Ion-pair formation in electron recombination with molecular ions

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Abstract. By studying ion-pair formation in electron recombination with molecular ions, fundamental knowledge on the molecular dynamics can be obtained. In order to study these types of reactions, both the electron recombination as well as the dynamics all the way to the asymptotic limits must be well described. We have used the wave packet technique to study ion-pair formation in electron recombination with HeH⁺, HD⁺, H⁺³ and HF⁺. We here discuss what will determine the general shape of the ion-pair cross section, the threshold effects, possible interference effects as well as the ratio of the cross sections of ion-pair formation to dissociative recombination.

1. Introduction
In electron recombination with molecular cations, both neutral and charged fragments can be formed. Dissociative recombination (DR) is the process where neutral fragments are formed. For a diatomic molecule the reaction is given by

\[ \text{AB}^+ + e^- \rightarrow \text{AB}^* \rightarrow A(n) + B(n'), \]  

(1)

where the neutral fragments can be in different excited states. Often, in the experimental studies of DR, all neutral fragments are detected and the total cross section for DR is measured. In ion-pair formation opposite charged fragments are formed as an ion-pair,

\[ \text{AB}^+ + e^- \rightarrow \text{AB}^* \rightarrow A^+ + B^- . \]  

(2)

When studying this reaction, only the cross section for this channel is measured and the reaction therefore provides fundamental understanding of the molecular dynamics. In this article we will describe how the ion-pair formation in electron recombination can be theoretically studied using the wave packet technique. In section 2, we describe how the relevant potentials and couplings are calculated. This is followed in section 3 with a description of the wave packet method. We have used this technique to study the ion-pair formation in electron recombination with HeH⁺ (section 4), HD⁺ (section 5), H⁺³ (section 6) and HF⁺ (section 7). In section 8, general conclusions from these studies are summarized.
2. Calculation of potentials and couplings

When the molecular ion captures the electron, an electronic state of the neutral molecule is formed. This electronic state is, in general, highly electronically excited and it will interact by electronic couplings to a manifold of states of the same symmetry. In many molecular systems, the electron recombination is dominated by electron capture into a doubly excited neutral state that crosses the ionic ground state potential. This is the case in e.g. electron recombination with HD\(^+\) as will be described below. Above the ion-potential, the doubly excited neutral state is not an electronically stable state, it is a resonant state that will interact with the ionization continuum and hence an autoionization width will be associated with it. Therefore, standard quantum chemistry techniques are not well suited for calculating these resonant states. Electron scattering calculations are carried out in order to determine both the energy positions and widths of the resonant states. We are using the Complex-Kohn variational method [1] to calculate the cross section for elastic scattering of electrons of the molecular ion target. By fitting the eigenphase sum to a Breit-Wigner form, the energy position and width for a fix target geometry can be determined.

Below the ground state of the ion, the adiabatic potentials are calculated using extensive structure calculations. For small molecular systems such as HeH, HD and H\(_3\), the full configuration interaction (FCI) method is used. For systems with more electrons, such as HF, a multi-reference configuration interaction (MRCI) description is employed. To be able to merge the results of these calculations with the scattering calculation, the same basis set, natural orbitals and the CI used for the target wave function must be used.

The excited adiabatic potentials are close in energy and will interact. One problem is to find a suitable representation of the potentials and couplings. Here we are not using the “strict diabatic” representation where all non-adiabatic coupling elements \(\langle \phi_i | \frac{\partial}{\partial R} | \phi_j \rangle\) vanish [2]. An infinite number of states interact and the strict diabatic representation is not practical. Instead, the “quasidiabatic representation” is used, where the resonant states are diagonalized relative to the Rydberg manifolds and will couple to these with electronic couplings of the form \(c_{ij}(R) = \langle \phi_{res}^i (R) | \hat{H}_{el} | \phi_{ryd}^j(R) \rangle\). Among the Rydberg states there will still be non-adiabatic couplings, but these couplings are generally neglected here. This approximation is valid for high collision energies. The diabatic potentials of the resonant states are generally constructed by following the compact resonant configurations when the internuclear distances are varied. These can quite easily be separated from both the Rydberg states and the ionization continuum.

If one of these excited neutral states is dissociating into an ion-pair limit, not only neutral fragments are formed. In order to calculate the cross section for ion-pair formation, the relevant potentials and couplings have to be determined from the Franck-Condon region where the electron is captured and all the way out to the asymptotic limits.

