ell-1}^{2\ell+1}(\rho)$$

(2.8)

where $\rho = \frac{2\pi r}{a_0 n'}$ $Z$ is the atomic number, $L$ is the Laguerre polynomial, $a_0$ is the Bohr radius, $\ell$ is the angular quantum number and $n'$ is the effective principal quantum number, $n - \delta_\ell$.

For potassium Rydberg atoms, the parameters above can be set as $Z = 1$, $\ell = 1$, and $\delta_\ell = 1.71 \sim 2$ leading to the radial probability density distribution in the xy plane shown in figure 2.6.

![Figure 2.6 Radial electron probability density distributions (a) in the XY-plane and (b) in the radial](image)
direction for a hydrogen atom in the 12p state used to approximate that for a potassium atom in 14p state.

After the electron attachment occurs, classical orbital mechanics is used to propagate the motion of the positive Rydberg core ions and excited intermediates and filter out those pairs that do not have closed orbits. This is the problem of classical two-body central force motion which is well documented and understood. The Lagrangian in atomic units is written as

\[ \mathcal{L} = T - V = \frac{m_1 r_1^2}{2} + \frac{m_2 r_2^2}{2} + \frac{1}{r} \]  \hspace{1cm} (2.9)

Using the definitions of the relative separation \( \vec{r} = \vec{r}_1 - \vec{r}_2 \) and the reduced mass \( \mu = \frac{m_1 m_2}{(m_1 + m_2)} \), the Lagrangian can be written

\[ \mathcal{L} = \frac{\mu r^2}{2} + \frac{1}{r} \]  \hspace{1cm} (2.10)

which is equivalent to a one-body problem. From this we all know that the angular momentum \( \vec{L} \) of the system is conserved, \( \frac{d\vec{L}}{dt} = 0 \), and its motion is constrained to a plane perpendicular to the vector angular momentum. As a result, it can be described in terms of plane polar coordinates, \((r, \phi)\),

\[ \mathcal{L} = \mu (\dot{r}^2 + r^2 \dot{\phi}^2) + \frac{1}{r} \]  \hspace{1cm} (2.11)

with \( \frac{\partial \mathcal{L}}{\partial \dot{\phi}} = \mu r^2 \dot{\phi} = \text{constant} = \ell \). From the conservation of energy

\[ E = \frac{\mu r^2}{2} + \frac{\ell^2}{2\mu r^2} - \frac{1}{r} = \text{constant} \]  \hspace{1cm} (2.12)
and solving for $\dot{r}$,

$$\dot{r} = \sqrt{\frac{2(E+1/r)}{\mu} - \frac{l^2}{\mu^2 r^2}}$$  \hfill (2.13)\\

Noting that $d\phi = \left(\frac{d\phi}{dt}\right) \left(\frac{dt}{dr}\right) dr = \left(\frac{\dot{\phi}}{r}\right) dr$ and, substituting $\dot{\phi} = l/\mu r^2$

$$\phi(r) = \int \frac{l/r^2}{\sqrt{2\mu(E - \frac{1}{r} - \frac{l^2}{2\mu r^2})}} dr$$  \hfill (2.14)\\

By defining $u \equiv 1/r$ then we have

$$\cos(\phi) = \frac{(l^2/2\mu r^2)(1/r) - 1}{[1 + 2E l^2 / \mu]^{1/2}}$$  \hfill (2.15)\\

Therefore,

$$r = \alpha / (1 + \varepsilon \cos(\phi))$$  \hfill (2.16)\\

where the semi-latus rectum $\alpha \equiv l^2 / \mu$ and the eccentricity $\varepsilon = [1 + 2E l^2 / \mu]^{1/2}$.

If dissociation of the intermediate occurs, the ion-pair system comprising the Rydberg ionic core and excited intermediate is followed until the dissociation time $t_d$, whose distribution is given by

$$f(t_d) = \frac{e^{-t_d/\tau}}{\tau}$$  \hfill (2.17)\\

where $\tau$ and $\frac{1}{\tau}$ are the intermediate lifetime and normalization factor respectively.

At dissociation, the model assumes a specified translational kinetic energy release distribution (see figure 2.7) to describe the dissociation behavior of the negative intermediate ions. When electron capture by the target occurs, if the
attaching target molecule dissociates immediately with lifetime $\tau$ less than a vibrational period, there is little opportunity for the redistribution of the excess energy of the reaction among internal vibrational modes of the molecule. In consequence, most of the excess energy appears in translation of the product ion and the neutral molecule, producing a narrow energy distribution that approaches a $\delta$-function distribution.

