



Research article



Studies of mutual neutralization in collisions involving Mg^+/H^- , Na^+/H^- , Li^+/H^- and Li^+/Cl^-

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ABSTRACT

The Landau-Zener model is used to systematically compute mutual neutralization cross sections for collisions between Mg^+/H^- , Na^+/H^- , Li^+/H^- and Li^+/Cl^- . Potential energy curves for electronic states that are relevant for mutual neutralization are taken from available literature. Where non-adiabatic couplings are available, they are utilized to compute the diabatic potential energy curves, crossing distance and electronic couplings. In cases where non-adiabatic couplings are not available, they are approximated using a Lorentzian function. The reaction cross sections are computed for the energy range 0.001 eV to 1000 eV. The results are compared with other available experimental and theoretical results and are found to be very comparable. There is an observable trend in the reaction cross section involving ions of metals and hydrogen at collision energies below 10 eV, with the heaviest metal showing the largest reaction cross section and the lightest metal with the lowest cross section. At collision energies below 10 eV, isotope effect is also found to have an effect on the reaction cross section for Li^+/Cl^- .

1. Introduction

Mutual neutralization is a reaction where a cation and an anion collide, exchanging charge and forming a neutral resonant molecule, which then breaks apart into neutral fragments. The formed fragments could be electronically excited. This elementary reaction is of interest, given that quantitative reaction cross section or branching ratio information is needed for many collision systems that are of relevance in plasma physics or interstellar chemistry. Experimental studies of mutual neutralization have been carried out for collisions of systems involving H^+ and H^- [1, 2], He^+ and H^- [3, 4], O^+ and O^- and between N^+ and O^- [5, 6] to name just a few. On the other hand theoretical calculations have been carried out for systems such as He^+ and H^- [7, 8], Li^+ and H^- [9, 10], Li^+ and F^- [11], He^+ and H^- [12, 13, 14], Mg^+ and H^- [15] and collisions of H^+ and Cl^- [16].

A qualitative comparison of the computationally inexpensive semi-classical calculation with a full quantum calculation could give much insight into the most appropriate approach one could take to theoretically model a mutual neutralization reaction. A fully quantum model of the process is most dependable since it can fully account for many significant interactions like non-adiabatic effects, rotational couplings

and spin-orbit couplings [8, 14, 16]. However, this approach has limitations due to the mammoth task one has to undertake in performing high level electronic structure calculations for potential energy curves of highly excited and coupled states. This approach, often time, also has to go with very sophisticated calculations of the non-adiabatic couplings between the states. This is proving a challenge to adequately undertake, in particular for systems with many electrons. On the other hand, the Landau-Zener model [17, 18], can provide mutual neutralization reaction cross sections that are comparable with the fully quantum studies [16, 19, 20, 21]. The Landau-Zener model is only dependent upon parameters like the asymptotic energies for the states involved, electronic couplings and the crossing distance. These parameters can be systematically obtained without having any electronic structure data and non-adiabatic couplings [19]. The mutual neutralization reaction involves an ion-pair potential and covalent states potential. The ion-pair will exhibit a long range Coulombic form, while the covalent states are asymptotically converging, such that the potential energy curves for such states will be flat at larger internuclear distances.

Mutual neutralization involving ions of metals and hydrogen systems, like collisions between Mg^+ and H^- , are of interest to the astrophysics community. The reaction cross sections and reaction rates are a

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major objective for astrophysicists involved in the three-dimensional modeling of stellar atmospheres. Here, such a process will compete with the radiative processes to populate the atomic levels [22]. In cold plasma environments, it is believed that such collisions are predominant and it is of interests to the astrophysics community to understand the driving mechanisms and fragments formed [23, 24]. However, most of these collision reaction rates are unknown or often estimated with very large uncertainties [25].

This study is carried out in order to obtain reaction cross section for mutual neutralization of the systems as depicted by equations (1)- (4);



First, diabatic potential energy curves, electronic couplings and crossing distance are computed. Then the nuclear dynamics are studied using the Landau-Zener [17, 18] model. The reaction cross section is computed for collision energies of 0.001 eV to 1000 eV.

This article is arranged as follows; Section 2 briefly outlines the Landau-Zener model and methods for computing non-adiabatic coupling elements, electronic couplings and the mutual neutralization cross section. Section 3 reports on the reaction cross section results, with the mutual neutralization reaction for $\text{Mg}^+ + \text{H}^-$, $\text{Na}^+ + \text{H}^-$, $\text{Li}^+ + \text{H}^-$ and $\text{Li}^+ + \text{Cl}^-$ discussed in subsection 3.1, subsection 3.2, subsection 3.3 and subsection 3.4, respectively. Finally, the discussion and conclusion are given in section 4.