3. Molecular dynamics

The molecular dynamics on the coupled potentials is studied using wave packet propagation. In the following analysis atomic units are used. Since, the non-adiabatic couplings to the Rydberg states are generally neglected, the electron capture will induce wave packets on the resonant states. The initial conditions for the wave packets are

\[
\Psi_i^{res}(R, t = 0) = \sqrt{\frac{\Gamma_i(R)}{2\pi}} \chi_{v=0}(R),
\]

where \(\Gamma_i\) is the autoionization width and \(\chi_{v=0}\) is the ground vibrational level of the ion. The wave packets are then propagated by numerically integrating the time-dependent Schrödinger equation

\[
i \frac{\partial}{\partial t} \Psi = (T1 + V) \Psi,
\]

\(2\)
where the $V$ is the diabatic potential matrix. Autoionization is included by letting the resonant states be complex above the ion potential $V_i(R) = E_i(R) - i\Gamma_i(R)/2$. Since the ion-pair state is a long-range potential, the cross section for ion-pair formation is calculated by e.g. projecting the asymptotic wave packet onto the energy-normalized eigenstates of the ion-pair potential. For the one-dimensional systems described below (HeH, HD and HF) the wave packets have been propagating using the Cranck-Nicholson method [3]. For the $H_3$ system, two degrees of freedom are included, and the wave packets are propagated using the MCTDH (Multi-Configuration Time-Dependent Hartree) method [4] developed in Heidelberg.

4. HeH$^+$

The dissociative recombination of HeH$^+$ at low collision energies has been carefully investigated both experimentally [5] and theoretically [6] during the last decades. This is a molecular ion where there is no resonant states crossing the ionic ground state close to its minimum. Instead the DR is driven by non-adiabatic couplings into rovibrationally excited Rydberg states situated below the ionic potential.

However, for collision energies above 10 eV resonant states can be reached. Measurements [7] of the DR cross section show that when the energy is high enough to reach these states, a peak in the cross section can be observed. This has also been confirmed by theoretical studies of the reaction [8]. One of these resonant states is an ion-pair state dissociating into the He$^+$ + H$^-$ limit. In a diabatic representation, this resonant state will cross the other resonant states at large internuclear distances ($R \approx 7 - 15$) a$_0$ and electronic couplings will here be induced.

In figure 1, we show the calculated [9] cross section for ion-pair formation in electron recombination with HeH$^+$. The cross section for ion-pair formation shows a peak if the energy is high enough to reach the ion-pair state. In this study the wave packets were propagated on seven coupled resonant states simultaneously. Since there is no structure in the cross section, the interference effect from the wave packets propagating on the coupled potentials is negligible. Also there is no strong threshold in the cross section where the ion-pair limit becomes energetically open (13.6 eV above the $v = 0$ level of the HeH$^+$ ion). The rise of the ion-pair cross section is thus limited by the Franck-Condon overlap between the initial vibrational level of the ion and the neutral resonant state. For HeH$^+$, the ion-pair cross section corresponds to about 10% of the total DR cross section.

![Figure 1](image)

**Figure 1.** Calculated ion-pair cross section for $^4$HeH. The arrow shows the threshold energy for ion-pair formation.
5. HD$^+$
For H$_2^+$ there is a neutral resonant state with a potential that crosses at the minimum of the ion potential. Dissociative recombination of H$_2^+$ is thus driven by the direct capture and dissociation along this resonant state. In the quasidiabatic representation, this resonant state dissociates into the ion-pair limit. In order to obtain vibrationally relaxed ions in the ion-storage ring experiments, the HD$^+$ ions are stored instead of H$_2^+$. By detecting the D$^-$ ions, the cross section for ion-pair formation has been measured [10]. The cross section showed a sharp threshold at 1.9 eV where the ion-pair formation becomes energetically possible, followed by 14 well resolved peaks. The peaks continued for energies higher than the dissociation energy of the HD$^+$ ion and could therefore not be explained by indirect resonant capture into Rydberg states situated below the ion potential. We have studied the ion-pair formation in electron recombination with HD$^+$ using both a semi-classical Landau-Zener-Stückelberg method [11] and the wave packet technique [12]. Both methods used the quasidiabatic representation of the potentials and it was found that the oscillations could be explained by quantum interference between competing dissociative pathways. In the electron recombination, the doubly excited resonant state will be formed. During dissociation, this resonant state can be followed diabatically all the way to the ion-pair limit. Alternative paths are produced by the electronic couplings to the Rydberg states both at small and large internuclear distances. The calculation shows that most of the structure observed in the cross section could be explained by interference between the ion-pair state and the lowest $n = 3$ Rydberg states. The sharp threshold behavior of the ion-pair cross section can here be understood by the fact that the electron capture into the resonant state is allowed already at zero collision energy. For HD$^+$, the cross section for ion-pair formation corresponds to about 5% of the total DR cross section.