In contrast, for long-lived intermediates, a significant amount of the excess energy couples into the internal vibrational modes of the molecule. Therefore, not much of the energy is converted into the translational kinetic energy of the products. According to unimolecular decay theory, the translational energy release distribution is of the form of a Boltzmann-like distribution given by [39]

$$f(\varepsilon) = \frac{e^{-\varepsilon}}{\varepsilon}$$  \hspace{1cm} (2.18)

For an incident electron with the kinetic energy $E_e$ captured by a molecule $XY$, the excess energy of the reaction, $e^- + XY \rightarrow XY^* \rightarrow X^- + Y$, is given by

$$\varepsilon = E_e + EA(X) - D(XY) + E_{int}$$  \hspace{1cm} (2.19)

where $E_{int}$ denotes the internal energy in the target molecule. $EA(X)$ and $D(XY)$ are the electron affinity of $X$ and the dissociation energy of $XY$, respectively. Thus, the most probable kinetic energy $E_K$ of the product $X^-$ can be written as

$$E_K = \left(1 - \frac{m_X}{m_{XY}}\right) (\varepsilon - E_e)$$  \hspace{1cm} (2.20)
where $m_X, m_{XY}$ are the mass of the fragment $X$ and $XY$ and $E_E$ is the internal excitation energy of the fragments.

After the target molecule dissociates, the Rydberg core ion interacts with the fragment anion which has gained some kinetic energy from the dissociation process. The total energy of the ion pair is calculated by using $E_{total} = \frac{1}{2} \mu \dot{r}^2 - 1/r$ where $\mu$ is the reduced mass of the potassium and the fragment ions, $\dot{r}$ is their relative velocity and $r$ is their separation. If $E_{total} > 0$, the ion-pair system is unbound. If $E_{total} < 0$, the ion pairs are bound and their motions are followed. For comparison to experimental data weakly-bound ion pairs (their binding energy is less than 30 meV) are selected. Their velocity and angular distributions are computed. The simulated results are then compared to the experimental data to determine the lifetimes and decay energetics of the intermediates.

Figure 2.7 Model translational energy release distributions for K(14p)-CF$_3$I collisions comprising (a) a $\delta$-function at 0.7 eV (b) a Gaussian distribution of 0.2 eV FWHM (c) a linearly increasing distribution (d) a flat distribution (e) a linearly decreasing distribution, and (f) a Boltzmann-like distribution.
The probability of electron capture by the target molecule is related to the available interaction time, $t$, defined as the time available for electron attachment to occur and is expressed as

$$P(t) = 1 - e^{-\rho kt} \approx \rho kt \text{ when } \rho kt \ll 1$$

(2.21)

where $\rho$ is the gas density, $k$ is the rate constant, and $t$ is the available interaction time. Thus, the probability of electron attachment is only proportional to the available interaction time $t$, which begins with a creation of Rydberg atom by the laser pulse and ends with Rydberg atom decay.
Chapter 3

Results and discussion

This section provides a discussion of calculated and experimental results for ion pairs formed by Rydberg atom collisions with the target species CF$_3$I, CH$_2$Br$_2$, and CCl$_4$.

3.1 Heavy-Rydberg ion pair formation in K(14p)-CF$_3$I collisions

3.1.1 Model discussion

Collisional destruction of potassium Rydberg atoms by CF$_3$I can create ion-pair states by the reaction,

$$K(14p) + CF_3I \rightarrow K^+ + CF_3I^- \rightarrow K^+ \cdots I^- + CF_3 \quad (3.1)$$