2. Landau-Zener model

The Landau-Zener model, developed independently by Landau [17] and Zener [18], is a semi-classical model that approximates the probability, p_ℓ , of transition at a curve crossing (or at an avoided crossing) as equation (5),

$$p_\ell = \exp\left(\frac{2\pi H_{12}^2}{v_x^\ell k}\right) \quad (5)$$

where $H_{12} = H_{12}(R_x)$ is the off-diagonal element of the diabatic potential energy matrix at the curve crossing also known as the electronic coupling [26], v_x^ℓ is the classical radial velocity at the curve crossing, k relates the diabatic potential energies, V_{ii}^d and V_{jj}^d , of the two interacting states, i and j , at the curve crossing. For this model the difference between the diabatic potentials is assumed to be linear, such that k is approximated to be a constant and in the vicinity of an avoided crossing,

$$V_{ii}^d - V_{jj}^d = kR, \quad (6)$$

where R , in equation (6), is the internuclear separation distance. Theoretically, the diabatic potential energy curves are nothing but eigenfunctions of the electronic Hamiltonian, as shown by equation (7),

$$\langle \phi_i^d | \mathbf{H}_e | \phi_j^d \rangle = V_{ij}^d, \quad (7)$$

where \mathbf{H}_e is the electronic Hamiltonian and ϕ_i^d is the diabatic electronic wave-function.

The attractive ion-pair potential is assumed to take the form of equation (8),

$$V_{\text{ion-pair}} = E_{\text{asy}} - \frac{1}{R} - \frac{\alpha(A^+) + \alpha(B^-)}{2R^4}, \quad (8)$$

where E_{asy} is the asymptotic energy, $\alpha(A^+)$ and $\alpha(B^-)$ are the polarizabilities of the positively charged and negatively charged ions, respectively. Polarizabilities of the ions considered in the study are listed in

Table 1. Polarizabilities of ions considered in the current study.

Species	α (a_0^3)
Mg^+	35.04 [27]
Na^+	1.22145 [28]
Li^+	0.195702 [28]
Cl^-	24.901384 [28]
H^-	216 [29]

Table 1, where a_0 is the Bohr radius. The adiabatic to diabatic transformation is carried out using a transformation matrix, as outlined in refs. [11, 19, 21]. The two-by-two transformation matrix, \mathbf{T} , is of the form

$$\mathbf{T} = \begin{pmatrix} \cos[\theta_{ij}(R)] & \sin[\theta_{ij}(R)] \\ -\sin[\theta_{ij}(R)] & \cos[\theta_{ij}(R)] \end{pmatrix}, \quad (9)$$

where $\theta_{ij}(R)$ is defined a transformation rotational angle. It is obtained by integration of the non-adiabatic couplings,

$$\theta_{ij}(R) = \int_0^\infty f_{ij}(R) dR, \quad (10)$$

$f_{ij}(R)$ are the non adiabatic elements and are known to peak near an avoided crossing [11, 19, 20]. Where none are reported from literature, the non-adiabatic coupling between the two states is approximated using a Lorentzian function of the form as given by equation (11),

$$f_{ij}(R) = \frac{\Gamma}{4(R - R_x)^2 + \Gamma}, \quad (11)$$

where Γ is a constant and is optimized to ensure a complete diabatic switch at the curve crossing [11].

The collision energy dependent mutual neutralization reaction cross section, $\sigma_i(E)$, for state i is obtained by equation (12)

$$\sigma_i(E) = \frac{\pi}{k_i^2} \sum_{\ell=0}^{\ell_{\text{max}}} (2\ell + 1) \wp_i^\ell, \quad (12)$$

where \wp_i^ℓ is the multistate Landau-Zener probability, ℓ is the rotational quantum number, and k_i is the asymptotic wave number of the incoming channel,

$$k_i = \sqrt{2\mu E}, \quad (13)$$

when assuming that the threshold energy for the incoming channel is zero and E is the collision energy, while μ is the reduced mass.

3. Results

3.1. Mutual neutralization of $\text{Mg}^+ + \text{H}^-$

Using the adiabatic potential energy curves and non-adiabatic couplings between eight $^1\Sigma$ states of the MgH system that are reported by Guitou et al. [30], a two-by-two strict diabatization [26] procedure is carried out in order to obtain the electronic couplings and crossing distance required as input for the Landau-Zener formula. The transformation is of the form given by equation (14)

$$\mathbf{V}^d = \mathbf{T} \mathbf{V}^a \mathbf{T}^T, \quad (14)$$

where \mathbf{T} is the two-by-two transformation matrix as described by equation (9). \mathbf{V}^a and \mathbf{V}^d are the two-by-two matrices containing the adiabatic potential energies and diabatic potential energies, respectively. The transformation yields adiabatic potentials of the covalent states that are crossing with the ion-pair potential. These potentials are shown in Fig. 1, where they are assigned using the asymptotic states of Mg. The diabatic potential energy curves do not exhibit the sharp avoided crossings that are exhibited by potential energy curves in the diabatic

