Low collision energy mutual neutralization reaction of He\(^+\) and H\(^-\)

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Abstract

A Semi-classical Landau-Zener model is employed to theoretically study mutual neutralization in the collisions of \(^4\)He\(^+\) and H\(^-\)/D\(^-\). The model includes ten covalent states and an ion-pair state of \(^2\Sigma^+\) symmetry for the HeH molecular system. Here the assumption is that only two states are interacting at a given internuclear position. In the diabatic representation, the nuclear dynamics relevant for mutual neutralization is modelled for collision energies below 100 eV. The mutual neutralization reaction cross section and final states distribution are computed and compared with previous theoretical and experimental results.

1. Introduction

Mutual neutralization is a process where positively and negatively charged ions collide, resulting in charge transfer and the formation of neutral fragments. When the rate of mutual neutralization reaction is very large, Whitten et al.\(^1\) alluded to the fact that it can be an important escape channel for the formation of the excimer species. When a helium cation and a hydrogen anion collide, the mutual neutralization reaction is

\[
\text{He}^+ + \text{H}^- \rightarrow \text{He}^* + \text{H}.
\]

Here the asterisk (*) denotes the fact that the helium may be in an excited quantum state.

The process is of interest in many fields of research, such as the chemistry of the interstellar medium\(^2\) and the gas evolution of the early universe\(^3,4\). Helium and hydrogen ions are believed to have played a crucial role in the formation of important species like HeH\(^+\), He\(^2\) and H\(^2\). At the divertor section of a fusion reactor, like Iter\(^5\), there is a belief that ions of helium and hydrogen could be present\(^6-8\). Thus it is of importance to study all the possible reactions, involving the ions, that may take place, including the mutual neutralization reaction. With the advent of cold ion storage rings, like Desiree\(^9,10\) and merged beam facilities, the mutual neutralization reaction can be studied experimentally.

This reaction\(^1\) is good enough for testing theory, due to the size of the species involved. A fully quantum study for this reaction has recently been reported\(^11\), where eleven coupled \(^2\Sigma^+\) electronic states of HeH were included in modeling the nuclear dynamics using the log-derivative\(^12\) method. Rotational couplings of the \(^2\Sigma^+\) electronic states to six \(^2\)I electronic states was also considered and found to contribute significantly to the total cross section at energies above 1 eV. In the study auto-ionization amongst the coupled electronic resonant states was also included at short internuclear distances. However, auto-ionization was found to have a very low contribution to the mutual neutralization reaction total cross section, for energies below 10 eV. The study yielded a large cross section, comparable with previous results\(^13-16\). The final states distribution showed a dominance of the state going to the He[1s3s \(\Sigma^+\)S] + H asymptotic limit, followed by the state going to the He[1s3p \(\Pi^+\)P] + H asymptotic limit, with ratios of approximately 50% and 30%, respectively, at low collision energies.

In the current study, a multi-state Landau-Zener\(^17,18\) model is used to compute the mutual neutralization reaction\(^1\) cross section. This study includes eleven electronic states of the HeH system and the aim is to test the reliability of the model for this system. The Landau-Zener model is not as computationally demanding as the fully quantum log-derivative method employed recently by Larson et al.
Using a multi-state Landau-Zener model, Olson et al [19] calculated the mutual neutralization reaction (1) cross section, by incorporating eleven covalent electronic states of the HeH system. The electronic couplings, were approximated using two methods; a parametrized empirical equation and an equation based on asymptotic wave function expansions. Without any \textit{ab initio} data, the electronic couplings can vary significantly from one approximation method to another, as shown in the study by Olson et al. The quality of the reaction cross section obtained, however, is very much dependent on the values of the electronic couplings. In their study, the lowest state, in energy, associated with the He[1s2s^2S] + H asymptotic limit was neglected, while a state higher, in energy, with an avoided crossing larger that 100 \( a_0 \) (associated with the He[1s4s^2S] + H asymptotic limit) was included. In the current study, we assume that the potential energy curves have reached their asymptotic limit at internuclear distances larger than 50 \( a_0 \). Thus the lower state, neglected by Olson et al., has been included here. Additionally the higher state, considered in their study, is not included in our current study.

In section 2, of this paper, details on the computations of the transformation matrix, diabatic potential energy curves and electronic couplings are discussed. The results and conclusion are given in section 3 and section 4, respectively.

