Formation of the ion-pair in electron recombination with $H_3^+$

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Abstract. We present a two-dimensional theoretical study of the formation of the ion-pair, $H_2^+ + H^-$, in electron recombination with $H_3^+$ in its ground electronic and vibrational state. The relevant potential energy surfaces, electronic couplings and autoionization widths are calculated by combining electron scattering calculations with quantum chemistry calculations. The nuclear dynamics on six coupled electronic states is studied by propagating wave packets using the MCTDH (Multi Configuration Time-Dependent Hartree) method. Also the cross section for ion-pair formation in electron recombination with $D_3^+$ is calculated.

1. Introduction

When an electron recombines with the $H_3^+$ ion in its ground electronic and vibrational state, several processes are possible. In the first step an excited state of $H_3$ system is formed. This state can then be stabilized through dissociation into neutral fragments - dissociative recombination - where both the two- ($H_2 + H$) and three-body ($H + H + H$) channels are possible. Dissociative recombination is energetically available even at zero collision energy. The $H_3$ system can also be stabilized through autoionization, i.e., re-emitting the electron. If the system autoionizes into a bound vibrational state of the $H_3^+$ ion, vibrational excitation occur. If the autoionization goes into the vibrational continuum, the process is dissociative excitation. These reactions require a threshold energy $\Delta E$ that will depend on the state of the remaining ion.

In the process of ion-pair formation, the system is stabilized through dissociation into opposite charged fragments. In electron recombination with $H_3^+$, there are two different ion-pair channels

$$H_3^+ + e^- \rightarrow \left\{ \begin{array}{l} H^- + H_2^+ \\ H^- + H^+ + H \end{array} \right.$$

(1)

The first channel has a threshold energy of $\Delta E = 5.4$ eV and for the second channel the threshold energy is $\Delta E = 8.1$ eV. In the present study, only the first channel (formation of $H_2^+ + H^-$) is included and therefore we will not be able to predict the total cross section for ion-pair formation above 8.1 eV where the second channel becomes energetically available.

Already in 1979, Kulander and Guest [1] calculated the resonant states of $H_3$ by combining the Configuration Interaction method with Feshbach projection operators. One-dimensional slices of the diabatic potential energy surfaces were calculated where the H-H distance was frozen to

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1.65 \text{ a}_0 \text{ and the Jacobi angle } \theta \text{ was set to } 90^\circ. \text{ They found that the lowest resonant state of H}_3 \text{ does not cross the ion potential close to its minimum. The resonant state was not able to explain the dissociative recombination cross section at low collision energies. However, when the collision energy is high enough to capture into this resonant state, a peak in the cross section will be seen. Furthermore, they predicted that the lowest resonant state diabatically correlates with the ion-pair limit, } \text{H}_2^+ + \text{H}^-. \text{ Therefore, the recombination into the lowest resonant state will produce both neutral fragments as well as the ion-pair. Similar one-dimensional potentials have also been calculated by Michels and Hobbs [2].}

More detailed electron scattering calculations were carried out by Orel \textit{et al.} [3] using the Complex Kohn variational method [4]. Using this method, both the resonance energy positions as well as the autoionization widths are obtained. These scattering calculations were carried out in two dimensions where both radial Jacobi coordinates were varied. The Jacobi angle \theta \text{ was still frozen to } 90^\circ. \text{ They found that there are four resonant states, two states of } ^2A_1 \text{ symmetry and two of } ^2B_1 \text{ symmetry. Furthermore, three of these states (the two } A_1 \text{ states and the lowest } B_1 \text{ state) have a triple intersection at the equilibrium geometry of the H}_3^+ \text{ ion. A few scattering calculations were carried out where also the Jacobi angle was varied. It was found that while all resonant states are strongly repulsive with respect to both radial coordinates, they are flat with respect to variations in the angle.}

The high energy peak in the cross section for dissociative recombination was first measured in 1993 using the CRYRING ion-storage ring [5]. In this measurement, the neutral fragments were detected and a peak in the cross section centered around 9 eV was observed. The same year, Orel and Kulander [6] used their calculated resonant states to carry out wave packet propagation to predict the high-energy peak in the dissociative recombination cross section. The two radial dimensions were included and it was assumed that everything dissociated into neutral fragments. No couplings between the neutral states were included and the resonant states became flat as soon as they crossed the ion potential. The theoretical study gave a peak in the cross section with a similar shape and position as the one measured in the experiment.