The excess energy $E_E$ released from the electron capture reaction in (3.1) can be derived from $E_E = E_e + EA(I) - D(CF_3 - I)$, with the electron affinity $EA$ of I, 3.06 eV, the ground state to ground state bond dissociation energy of the neutral, $D_0$, measured as 2.39 eV [40] and 2.33 eV [41], and the Rydberg electron kinetic energy $\sim 15$ meV which is much smaller than its mean binding energy $\sim 90$ meV. Since the attached electrons in $np$-Rydberg states have highly-elliptical orbits, electron capture most likely occurs near the outer classical turning point where the electrons travel with very low kinetic energy. Additionally, the contribution from the usable internal energy can be ignored because the internal rovibrational modes are not strongly excited [32]. For the lowest excited vibrational mode, the stretching
vibrational mode of CF$_3$-I with a vibrational spacing of $\sim$ 35.5 meV, the probability of excitation is only 0.256 at room temperature. These considerations suggest an available excess energy of $\sim$ 0.7 eV, a number in reasonable agreement with the value $E_E \sim 0.8$ eV obtained from earlier measurements using high $n$, $n \sim 55$, Rydberg atoms [42]. Not all $E_E$ is acquired by the I$^-$ ion. 65% of the released energy is given to the lighter CF$_3$ fragment. The fraction given to the I$^-$ ion is simply calculated from the mass ratio $1 - \frac{m_{I^-}}{m_{CF_3}}$, where $m_{I^-}$ and $m_{CF_3}$ are the masses of the I$^-$ and CF$_3$ fragments.

As discussed in section 2.6, the lifetime (and decay energetics) of excited intermediates is inferred from their translational kinetic energy release distributions. The calculated spatial $K^+ \cdots I^-$ distributions at delay time, $t_D$, for different assumed energy release distributions for $K(14p)$-CF$_3$I collisions are shown in figure 3.1. In the figures the color scale in each panel is normalized 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. Firstly, figure 3.1a illustrates spatial distributions calculated assuming that the energy release distribution is a $\delta$-function at 0.7 eV, that all of the excess energy $E_E$ is transferred to translation, and that the CF$_3$I$^{--}$ intermediate is short lived (intermediate lifetime $\tau = 0$). As the delay time, $t_D$, increases the bound ion pairs move away from the center of the gas cell with a narrow range of speeds centered near $\sim$ 6x10$^4$ cm s$^{-1}$ over a broad range of scattering angles, $\theta$, centered in the direction of the potassium atom beam. This is
also evident in figure 3.2 which shows ion-pair velocity distributions derived for different scattering angles. Each set of data is for an angular width of $\pm 5^\circ$ centered on the labeled angle. Inspection of the figure shows that those ion pairs with the highest velocity, $\sim 6 \times 10^4 \text{ cm s}^{-1}$, travel in the forward direction, $\theta \sim 0^\circ$, and their number and velocities decrease for larger scattering angles.
Figure 3.1 Calculated position distributions for K⁺⋯I⁻ ion pairs formed in K(14p)-CF₃I collisions for a laser pulse width of 1 μs and indicated delay times τᵰ. The assumed translational energy release distributions are illustrated in the right panels and comprise (a) a δ-function at ε = 0.7 eV, (b) a Gaussian distribution of 0.2 eV FWHM centered on ε = 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 ε = 0.3 eV.

Figure 3.2 Calculated velocity distributions of K⁺⋯I⁻ ion pairs that travel at the scattering angles θ indicated for a δ-function translational energy release of 0.7 eV.
The simulated position distributions for a broader translational energy release distribution using the same excess energy is illustrated in figure 3.1b. The assumed distribution is a Gaussian with a FWHM of 0.2 eV centered on a mean value $\bar{\epsilon} = 0.7$ eV. In comparing figure 3.1b to figure 3.1a, there is a little change in ion-pair positions and velocities (see figure 3.3) because the most probable excess energy is still at $\bar{\epsilon} = 0.7$ eV. Furthermore, the dependence of speed $v$ on kinetic energy $\epsilon$ of the ion pairs scales as $v \propto \sqrt{\epsilon}$. The predicted spatial distributions are relatively insensitive to the assumed width of the distribution.

If the internal rovibrational modes in the intermediate are available to redistribute the excess energy before dissociation, the excited intermediate can be temporarily stabilized. This results in an increase in the intermediate lifetime and a decrease in the excess energy that appears in translation. The calculated position distributions for different assumed distributions with decreasing translational energy are displayed in figures 3.1c to 3.1f. In each case, the model assumes the lifetime of the intermediate to be zero. As the mean translational energy release decreases, the momenta of the I$^-$ ions are reduced. Therefore the average velocities of the product K$^+$ ... I$^-$ ion pairs decrease and their angular distributions become increasingly forward peaked in the direction of the potassium beam as can be seen in figure 3.3.
Figure 3.3 Calculated velocity and angular distributions of $K^+ \cdots I^-$ ion pairs formed in $K(14p)$-CF$_3$I collisions for the assumed energy release distributions labeled as (a) to (f) in figure 3.1 are shown in the left and right hand panels respectively.