2. Computations

The mutual neutralization reaction can be theoretically studied by viewing the ionic and covalent interaction of the potential energy curves. In the adiabatic picture [20], the potential energy curves for a diatomic system do not cross [20, 21]. Such curves, however, do not preserve the ionic/covalent character of the states. Thus a potential energy curve may exhibit an ion-pair state character at short internuclear distances and a covalent state character at large distances. On the other hand, if the potential energy curves are transformed to a diabatic representation, the character can be preserved at all internuclear distances. Nevertheless, the diabatic potential energy curves of the same symmetry may cross, even if they are for a diatomic system.

The Landau-Zener model assumes only two states are interacting at an avoided crossing. The adiabatic potential energy curves obtained by some of us previously [11], are used in this study. These states are for the \( ^5\Sigma^+ \) symmetry and do not cross each other, but instead have avoided crossings as depicted by figure 5 of [11]. First the electronic states are transformed to a diabatic representation. The adiabatic-to-diabatic transformation matrix, \( T_{ij} \), is a two-by-two matrix of the form

\[
T_{ij} = \begin{pmatrix}
\cos[\gamma_{ij}(R)] & \sin[\gamma_{ij}(R)] \\
-\sin[\gamma_{ij}(R)] & \cos[\gamma_{ij}(R)]
\end{pmatrix},
\]

(2)

The rotational angle, \( \gamma_{ij} \), is obtained from integrating the first derivative non-adiabatic coupling element [20],

\[
\gamma_{ij}(R) = \int_{R}^{\infty} F_{ij}(R') dR',
\]

(3)

where \( F_{ij}(R) \) is the first derivative non-adiabatic coupling element between states \( i \) and \( j \). The non-adiabatic couplings used here are those reported by Larson \textit{et al} [11]. These couplings have a bigger magnitude at larger internuclear distances and are known to drive the mutual neutralization reaction in other systems [21–24].

These coupling elements are peaked at the avoided crossing. Thus the rotational angle will exhibit a drop by a factor of \( \frac{\pi}{2} \) near the avoided crossing. This drop has been observed previously for other systems [22, 24]. The rotational angles, obtained by using equation (3) for the HeH system are shown in figure 1, where the drop by a factor of \( \frac{\pi}{2} \) is observed at the internuclear positions corresponding to an avoided crossing.

Once the rotational angles are obtained, a transformation matrix (2) is set up and used to perform a two-by-two transformation of the adiabatic potential energy curves for the system, using

\[
T \begin{pmatrix}
V_{1}^{ad} \\
0
\end{pmatrix}
T_{ij}^{T} \begin{pmatrix}
0 \\
V_{2}^{ad}
\end{pmatrix} = \begin{pmatrix}
V_{1}^{di} \\
H_{12} \\
H_{21} \\
V_{2}^{di}
\end{pmatrix},
\]

(4)

\( V_{1} \) and \( V_{2} \) are the potential energies for the two interacting states. The superscripts ‘\( ad \)’ and ‘\( di \)’ denotes \textit{adiabatic} and \textit{diabatic}, respectively. Since the diabatic electronic states are not eigenfunctions of the electronic Hamiltonian, the diabatic potential matrix has off-diagonal elements, \( H_{12} = H_{21} \), known as electronic couplings. The diabatic potential energy curves for the electronic states are the diagonal elements of the matrix for the HeH system are shown in figure 2. The diabatic curves now are depicting electronic states that are preserving their ionic/covalent character at short and larger internuclear distances. The potential energy curve for the ion-pair state is crossing the potential energy curves of the covalent states. In the Landau-Zener model, the diabatic potential energy curves are assumed to vary linearly with the internuclear distance, \( R \), in the vicinity of a crossing \( R_c \), i.e

\[
V_{1}^{di}(R) - V_{2}^{di}(R) = cR,
\]

(5)

where \( c \) is a constant.
Electronic couplings obtained using the two-by-two state transformation are shown in figure 3. The electronic couplings show a smooth variation with internuclear distance and are peaked at the non-adiabatic avoided crossing. This is a stark contrast to the non-adiabatic couplings (as reported in [11]), where there is no smooth variation with internuclear distance.