**Figure 2.** Ion-pair cross section for HD$^+$ calculated using the semi-classical Landau-Zener-Stückelberg method.

**Figure 3.** Ion-pair cross section for HD$^+$ calculated using the wave packet technique.
6. $H_3^+$

$H_3^+$ is another system where there is no direct mechanism for DR at low collision energies. The lowest resonant states are reached for collision energies in the range 5-20 eV. Electron capture and dissociation along these resonant states will induce a high-energy peak in the DR cross section which has been seen both experimentally [13] and theoretically [14]. Early quantum chemistry studies [15] indicated that the lowest of these resonant states is diabatically associated with the ion-pair limit $H_2^+ + H^-$ at infinity.

Ion-pair formation in electron recombination with $H_3^+$ consists of two channels where either $H_2^+ + H^-$ is formed with a threshold of $E_{th} = 5.4$ eV or $H + H^+ + H^-$ with the threshold $E_{th} = 8.1$ eV. The cross section for ion-pair formation has been measured using both inclined beam experiment [16], a single pass merged-beam experiment [17] and using the ion-storage ring CRYRING [18]. In all these experiments, the $H^-$ fragments were detected and therefore the two ion-pair channels could not be separated. In a very recent experimental study, using the TSR ion-storage ring, the $H_2^+$ and $H^-$ fragments were measured in coincidence [19]. The measurement could therefore separate between the two-body and three-body channels of ion-pair formation. However, absolute cross sections were not measured, but the magnitude of the peak of the total ion-pair cross section was set to agree with the cross section measured in CRYRING [18].

In the ion-storage ring experiments, the molecular ions have time to vibrationally relax. In the former two experiments, the vibrational distribution is suppressed by collisional quenching. These experiments show more sharp thresholds in the cross section where the ion-pair channel opens up. They all agree on the absolute magnitude of the cross section of about $2 \cdot 10^{-18}$ cm$^2$. This corresponds to approximately 2 % of the total DR cross section at this energy.

We have carried out a series of calculations on the formation of $H_2^+ + H^-$ in electron recombination with $H_3^+$. The first study [18], was an one-dimensional study where the H-H distance was frozen to 1.65 $a_0$ and the Jacobi angle, $\theta = 90^\circ$ ($C_{2v}$ symmetry). In this study, we included six coupled neutral states, two resonant states that interact in the Franck-Condon region as well as the four lowest Rydberg states situated below the ionic ground state. The ion-pair state crosses some of these Rydberg states twice, both at small and large internuclear distances. In that sense it is similar to the $H_2$ potentials discussed above. The one-dimensional model produced a cross section that was a factor of five larger than the measured cross section. Also the threshold was very sharp and it had a double-peak structure that could be explained as an interference effects from the two coupled resonant states.

The next study [20] was a two-dimensional study where also the H-H distance was included in the molecular dynamics. The Jacobi angle $\theta$ was frozen at 90$^\circ$. The motivation for this was that electron scattering calculations [14] show that the resonant states are strongly repulsive with respect to the two Jacobi coordinates, but almost flat with respect to the angle. In this study, the dynamics on the two coupled resonant states was studied using the Chebyshev propagator [21] to propagate the wave packets. The loss to the Rydberg states was included using a semiclassical Landau-Zener model. This gave a cross section that was smaller in magnitude than the measured cross section. It had no signs of interference effects and the threshold was removed.

In more recent calculations, we have included all six coupled states in the molecular dynamics. Still, the Jacobi angle is frozen at 90$^\circ$. We have improved the extrapolation of the resonant states, autoionization widths and couplings. The molecular dynamics is studied using the MCTDH method [4]. Using this program, the potentials, widths and couplings must be fitted to a desired product form. This is done using up to 68 parameters. The two-dimensional study shows that the cross section of ion-pair formation is reduced by the electronic coupling between the two resonant states. No double-peak is observed. Also flux will be lost by the electronic couplings to the Rydberg states. The largest drop in the cross section comes from the interaction with the third Rydberg state. In figure 4, we compare our calculated cross section using the 1D model with the corresponding 2D cross section. In figure 5, we show our calculated cross section using
Figure 4. Comparison of the cross section for formation of H$_2^+$ + H$^-$ in electron recombination with H$_3^+$ calculated using the 1D and 2D models of the nuclear dynamics.

Figure 5. Ion-pair cross section for H$_3^+$ calculated using the 2D model is compared with measured cross sections.

the recent 2D study with the measured cross sections of ion-pair formation. Remember that the former three experiments [16, 17, 18] measure the total cross section of ion-pair formation, while the theoretical study only included the formation of H$_2^+$ + H$^-$ . Therefore, we are not able to predict the cross section above 8.1 eV, where the second channel opens up. We see an agreement with all experiments on the absolute magnitude of the cross section. However, our cross section is shifted toward lower energies compared with the storage-ring experiments and the energy-dependence agrees better with the measured cross section by Yousif et al. [17]. We are presently running further electron and structure calculations in the Franck-Condon region of the ion in order to improve the surfaces and check if the shift in energy is real.