Figure 3.4 Ion-pair velocity distributions versus the scattering angle $\theta$ for a Boltzmann-like distribution with $\varepsilon = 0.3$ eV.
The velocity distributions for different assumed scattering angles for Boltzmann-like energy release distribution are shown in figure 3.4. Comparing these to those for the δ-function distribution, the ion pairs move slower and the spatial distributions are more strongly focused in the forward direction, figure 3.1f. Because the Boltzmann-like distribution can provide a wide range of translational energy releases $\sim 0 - 1$ eV, ion pairs have broader possible values of velocities.

\[ \tau = 0 \text{ ps} \quad (a) \quad (b) \]
\[ \tau = 10 \text{ ps} \]
\[ \tau = 100 \text{ ps} \]
\[ \tau = 1 \text{ ns} \]

Figure 3.5 Calculated arrival position distributions at $t_0 = 30 \mu s$ for K$^+ \cdots$I$^-$ ion pairs formed in K(14p)-CF$_3$I collisions and the CF$_3$I$^-$ intermediate lifetimes $\tau$, indicated. The assumed distributions are (a) a δ-function translational energy release of 0.7 eV and (b) a Boltzmann-like distribution with the mean energy of 0.3 eV.
Figure 3.6 Angular distributions of $K^+ \cdots I^-$ ion pairs formed in $K(14p)$-CF$_3$I collisions with (a) a $\delta$-function translational energy release distribution with $\varepsilon = 0.7$ eV and (b) a Boltzmann-like distribution with $\bar{\varepsilon} = 0.3$ eV.

The dependence of the arrival spatial distributions on assumed intermediate lifetimes is displayed in figure 3.5a and 3.5b for the limiting cases of a $\delta$-function and a Boltzmann-like translational energy release distribution and a $t_D$ of 30 $\mu$s. The model simulation assumes the excited intermediate CF$_3$I$^*$ decays exponentially as $e^{-t/\tau}$, where $\tau$ is the mean lifetime as discussed in section 2.6. The angular distributions of the two cases are also calculated and presented in figure 3.6a and 3.6b. The spatial and angular distributions are relatively insensitive for both assumed cases to intermediate lifetime on time scales of a few tens of picoseconds. However, their angular distributions spread considerably to larger scattering angles when the intermediate lifetimes approach the characteristic Kepler orbital periods of $K^+ \cdots$CF$_3$I$^*$ ion pairs given by $T = \pi \sqrt{\frac{\mu}{2|E_B|^3}}$, for binding energies of $\sim 100$ and 15 meV, $T \sim 60$ ps and 1 ns (see section 1.4.1). This is because in the center of mass
frame of reference the orbiting $K^+ \cdots CF_3I^+$ ion pairs have randomized their orientations. Moreover, as seen in figure 3.6, the angular distribution in the case of a $\delta$-function distribution responds more sensitively to changes in intermediate lifetimes than in the case of a Boltzmann-like distribution. This is due to the fact that ion pairs associated with the $\delta$-function distribution are more tightly bound (their velocities are comparable to those of parent Rydberg atoms) and have smaller values of the orbital periods. As a result, the $K^+ \cdots CF_3I^+$ ion pairs have more randomized their orientations than for a Boltzmann-like distribution. Even though measurements of angular distributions do not provide a sensitive measure of the lifetimes of short-lived intermediates, they might be used to classify very long-lived ($\tau \geq 100$ ps) intermediates.