In the HeH system, for the reaction (1) under study, the potential energy curve for the ion-pair state crosses ten potential energy curves for the covalent states, in the diabatic picture (see figure 2). The reaction starts in the ion-pair electronic state and ends in the covalent state. Values of internuclear distances where the ion-pair potential energy curve crosses the covalent states, $R_{e}$, are displayed in table 1. Electronic couplings values at the curve crossings are also shown in the table. The electronic couplings used are from the off-diagonal elements of the two-by-two diabatic matrix elements (a method reported as the ‘ATD’ method in [24]). A comparison of the electronic couplings with the analytic approximation is also shown. These are reported by Olson et al [19], where the electronic couplings were approximated using the equations

$$H_{12} = \gamma^2 [8.0 \exp(-0.91\gamma R_{e}) - 7.5 \exp(-0.99\gamma R_{e})],$$

and

$$H_{12} = \gamma \frac{\alpha^2 A^2}{2 R_{e}^2} \left(\frac{4}{\epsilon}\right)^{1/\gamma} (\alpha R_{e})^{2/\gamma} (2\epsilon + 1) \left[\left(\frac{1}{\alpha}\right)^{\beta} + \epsilon^\gamma \right] \frac{1}{\Gamma^\gamma}$$

$$\times \left[\left(\frac{1}{\alpha}\right)^{\beta} - \epsilon^\gamma \right] \exp\left(-\alpha + \gamma R_{e}\right).$$

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$$\times \left[\left(\frac{1}{\alpha}\right)^{\beta} - \epsilon^\gamma \right] \exp\left(-\alpha + \gamma R_{e}\right).$$
\( \gamma^2 \) is the binding energy of \( H^- \), \( \ell \) is the orbital angular momentum quantum number for the electron in the excited atom, \( \alpha^2 \) is the binding energy of the outer electron in the excited atom, while \( \lambda^2 \) has a value of 2.65 and \( e \) is the elementary charge. \( \Delta E \), the asymptotic energy difference between the potential energy curve of the ion-pair state and the covalent state, is also shown in the table. The values in brackets are those reported by Olson et al [19]. Superscripts \( ^{(a)} \) and \( ^{(b)} \) in the table denote results of equation (6) and equation (7), respectively.

The Landau-Zener probability, \( p_\ell \), for staying in a diabatic curve at the curve crossing is given by [17, 18]

\[
p_\ell = \exp \left( -\frac{\eta}{\nu_\ell} \right),
\]

where

\[
\eta = \frac{2\pi H_{12}^2}{c},
\]

\( H_{12} \) is the electronic coupling element, while \( \nu_\ell \) is the radial velocity at the curve crossing. As pointed out in previous studies [22, 24], the electronic couplings play a crucial role on the quality of the results one may obtain by using the Landau-Zener method. The probability, \( \varphi(\text{ion}, 1) \) (where \( \text{ion} \) is the incoming channel and \( 1 \) is the the outgoing channel), for ending in the highest covalent state (here the covalent states are numbered 1-10, starting from the highest in energy, refer to figure 2) is given by

\[
\varphi(\text{ion}, 1) = \begin{cases} 
2P_{\text{ion}}P_{\ell_2}P_{\ell_1}P_{\ell_1}P_{\ell_1}P_{\ell_1}P_{\ell_1}P_{\ell_1}P_{\ell_1}\times P_{\ell_1}P_{\ell_1}P_{\ell_1}P_{\ell_1}(1 - p_\ell), & \text{if } \ell < \ell_1 \\
0, & \text{otherwise}.
\end{cases}
\]

Figure 3. Electronic couplings for the diabatic \( ^3\Sigma^+ \) electronic states of the HeH system.

Table 1. Diabatic curves crossing distances, electronic couplings and values of \( \Delta E \) for the diabatic covalent states of the HeH system used in the study.

| \( R_e (\text{a}) \) | \( H_{12} (\times 10^{-4} \text{eV}) \) | \( \Delta E (\text{eV}) \) |
|------------------|-----------------|-----------------|
| \( 2s^2S \)      | 7.74            | 128.17          | 3.3760          |
| \( 2s^1S \)      | 9.28 (8.5)      | 37.956 (150)\(^a\) (400)\(^b\) | 2.580 (3.22)    |
| \( 2p^1P \)      | 10.38 (9.5)     | 63.394 (130)\(^a\) (310)\(^b\) | 2.2301 (2.87)   |
| \( 2p^1P \)      | 11.51 (10.4)    | 7.8453 (110)\(^a\) (260)\(^b\) | 1.9750 (2.62)   |
| \( 3s^1S \)      | 23.89 (24.4)    | 6.9397 (9.7)\(^a\) (18)\(^b\) | 0.4803 (1.12)   |
| \( 3s^1S \)      | 28.88 (29.7)    | 1.9948 (3.6)\(^a\) (6.8)\(^b\) | 0.2783 (0.92)   |
| \( 3p^1P \)      | 32.15 (32.9)    | 2.4096 (1.9)\(^a\) (4.5)\(^b\) | 0.1885 (0.83)   |
| \( 3p^1P \)      | 35.39 (36.0)    | 1.5679 (1.0)\(^a\) (1.5)\(^b\) | 0.1069 (0.76)   |
| \( 3d^1D \)      | 35.39 (36.0)    | 1.5679 (1.0)\(^a\) (1.5)\(^b\) | 0.1069 (0.76)   |
| \( 3d^1D \)      | 36.52 (36.5)    | 1.5246 (0.95)\(^a\) (2.4)\(^b\) | 0.0792 (0.75)   |
The Landau-Zener probability for a transition from the ion-pair state to a covalent state \( n \) \((2 \leq n \leq 10)\) is