7. HF$^+$

Also for HF the cross section for ion-pair formation has been measured previously [22]. The formation of H$^+$ + F$^-$ in electron recombination with HF$^+$ has a threshold of about 0.017 eV, which is within the energy spread from the rotational distribution of the ions in the experiment. Therefore, the measured cross section for ion-pair formation (see Figure 6) shows no indications of a threshold. In this experiment also the cross section for DR of HF$^+$ was measured and a smaller cross section than for most diatomic molecular ions was obtained with a corresponding thermal rate coefficient of about $1.96 \times 10^{-8}$ cm$^3$s$^{-1}$ at room temperature. The ratio of ion-pair formation to DR is about 13% at a collision energy of 0.1 eV.

We are carrying out a theoretical study of the direct process in electron recombination with HF$^+$. With direct, we refer to the process where the electron is captured into the resonant
states and dissociates along these resonant states diabatically. No electronic couplings between
the resonant states or to the Rydberg manifolds are included. Combining electron scattering
calculations with structure calculations, we determined the potentials and widths of 30 resonant
states of all symmetries. There has been a debate on the curve crossing between the ion-pair
state ($V^1\Sigma^+$) and the ground state of the ion. The present study shows that the ion-pair state
indeed crosses the ion potential, but it crosses the potential at an internuclear distance smaller
than the equilibrium distance of the ion. In the wavepacket study the molecular dynamics on the
30 resonant states was included and several resonant state contribute to the total cross section.
In figure 6, we show the cross section for the four lowest singlet resonant states. The lowest $^1\Sigma^+$

Figure 6. Calculated cross section for direct electron capture and dissociation along the four
lowest singlet states of HF. The $^1\Sigma^+$ state is the diabatic ion-pair state. Also the measured
cross sections for dissociative recombination and ion-pair formation in electron recombination
with HF$^+$ [22] are shown.

resonant state is the ion-pair state mentioned above. We see that the direct process for ion-pair
formation underestimates the cross section by more than one order of magnitude. In order to
accurately describe the ion-pair formation, the molecular dynamics on the coupled states must
be studied. For the moment we are working on the diabatization of the HF potentials. Also
note, that since the ion-pair formation in electron recombination with HF$^+$ has a threshold at
low energies, the cross section follows Wigner’s $1/E$ threshold law [23].

8. Summary and Conclusions
We have theoretically studied ion-pair formation in electron recombination with diatomic and
triatomic molecular cations. Since these reactions both start and end in well defined states,
they provide sensitive tools to obtain knowledge on the complex dynamics taking place on
the manifold of coupled electronic states of the neutral system. We have used the wave
packet technique to study the molecular dynamics. The quasidiabatic potentials are obtained
by combining electron scattering calculations with extensive structure calculations. Relevant
potentials, coupling and widths must be known for all distances. The ratio of the cross sections
of ion-pair formation to total dissociative recombination varies from 2\% ($\text{H}_2^+$) to 13 \% ($\text{HF}^+$). There is no simple rule of thumb determining what this ratio will be. The cross section for
ion-pair formation of HD$^+$ shows a sharp threshold effect where the ion-pair limit becomes
energetically open. For HeH$^+$ no such limit can be seen, but the cross section consists of a peak with a smooth onset. This can be understood that for HD$^+$ the electron can be captured into the diabatic ion-pair state already at zero collision energy, but the ion-pair limit opens up at 1.9 eV. For HeH$^+$ the threshold energy for ion-pair formation is 13.6 eV, while the capture probability into the ion-pair state starts just above this threshold energy. For H$_3^+$ we see that the 1D model gives a much sharper threshold for ion-pair formation than the 2D models.

The shapes of the ion-pair cross sections for H$_3^+$ and HeH$^+$ are given by smooth peaks at higher energies. This can be understood since for these molecules the interference effects are negligible and it is the high-energy capture probability into the resonant ion-pair state that will give the shape of the cross section. For HF$^+$ the ion-pair channel becomes energetically available at low energies and for this ion, the ion-pair cross section will follow Wigner’s $1/E$ threshold law.

For HD$^+$ the interference effects from the dynamics on competing dissociative pathways will cause oscillations in the cross section of ion-pair formation. For this system, the ion-pair state crosses some of the Rydberg states twice, both at small and large internuclear distances. The same is true for H$_3^+$, however, for this system the second dimension will smear out the possible interference effects.

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