The ion-pair motions seen from figure 3.1 to 3.6 can be qualitatively explained in terms of their binding energies. Rydberg Potassium atoms interact with the target molecules forming ion-pair states whose energies are classically given by $E_{total} = E_{krel} + V_{coul}$. The Coulomb potential $V_{coul}$ of the ion pairs is similar to that of the parent Rydberg atoms because electron capture occurs at the same distribution of separations with a mean value similar to the radius of Rydberg electron $r \sim n^2$, $n \sim 12$. Thus, their relative kinetic energies are important in determining their binding energies where $E_{krel} = \frac{1}{2} \mu v_{rel}^2$, and $v_{rel}$ is the relative velocity between the positive core ion and the fragment anion. For a near $\delta$-function translational energy release distribution the velocity distribution of the fragment $I^-$ in the laboratory frame is narrow and centered near $\sim 6 \times 10^4$ cm s$^{-1}$ which is much
higher than the initial velocities of the excited intermediate CF$_3$I$^{-*}$ ions themselves, \( \sim 2\times10^4 \text{ cm s}^{-1} \). As mentioned earlier, the mean velocity of the Rydberg atoms is \( \sim 6\times10^4 \text{ cm s}^{-1} \) comparable to that of the negative I$^-$ ions. Therefore, \( E_{k\text{rel}} \) is minimized when the parent Rydberg atom and the anion I$^-$ travel in the same forward direction. As the angle, \( \phi \), defined as an angle between the direction of the Rydberg core ion and product I$^-$ ion, increases the value of \( E_{k\text{rel}} \) becomes greater and is maximized when \( \phi = 180^\circ \). In other words, the average binding energy increases as \( \phi \) decreases, producing bound ion pairs that preferentially travel in the forward direction. In the limit of \( \phi \sim 180^\circ \), the I$^-$ ions travel in the opposite direction to the K$^+$ ions which minimizes their average binding energies and few ion pairs can remain bound. In consequence, the angular distribution associated with the production of free I$^-$ ions is expected to peak in the back direction as has been observed previously [43]. In addition to the energy considerations, conservation of momentum also plays a role when discussing angular distributions. As \( \phi \) increases, the resulting ion pairs gain an increasing component of transverse momentum and are therefore dispersed through ever larger scattering angles \( \theta \). The relationship between the binding energies of the K$^+$ \( \cdots \) I$^-$ ion pairs and their scattering angles are shown in figure 3.7. Their average binding energies are greatest at small scattering angles and the more weakly bound ion pairs are concentrated at larger scattering angles as expected.
Figure 3.7 Dependence of the calculated angular distributions of \( \text{K}^{+} \cdots \text{I}^{-} \) ion pairs formed in \( \text{K}(14\text{p})\)-\( \text{CF}_3\text{I} \) collisions on their binding energies. Each curve is associated with the binding energy ranges indicated. The assumed translational energy release distribution is a \( \delta \)-function distribution with \( \varepsilon = 0.7 \) eV.

A decrease in the assumed mean translational energy release causes the anion fragments \( \text{I}^{-} \) to be formed with lower velocities, resulting in a reduction in ion pair velocities and a shrinking of the spatial distributions as seen clearly in the limiting case of a Boltzmann-like distribution (see figure 3.1f). In this limit, the main contribution to the final \( \text{I}^{-} \) velocities comes from the thermal velocities of \( \text{CF}_3\text{I} \) target molecules which are peaked at \( \sim 3 \times 10^4 \) cm s\(^{-1}\). This value is two times less than the velocity of the parent Rydberg atoms and therefore the resulting center of mass velocities of the ion pairs are in the range of \( \sim 3 \) to \( 5 \times 10^4 \) cm s\(^{-1}\), leading to larger relative kinetic energies \( E_{\text{Krel}} \) and smaller binding energies as compared to the \( \delta \)-function distribution case. As a result, a smaller fraction of the ion pairs remains bound and their average binding energy is highest when the \( \text{I}^{-} \) ions move in the
forward direction, the same direction as the Rydberg atoms. Furthermore, due to the relatively small initial transverse components of momentum of the I\(^-\) ions, ion pairs are more focused in the forward direction. This can be seen from figure 3.8. As the assumed mean translational energy release decreases the angular distribution becomes more strongly peaked in the forward direction.

**Figure 3.8** Calculated angular distributions of K\(^+\) \(\ldots\) I\(^-\) ion pairs formed in K(14p)-CF\(_3\)I collisions with different assumed translational energy release distributions; (a) a \(\delta\)-function distribution at \(\varepsilon = 0.7\) eV, (b) a distribution that is flat from 0 to 0.7 eV and, (c) a Boltzmann-like distribution with \(\bar{\varepsilon} = 0.3\) eV. The results are normalized by their highest peaks.
### 3.1.2 Comparison with experimental results