The cross section for ion-pair formation has been measured using an inclined beam experiment [7], a merged beam experiment [8] as well as using the CRYRING [9] and TSR [10] ion-storage ring experiments. The resulting cross sections from these experiments will be displayed in figure 4 below. In the first two experiments, vibrational relaxation is obtained by collisional quenching. The advantage with the ion-storage ring experiments is that the ions are stored in the ring prior to the experiments and the ions will have time to vibrationally relax to its ground vibrational state. In the first three experiments, the H$^-\text{ fragments were detected and therefore these measurements can not separate between the two channels of ion-pair formation. In the most recent experiments [10], the H}_2^+ \text{ fragments were measured in coincidence with the H}^- \text{ fragments and therefore the branching for the two- and three-body ion-pair channels can be determined. However, in this experiment, the absolute cross section was not obtained and therefore, the peak of the total cross section for ion-pair formation was normalized relative to the cross section measured in CRYRING. As can be seen in figure 4, all measurements agree on a magnitude of } 2 \cdot 10^{-18} \text{ cm}^2 \text{ of the cross section for ion-pair formation. However, the shape of the cross sections differ. The merge-beam experiment shows a sharper onset of the cross section above the threshold energy for ion-pair formation. The recent TSR experiment shows that the two-body ion-pair channel dominates over the three-body channel and some structures are seen in the two-body cross section that are not present in the cross sections for three-body formation.}

We have previously carried out an one-dimensional study on the formation of the ion-pair H}_2^+ + \text{H}^- \text{ in electron recombination with H}_3^+ [9]. In this study, the Jacobi angle was frozen to 90° (C_{2v} \text{ symmetry) and the H-H distance was set to } 1.65 \text{ a}_0. \text{ A diabatic representation of the two } ^2A_1 \text{ resonant states as well as four Rydberg states of the same symmetry were included.}
The molecular dynamics were studied by propagating wave packets on coupled one-dimensional potentials. The calculated cross section for ion-pair formation had a shape and magnitude very different from what has been measured [9]. It had a very sharp threshold where the ion-pair channel opens up and it was followed by a double peak structure that can understood as an interference effect induced by the electronic couplings between the two resonant states. Furthermore, the magnitude of the calculated cross section was about a factor of five larger than all measured cross sections. From this study, we concluded that we have to perform a two-dimensional study of the reaction including all relevant coupled potentials. This is what we intend to do in the present study. The article is outlined as follows: In section 2 it is described how the diabatic representation of the relevant potential energy surfaces, electronic couplings and autoionization widths are obtained. This is followed in section 3 with an outline of how we describe the nuclear dynamics using the wave packet technique. In the following study, we are using the Multi-Configuration Time-Dependent Hartree (MCTDH) method developed in Heidelberg [13] to propagate the wave packets. The numerical details are given in section 3.1. The results are then summarized, where we show the influence on the cross section from the electronic couplings between the ion-pair state and the other neutral states included in the model. We also study ion-pair formation in electron recombination with D$_3^+$. Atomic units are used throughout the article.