\[
\psi(\text{ion}, n) = \begin{cases} 
P_{\text{ion}}(1 - P_{\text{ion}}), & \text{if } \ell_{n-1} < \ell < \ell_n \\
P_{\text{ion}}^2 \cdot \cdots \cdot P_{\text{ion}}(1 - P_{\text{ion}})^2, & \text{if } \ell_{n-2} < \ell < \ell_{n-1} \\
\vdots \\
P_{\text{ion}}^2 \cdot \cdots \cdot P_{\text{ion}}^2(1 - P_{\text{ion}})^2, & \text{if } \ell_{1} < \ell < \ell_{2} \\
P_{\text{ion}}^2 \cdot \cdots \cdot P_{\text{ion}}^2(1 - P_{\text{ion}})^2, & \text{if } \ell_{2} < \ell < \ell_{3} \\
\vdots \\
P_{\text{ion}}^2 \cdot \cdots \cdot P_{\text{ion}}^2(1 - P_{\text{ion}})^2, & \text{if } \ell < \ell_{n}.
\end{cases}
\]

(11)

Here \( \ell_{n} \) denotes the largest rotational quantum number \( (\ell_{\text{max}}) \) required for the crossing point \( R_{\text{xc}} \) to be reached in the \( n^{-} \) state;

\[
\ell_{\text{max}} = 2R_{\text{x}} \sqrt{\mu(E_{n} + \Delta E)},
\]

(12)

where \( E_{n} \) is the collision energy of the system, in state \( n \), without including the centrifugal barrier term and assuming that the threshold energy is zero. \( \mu \) is the reduced mass for colliding species.

The mutual neutralization reaction cross section formula, for state \( n \), is calculated by

\[
\sigma_{n}(E_{n}) = \frac{\pi}{k_{n}^{2}} \sum_{\ell = \ell_{n}}^{\ell_{\text{max}}} (2\ell + 1) \psi(\text{ion}, n),
\]

(13)

where \( k_{n} \) is the asymptotic wave number of the outgoing channel,

\[
k_{n} = \sqrt{2\mu(E_{n} - E_{n}^{th})},
\]

(14)

and \( E_{n}^{th} \) is the asymptotic energy value for state \( n \).

3. Results

The mutual neutralization reaction cross section for collisions of \(^{4}\text{He}^{+} + \text{H}^{-}\) is computed using equation (13) for each of the ten states. The partial cross sections are shown in figure 4, together with the total cross section which has been computed using

\[
\sigma_{\text{total}}(E) = \sum_{n=1}^{10} \sigma_{n}(E_{n}).
\]

(15)

At low collision energy, the dominant channel is associated with the \(^{1s}\text{He}^{+} + \text{H}^{-}\) asymptotic limit, while at energies above 5 eV, the channel associated with the \(^{1s}3\text{s}^{2}\text{s}^{0}\text{He}^{+} + \text{H}^{-}\) limit dominates.

The final states distributions \( (\kappa_{n}) \) are computed using

\[
\kappa_{n}(E) = \frac{\sigma_{n}(E_{n})}{\sigma_{\text{total}}(E)}
\]

(16)