Figure 3.9 shows a comparison between experimental arrival position distributions recorded at the PSD following K(14p)-CF₃I collisions for different delay times and model simulations. To increase the experimental signal, the laser pulse width used in the experiment and in the simulation is $\sim 10 \, \mu s$. This results in a broadening of the arrival position distributions for both experiment and calculation since the ion pairs formed near the beginning of the laser pulse travel several millimeters towards the analysis region by the time ion pairs are formed at the end of laser pulse. Given the short effective Rydberg lifetime, $\sim 2 \, \mu s$, it is reasonable to assume that the ion pair production rate is constant during the laser pulse. As in figure 2.1 and 3.9, the location of the PSD is indicated by a white circle and the bottom left corner of the square is the center of the gas cell where ion-pair states are first created. Moreover, the electric dissociation field of $\sim 5 \, kV \, cm^{-1}$ is included in the simulation by identifying weakly-bound ion pairs with binding energies less than $30 \, meV$ and considering only their motion into the analysis region. As seen in the angular distributions of figure 3.7, such ion-pair states are mostly observed at non-zero scattering angles.
**Figure 3.9** Schematic diagram of the geometry used in comparing the experimental and calculated arrival position distributions. The white circle represents the PSD and the scattering angles defined by the slit at the entrance to the analysis region. The 3x3 cm$^2$ square is a background area shown by the black color panel in the arrival position distributions (see figure 3.10).
Figure 3.10 Experimented and calculated arrival position distributions at the PSD for weakly-bound \( K^+ \cdots I^- \) ion pairs formed in \( K(14p)\)-CF\(_3\)I collisions. Their binding energies are less than 30 meV. The experimental arrival position distributions are shown in the left hand panels with the delay times, \( t_D \), indicated. The model simulations use translation energy release distributions of (a) a \( \delta \)-function distribution with \( \varepsilon = 0.7 \) eV, (b) a flat distribution from 0 to 0.7 eV and (c) a Boltzmann-like distribution with \( \bar{\varepsilon} = 0.3 \) eV.

Considering the experimental results seen in the left hand panels of figure 3.10, ion pairs enter the analysis region and travel across the PSD from the side closest to the gas cell to its far side. Additionally, the ion pairs remain closely grouped together, indicating that they have a relatively narrow velocity distribution. Since the diameter of the analysis region is \( \sim 2 \) cm, the velocities of the ion pairs can be estimated as \( \sim 6.7 \times 10^4 \) cm s\(^{-1}\), which is much higher than expected for a Boltzmann-like translational energy release distribution. Comparison of the experimental and calculated results shows a good agreement between the model simulations assuming that all of the release excess energy \( E_E \sim 0.7 \) eV appear in translation (see figure 3.10a). As the assumed energy release distribution is broadened and has a lower mean excess energy \( \bar{\varepsilon} \), the simulated ion pair distributions become concentrated near the entering side of the PSD. The product ion pairs have lower velocities, leading to poor agreement between theory and experiment. As a consequence, the results in figure 3.10 demonstrate that electron attachment to CF\(_3\)I is not accompanied by conversion of excess energy into internal energy of intermediate. Therefore, CF\(_3\)I\( ^- \) is a very short-lived intermediate which dissociates immediately with all the excess energy of reaction appearing in translation.
In order to obtain the binding energy distribution of $K^+ \cdots I^-$ ion pairs, measurements of the field-induced detachment signal as a function of applied maximum field were performed. The experimental results can then be compared to model calculations which assume extreme translational energy release distributions; a $\delta$-function and a Boltzmann-like distributions. Since states with the same binding energy can dissociate over a range of fields, in the calculations, the relation between dissociation field and binding energy is chosen randomly from the distribution seen in the inset of figure 3.11 which corresponds to the dissociation of ion pairs with a broad distribution of angular momenta. Figure 3.11 illustrates that as the applied field increases, the detachment signal steadily increases and the simulations show little sensitivity in the type of translational energy release distributions assumed. However, both distributions are in a good agreement with the experimental data. The fact that the differences between those two limiting cases are small may be attributed to the broad distribution of fields over which states of a given binding energy dissociate.
Figure 3.11 Comparison between simulations assuming translational energy release distributions of (a) a δ-function distribution with $\varepsilon = 0.7$ eV and (b) a Boltzmann-like distribution with $\bar{\varepsilon} = 0.3$ eV and experimental data. The inset shows the assumed distribution of dissociation fields for an ion pair binding energy of 40 meV.
3.2 Heavy-Rydberg ion pairs formation in K(14p)-CH₂Br₂ collisions