2. Calculation of potentials and couplings
The four lowest resonant states of H$_3$ are calculated by Orel et al. [3] using the Complex Kohn Variational method [4]. In the present study, we include the two lowest resonant states of $^1A_1$ symmetry. In a “quasidiabatic representation”, these two resonant states will cross each other in the Franck-Condon region and one of the resonant states will correlate with the ion-pair limit at infinity. The neutral adiabatic states situated below the ion-potential are calculated with full configuration interaction calculation containing 63 000 configurations. Each H atom is represented by a (8s, 5p, 1d) basis set. The neutral states are diabatized using the $R$-dependence of the configuration interaction coefficients. The electronic couplings between the two resonant states as well as the couplings between the ion-pair state and the lower Rydberg states are determined using a two-by-two transformation of the adiabatic potentials [11]. In order to determine the couplings between the ion-pair state and the higher Rydberg states, the autoionization width and the effective quantum number of the Rydberg state can be used in a scaling relation [12]. The potentials have to be extrapolated to correct asymptotic forms. In the present study, the two resonant states are included as well as the four lowest Rydberg states. The highest Rydberg state is an “effective state” [11] with a coupling to the ion-pair state that is determined to compensate for the infinite number of Rydberg states not included in the present study. The potential surfaces included in the theoretical model are displayed in figure 1, where the H-H distance is fixed at $r = 1.65$ a$_0$.

3. Nuclear dynamics
The molecular dynamics is studied by propagating wave packets on the coupled potentials. As will be described below, the MCTDH [13] method is used to integrate the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi(t, r, z) = H \Psi(t, r, z).$$

Here $H$ is the $6 \times 6$ Hamiltonian matrix, where the diagonal elements contain the kinetic energy operator plus potentials and the off-diagonal matrix elements contain the electronic couplings to the ion-pair state. Autoionization is included by letting the potentials of the two resonant
states be complex above the ion-potential

\[ \tilde{V}_{1,2}(r, z) = V_{1,2}(r, z) - \frac{i}{2} \frac{\Gamma_{1,2}(r, z)}{2}. \]  

(3)

This is the so-called local “Boomerang approximation” [14] for treating autoionization. The electron recombination will initiate wave packets on the two resonant states [14]:

\[ \Psi_{1,2}(t = 0, r, z) = \sqrt{\frac{\Gamma_{1,2}(r, z)}{2\pi}} \chi_{00}(r, z). \]  

(4)

Here \( \chi_{00} \) is the ground vibrational state of the \( \text{H}_3^+ \) ion. The electron capturing into the bound Rydberg states, induced by the non-adiabatic couplings are here neglected.

3.1. MCTDH

The MCTDH method [13] that here is used is a method that is well suited for propagating wave packets in many dimensions. The method is based on the assumption that the time-dependent wave packets are written as a linear combinations of Hartree-products of single-particle functions. For our two-dimensional wave packets we obtain:

\[ \Psi(t, r, z) = \sum_{i=1}^{n_r} \sum_{j=1}^{n_z} A_{ij}(t) \phi_i^{(r)}(t, r) \phi_j^{(z)}(t, z). \]  

(5)

In the present study we include 10 single-particle functions for both the \( r \) and \( z \) coordinates (\( n_r = n_z = 10 \)) and these single-particle functions are represented in basis functions of discrete variable representation. We are using 200 sine-functions for the \( r \) dimension and 500 sine-functions for the \( z \) dimension with grids ranging from 0.5 – 10.0 \( a_0 \) for the \( r \)-dimension and 0.5 – 20.0 \( a_0 \) for \( z \). When the ansatz (5) is inserted into the time-dependent Schrödinger equation, coupled time-dependent differential equations for the coefficients and the single-particle functions are obtained. The wave packets are propagated using the constant mean-field scheme, where the single particle functions are integrated using the Bulirsch-Stoer extrapolation (BS) scheme of order 9 and an error tolerance of \( 10^{-7} \). For the \( A_{ij} \) coefficients, a Short Iterative Lanzos

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**Figure 1.** Diabatic potential energy surfaces of \( \text{H}_3^+ \) (dotted) and \( \text{H}_3 \) for fixed H-H distance, \( r = 1.65 \ a_0 \). The resonant states are displayed with thick curves and the Rydberg states are the thin curves.
algorithm (SIL) of order 15 is applied, with an error tolerance of $10^{-7}$. The wave packets are propagated for 60 fs.