figure 5 shows a graph depicting the final states distribution for the reaction, where the dominant \(^{1s}3\text{s}^{2}\text{He}^{+} + \text{H}^{-}\) asymptotic limit channel contributes about 43% to the total cross section, at energies below 5 eV. The channel associated with the \(^{1s}3\text{s}^{2}\text{s}^{0}\text{He}^{+} + \text{H}^{-}\) limit contributes about 22 % at low energies and its dominance increases to about 30 % at energies above 5 eV. The least significant channels are for the \( n = 2 \) states, associated with the the channels going to the \(^{1s}3\text{s}^{2}\text{s}^{0}\text{H} + \text{H}^{+}\) and \(^{1s}2\text{s}^{3}\text{He}^{+} + \text{H}^{-}\) asymptotic limits. The branching ratios are compared with the results from the fully quantum calculation of [11]. The dominance of the \(^{1s}3\text{s}^{2}\text{s}^{0}\text{He}^{+} + \text{H}^{-}\) and \(^{1s}2\text{s}^{3}\text{He}^{+} + \text{H}^{-}\) is confirmed by both calculations, although the magnitudes of the ratios are not the same. The dominance of the channel associated with the \(^{1s}2\text{s}^{3}\text{He}^{+} + \text{H}^{-}\) limit is, however, not seen at all in the fully quantum study. This could be due to the Landau-Zener model which only considers a two state interaction near an avoided crossing. Thus coupling to other states, which could alter the reaction cross section in each channel, is not fully captured.
The mutual neutralization reaction total cross section results for collisions of \(^4\text{He}^+ + \text{H}^-\) are shown in figure 6. Here, they are compared with the theoretical results from a fully quantum model \(^{11}\) and the semi-classical model results of Olson \(^{19}\) et al. The experimental results by Peart \(^{14}\) et al., Gaily \(^{25}\) et al. and Olamba \(^{13}\) et al. are also shown. The cross section from the Landau-Zener model is comparable with the fully quantum model at low collision energies. For energies above 1eV, the total cross section from the current model is larger. This is a phenomenon previously observed in other systems \(^{22, 23}\). Results obtained by Olson \(^{19}\) et al. by using electronic couplings from equation \(^{6}\) seem to agree with the current study in the energy range 1-10eV, and deviate at energies above 10 eV. The total cross section obtained from the electronic couplings of equation \(^{7}\) is higher at energies below 100 eV, although at 100 eV there seem to be an agreement. Both results by Olson \(^{19}\) et al. are higher than the result of the fully quantum study.

To study isotope dependence of the reaction the total cross section of the \(^4\text{He}^+ + \text{H}^-\) reaction is compared with that of \(^4\text{He}^+ + \text{D}^-\). Olson \(et\ al\) concluded that the cross section from the heavier reduced mass is smaller than the cross section from the lighter reduced mass. In figure 7, the isotope dependence of the total cross section is shown. For the current study and the fully quantum study by Larson \(et\ al\) \(^{11}\), the value of the cross section from the larger reduced mass is larger than the cross section from the lighter reduced mass.

4. Conclusion

The mutual neutralization reaction total cross section is theoretically studied using a semi-classical Landau-Zener model. The electronic couplings used in the study are calculated from \textit{ab initio} data and they vary...
significantly with those of Olson et al [19]. The total cross section is comparable with the recent results from a fully quantum study, at energies below 1 eV. At low collision energies the cross section follows the Wigner threshold law [26]. The mutual neutralization reaction is driven by non-adiabatic couplings, at large internuclear distances. Compared to the results of the fully quantum study, the total cross section from the present study is larger at energies higher than 1 eV, for both isotopes. This could be attributed to the classical nature of approximating the radial velocity, at the curve crossing. Olson et al [19] attributed this to the wrong asymptotic dependance of the cross section on $1/v_x$ (rather than $1/v_x^2$). The electronic couplings, $H_{12}$, used in the Landau-Zener method are assumed to be constant around the crossing point. Such an assumption leads to a wrong asymptotic behaviour of the transition probability, $p_{CT}$. The Born approximation [27, 28] points to a $1/v_x^2$ dependance which leads a total cross section that agrees with experimental results.

In contrast to the results by Olson et al [19], results from the present calculation and the fully quantum study point to a larger cross section for the heavier reduced mass. The difference in the total cross sections from the present calculation and the calculations of Olson et al [19] could be attributed to the quality of the electronic couplings used in the study and the states included. The final states distribution show a significant contribution for the He[1s2p $^3P$] + H channel followed by the He[1s3s$^3S$] + H channel. For the branching ratios, both the fully quantum and current study points to a significance of the He[1s3s$^3S$] + H channel by 50% and 22%, respectively.

Figure 6. Total cross section for mutual neutralization reaction of $^4$He$^+$ + H$^-$ compared with other theoretical (lines) [11, 19] and experimental (points) [13, 14, 25] results.

Figure 7. Isotope effects in the total cross section of mutual neutralization reaction in collisions of $^4$He$^+$ + H$^-$ (solid lines) and $^4$He$^+$ + D$^-$ (dashed lines). The cross section is compared with other theoretical (lines) and experimental (points) results [19].
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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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