Figure 3.12 shows arrival spatial distribution obtained for ion pair formation through electron attachment to CH₂Br₂ via the reaction

\[ \text{K}(14p) + \text{CH}_2\text{Br}_2 \rightarrow \text{K}^+ + \text{CH}_2\text{Br}_2^- \rightarrow \text{K}^+ \cdots \text{Br}^- + \text{CH}_2\text{Br} \]  (3.2)

The available excess energy \( E_E \) obtained from the difference between the CH₂Br·Br bond dissociation energy, \( \sim 3.06 \text{ eV} \) [44] and the electron affinity of Br, \( \sim 3.36 \text{ eV} \), is \( \sim 0.3 \text{ eV} \). Inspection of the experimental results shows that K⁺·⋯Br⁻ ion pairs display identical behavior to that seen for CF₃I and agree well with the predictions of a δ-function energy release distribution (see figure 3.12a). The Br⁻ ions must separate immediately following electron attachment and the total available excess energy is transferred into translational kinetic energy of the fragments. Furthermore, even though the energy release is more than two times less than that of CF₃I⁻, the velocities of Br⁻ or K⁺·⋯Br⁻ are similar to those seen for CF₃I \( \sim 6 \times 10^4 \text{ cm s}^{-1} \), and matches well the mean Rydberg velocity. This is because the lighter Br⁻ ions acquire more of the excess energy, \( \sim 54\% \) and have similar velocities to the I⁻ ions. Again, when the mean translational energy release \( \bar{\varepsilon} \) becomes smaller, the velocities and transverse momenta of the product K⁺·⋯Br⁻ ion pairs decrease and their angular distribution is more strongly focused in the forward direction as seen in figure 3.12 and 3.13. Note that the experimental signal levels for CH₂Br₂ are not as good as those of CF₃I because the rate constant for electron attachment to CH₂Br₂, \( \bar{k} \sim 7 \times 10^{-8} \text{ cm}^3\text{s}^{-1} \) [45] is much lower than that for
CF₃I, \( \bar{k} \sim 1.7 \times 10^{-7} \text{ cm}^3\text{s}^{-1} \) [46] resulting in lower signal levels. As seen from figure 3.12, the data indicate that essentially all the excess energy appears in translation and the CH₂Br₂⁻* intermediates are short lived.

**Figure 3.12** Arrival position distributions for K⁺⋯Br⁻ ion pairs formed in K(14p)-CH₂Br₂ collisions. The experimental results are shown in the left and panels. The right hand panels show calculations 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 \( \bar{\varepsilon} = 0.1 \) eV. The intermediate lifetime is taken to be zero. The other conditions are as in figure 3.10.
Figures 3.13 Calculated angular distributions of \( K^+ \cdots Br^- \) ion pairs formed in \( K(14p)\text{-CH}_2\text{Br}_2 \) collisions for (a) a \( \delta \)-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 \( \bar{\varepsilon} = 0.1 \) eV. The intermediate lifetime is taken to be zero.
3.3 Heavy-Rydberg ion pairs formation in K(14p)-CCl₄ collisions

Illustrated by figure 3.14, contrasting behavior is seen following electron transfer to CCl₄, which produces ion-pairs through the reaction

\[ \text{K}(14\text{p}) + \text{CCl}_4 \rightarrow \text{K}^+ + \text{CCl}_4^- \rightarrow \text{K}^+ \cdot \cdot \cdot \text{Cl}^- + \text{CCl}_3 \]  

(3.3)