The cross section for ion-pair formation is calculated using the technique [15] of integrating the flux absorbed by a Complex Absorbing Potential (CAP), placed in the asymptotic ion-pair channel. Here we placed the CAP at $z_c = 15.0 \, \text{a}_0$. The cross section for the individual vibrational states of $\text{H}_2^+$ is calculated by employing projection operators onto these states [15]. Then the total cross section for ion-pair formation is obtained by summarizing contributions from the vibrational states of $\text{H}_2^+$. The flux is integrated with time-steps of $dt = 0.2 \, \text{fs}$. In order to avoid reflections to the edge of the grids, complex absorbing potentials are not only used for the ion-pair state, but also for the other potentials.

In order to use the MCTDH method, the Hamiltonian has to be given in a product form. Here we are using the Jacobi coordinates and the kinetic energy operator is then automatically given in the desired format. However, the calculated potentials, couplings and widths all have to be fitted in the product form

$$V(r, z) = \sum_{i,j} c_{ij} v_i^{(r)}(r) v_j^{(z)}(z),$$

before they are implemented in the MCTDH program. In the present study we are using fits of the surfaces containing up to 49 parameters.

4. Results

In order to obtain a fundamental understanding of the molecular dynamics, we start by studying the reaction by propagating on the ion-pair state alone. Then, we add the couplings to the other resonant state one by one.

4.1. Propagation on the ion-pair state alone

We start by propagating the wave packet on the resonant ion-pair state alone. Autoionization from the resonant state is included. In figure 2, we compare our calculated cross section using the MCTDH method with the cross section we obtain using the one-dimensional model [9] and using a two-dimensional model, where the wave packet is propagated using the Chebyshev propagator [16].

**Figure 2.** Cross section for propagation on the ion-pair state alone. Comparison between the one- and two-dimensional models and different propagators.

**Figure 3.** Calculated cross section for ion-pair formation, obtained when different number of states are included in the theoretical model.
The magnitudes of the calculated cross sections are about the same, but the shapes and the positions of the peak differ. The cross section calculated using the one-dimensional model shows a sharp threshold where the ion-pair limit becomes energetically available at 5.4 eV. With the Chebyshev propagator [17] the threshold is not that sharp and the peak of the cross section is centered around 8 eV. When the wave packets are propagating using the MCTDH method, the peak is shifted slightly toward lower energies. This can partly be explained by the fact that we, when using the Chebyshev propagator, used a harmonic oscillator wavefunction for the initial ground vibrational state of the ion. When using the MCTDH method, we instead numerically calculate the vibrational ground state of H$_3^+$ by carrying out a two-dimensional relaxation on the H$_3^+$ surface of Meyer et al. [18]. As described above, the cross section for ion-pair formation is calculated by integrating the flux absorbed by a complex absorbing potential (CAP). In figure 2, we show the cross sections obtained when the CAP is placed at $z_c = 10$ a$_0$ and $z_c = 15$ a$_0$. Since the ion-pair state is a long-range potential, it has not reached its asymptotic energy at these finite distances. Therefore the threshold is shifted toward higher energies when the CAP is moved to larger distances. Except for the threshold behavior, the cross sections calculated with the two CAP distances do not differ. Hypothetically, a CAP placed at infinity should cut the cross section below the threshold energy of 5.4 eV.

4.2. The role of the electronic couplings

In the next step we start to add the couplings between the ion-pair state and the other neutral states of H$_3$. When we add the second $^2A_1$ resonant state and the couplings between the two states in the Franck-Condon region, the cross section decreases in magnitude with a factor of 0.27. The shape and position of the peak in cross sections does not change. This if different from what we found in the one-dimensional study [9], where the coupling between the two resonant states caused a double peak structure that could be explained by a quantum interference between the two resonant states. When the second dimension is included, this interference effect is smeared out.

We then begin to add the potential energy surfaces of the Rydberg states and the couplings between the Rydberg states and the ion-pair state. When we add the lowest Rydberg state, there is a small decrease of the cross section for ion-pair formation. Adding the next Rydberg state decreases the cross section slightly more, as can be seen in figure 3. The following Rydberg state (state five) has couplings to the ion-pair state both at small and large internuclear distances and we can see that there is a significant drop in the cross section when this state is added to the model. Also some structures in the cross section are induced. The last Rydberg state included in the model (state 6) is the effective Rydberg with the coupling set to compensate for the infinite number of Rydberg states not included in the model. There is only a minor decrease of the ion-pair cross section when the effective state is added. The total effect of including the Rydberg state is to reduce the magnitude of the cross section for ion-pair formation with a factor 0.56. In figure 4 we compare the calculated cross section for the formation of H$_3^+$ + H$^-$ with the measured cross section of ion-pair formation. Remember that in the first three experiments [7, 8, 9], the H$^-$ were detected and therefore the experiments do not separate between the two- and tree-body reactions of (1). We believe that in order to reproduce the cross section above 8.1 eV, where the three-body ion-pair channel becomes energetically available, higher excited electronic resonant states have to be included in the model.

In the figure, we also show the very recent cross section measured using the TSR ion-storage ring [10]. As mentioned above, in this experiment, the branching ratio for the two- and tree-body channel of ion-pair formation was measured. The total cross section was not obtained and the therefore it has been normalized relative to the peak of the cross section measured in the CRYRING experiment. The two-body channel dominated at lower energies and also some structures are seen in the two-body cross section that are not present in the cross section for
three-body formation. Our calculated cross section has the same magnitude of $2 \cdot 10^{-18}$ cm$^2$ as all measured cross sections. It is shifted in energy relative to the more recent storage ring experiments. The shape of the calculated cross section agrees better with the measured cross section by Yousif et al. [8]. We see some structures in the calculated cross section that resemble the structures observed in the two-body cross section measured in TSR [10], although shifted in energy.

4.3. Isotope effects
The ion-pair formation has only been studied experimentally for the $\text{H}_3^+$ isotope. However, the high-energy peak in the cross section for dissociative recombination has been studied experimentally [19] and theoretically [20] both for $\text{H}_3^+$ and $\text{D}_3^+$. According to both the measurement and the theoretical calculations, the positions and shapes of the high-energy peaks in the DR cross section are very similar, although with different magnitudes. The magnitude of the peak found for $\text{H}_3^+$ is about a factor of 3.1 (1.9 theoretically) larger than the peak found in the cross section for $\text{D}_3^+$.

We have carried out calculations on ion-pair formation with electron recombination with $\text{D}_3^+$. We use the same relevant potentials, couplings and widths as above, but change the reduced masses when we carry out the relaxation to calculate the vibrational wave function of the target ion and when we run the wave packet propagation. The calculated cross section (see figure 5) for $\text{D}_3^+$ has similar shape as the cross section for $\text{H}_3^+$. The structure is slightly more pronounced. The magnitude of the cross section for $\text{H}_3^+$ is a factor of 2.7 larger than for $\text{D}_3^+$. This is a similar ratio as found for the high-energy peak in the DR cross section. This can be understood since the same resonant states are important in both reactions.

5. Conclusions
We have carried out a two-dimensional theoretical study of the formation of $\text{H}_2^+ + \text{H}^-$ in electron recombination with $\text{H}_3^+$ by including two coordinates and six coupled electronic states. In order to describe the reaction, both radial Jacobi coordinates are crucial. The second dimension will smear out the sharp interference effect observed in a previous one-dimensional study. The role of the Rydberg states is to reduce the cross section. We obtain a cross section that is shifted toward lower energies than found in the more recent storage ring experiments [9, 10]. The shape of the cross sections has a good agreement with cross section obtained with the
merged beam measurement [8]. The magnitude of the calculated cross section agrees perfectly with all measured cross sections. We believe that in order to obtain the cross section above 8.1 eV, higher excited resonant states have to be included in the model.

The calculated cross section for ion-pair formation in electron recombination with D$^+\_3$ has a similar shape as the corresponding cross for H$^+_3$. The cross section for H$^+_3$ is a factor of 2.7 larger and a similar ratio has been observed for the high-energy peaks of the cross sections for DR of H$^+_3$ and D$^+_3$.

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