The CCl₃-Cl bond dissociation energy, ~ 3.07 eV [47], and the electron affinity of Cl, ~ 3.61 eV, suggests an excess energy \( E_E \) of ~ 0.5 eV. If the excited \( \text{CCl}_4^+ \) intermediate dissociates immediately after capture ~ 70% of this energy will be acquired by the light \( \text{Cl}^- \) ions, resulting in \( \text{Cl}^- \) ions with very large velocity ~ 1.6x10⁵ cm s⁻¹ in the rest frame of the intermediate. This velocity is much higher than the mean velocities of the parent Rydberg atoms and therefore the only possible way that the ion pairs can be produced is the formation of \( \text{Cl}^- \) ions with Rydberg atoms with velocities near the maximum of their effusive velocity distribution. As a result, bound ion pairs will move across the PSD with large velocities ~ 1x10⁵ cm s⁻¹ and, according to the model simulations, most of them will escape the analysis region for delay times \( t_D \) ~ 20 μs, see figure 3.14a. As the \( \delta \)-function energy release distribution develops into a Boltzmann-like distribution, velocity matching improves. The velocities of the product \( \text{K}^+ \cdot \cdot \cdot \text{Cl}^- \) ion pairs are much reduced and their angular distribution becomes narrower and more focused in the forward direction (see figure 3.14 and 3.15). This behavior is evident in the experimental data. Comparison of the theory to the experimental results indicates that not all the excess energy \( E_E \) appears in translation, a large fraction of the energy
is redistributed among the vibrational modes of the intermediate $\text{CCl}_4^+$ pointing to lifetimes which are long compared to typical vibrational periods which is in an agreement with earlier studies that suggest a mean intermediate lifetime of $\sim 7.5$ ps [48].
Figure 3.14 (a) Calculated arrival position distributions for K⁺⋯Cl⁻ ion pairs formed in K(14p)-CCl₄ 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 ε = 0.5 eV, (ii) a rectangular distribution flat from 0 to 0.5 eV, and (iii) a Boltzmann-like distribution with ε = 0.1 eV. The intermediate lifetime is taken to be zero. (b) The comparison between theory and experiment for the laser pulse width of 20 μs. The experimental results are in the left hand panels. The assumed translational excess energy distributions are in the forms of (iv) a flat distribution from 0 to 0.5 eV and (v) a Boltzmann-like distribution with ε = 0.1 eV.

Figures 3.15 Calculated angular distributions of K⁺⋯Cl⁻ ion pairs formed in K(14p)-CCl₄ collisions for (a) a δ-function translational energy release distribution with ε = 0.5 eV, (b) a rectangular distribution flat from ε = 0 to 0.5 eV, and (c) a Boltzmann-like distribution with ε = 0.1 eV. The intermediate lifetime is taken to be zero.
Chapter 4
Conclusions and Future work

4.1 Conclusions

An investigation of the lifetimes and decay energetics of excited intermediate has been performed by measurements of the angular and velocity distributions of heavy-Rydberg ion-pair states formed through electron transfer in thermal-energy collisions between Rydberg atoms and targets that attach free low-energy electrons. While ion pairs associated with short-lived intermediates have broad angular and narrow high-velocity distributions, ion pairs formed via long-lived intermediates yield more strongly forward peaked distributions and lower ion pair velocities. The experimental data suggest that low-energy electron attachment to CF₃I and CH₂Br₂ leads to formation of excited intermediates that dissociate on time scales short compared to those for intramolecular vibrational relaxation (IVR) whereas electron attachment to CCl₄ leads to creation of excited CCl₄⁺ intermediates whose lifetimes permit efficient vibrational redistribution of the excess energy of reaction before dissociation occurs. All of the results are also summarized in Table 4.1.
Table 4.1 Summary of target species

<table>
<thead>
<tr>
<th>Species</th>
<th>Anion Product</th>
<th>Mean translational energy release $\bar{\varepsilon}$ (meV)</th>
<th>Types of intermediates</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$I</td>
<td>I$^-$</td>
<td>0.7</td>
<td>short lived</td>
</tr>
<tr>
<td>CH$_2$Br$_2$</td>
<td>Br$^-$</td>
<td>0.3</td>
<td>short lived</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>Cl$^-$</td>
<td>0.1</td>
<td>long lived</td>
</tr>
</tbody>
</table>

4.2 Future work

The more detailed investigation of the decay energetics of excited intermediates might be obtained by varying the initial conditions for the collisions. For example, the velocity of the Rydberg atoms can be controlled by using an off-normal laser beam and tuning to the appropriate point in the Doppler profile. The differential measurement of binding-energy-resolved velocity and angular distribution for target species that have multiple decay channels, such as, 1,1,1-C$_2$Cl$_3$F$_3$, can be achieved by changing dissociation field strengths and principal quantum numbers of the Rydberg atoms. This results in a substantial decrease of the signal levels. However, it can be solved by the use of strontium Rydberg atoms which have much higher production rates than those of potassium Rydberg atoms [49-51].
References