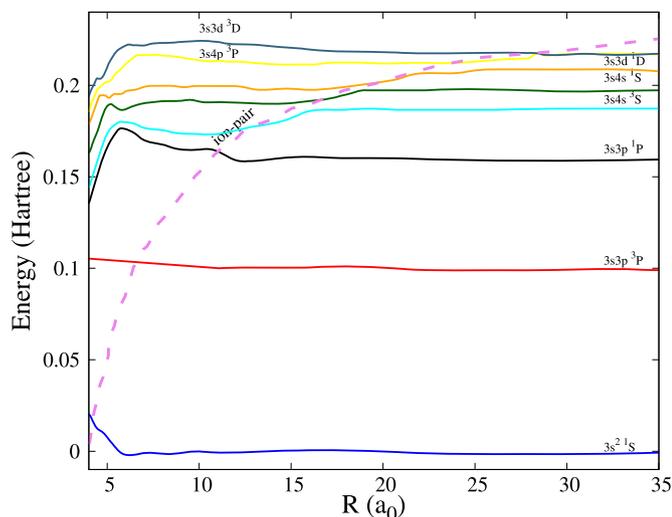


Fig. 1. Diabatic potential energy curves for MgH, obtained using the two-by-two strict diabaticization procedure.

Table 2. Landau-Zener formula input parameters for $\text{Mg}^+ + \text{H}^-$. Asymptotic energies are from ref. [30].

State	R_x (a_0)	H_{12} (eV)	E_{asy} (eV) [30]
$3s^2 \ ^1S$	10.84	0.04996	0
$3s3p \ ^3P$	18.09	0.03065	2.712
$3s3p \ ^1P$	19.90	0.01385	4.38
$3s4s \ ^3S$	22.24	0.0003485	5.13
$3s4s \ ^1S$	25.07	0.005978	5.42
$3s3d \ ^1D$	30.91	0.004903	5.75
$3s4s \ ^3P$	31.98	0.00003639	5.93
$3s3d \ ^3D$	32.19	0.002631	6.89

representation. In reality, each state is interacting with all other states, at all internuclear distances, hence the non-smoothness of the potential energy curves. The Landau-Zener input parameters obtained are as shown in Table 2.

The mutual neutralization reaction cross section obtained using the parameters in Table 2 is shown in Fig. 2. Here the results are compared with the results reported by Belyaev et al. [15].

3.2. Mutual neutralization of $\text{Na}^+ + \text{H}^-$

The adiabatic potential energy curves for the NaH system are those reported in ref. [31] and ref. [10]. Only five states of $^1\Sigma$ symmetry are reported, together with their non-adiabatic couplings. Using these states and the couplings, electronic couplings are computed by performing an adiabatic-to-diabatic transformation. Dickinson et al. [10] employed a two-by-two transformation to transform the adiabatic potential energy curves of the electronic states to a diabatic representation. The same method is employed here, with the aim of obtaining values for the electronic couplings which are critical in the Landau-Zener formula [19]. The diabatic states obtained are similar to those reported by Dickinson et al. The Landau-Zener input parameters obtained are as shown in Table 3.

The mutual neutralization reaction cross section is then computed and here is compared with a previous theoretical result of Dickinson et al. [10], and are shown in Fig. 3. Dickinson et al. used a fully quantum model to compute the reaction cross section. This was compared with some semi-classical calculations by Janev et al. [32] and Olson et al. [33]. The interest in the present work is to increase the energy range to 1000 eV for comparison with other systems. At collision energies above 10 eV, the present results deviates and gets smaller, even though at lower energies both results are equal and following the same trend.

Table 3. Landau-Zener formula input parameters for $\text{Na}^+ + \text{H}^-$. Asymptotic energies are from [10], while crossing distances are adapted from [31] and [10].

State	R_x (a_0)	H_{12} (eV)	E_{asy} (eV) [10]
3s	7.85 [31]	0.8604	0.012
3p	13.67 [31]	0.214	0.0091
4s	21.96 [10]	0.0234	0.007
3d	35.4 [10]	0.0108	0.0056
4p	43.0 [10]	0.00542	0.0051

3.3. Mutual neutralization of $\text{Li}^+ + \text{H}^-$

The input parameters for the Landau-Zener formula were taken directly from the work of Launoy et al. [6]. Five $^1\Sigma^+$ states of the LiH system are considered important for mutual neutralization. These are states whose interactions (crossing distances) are below $50 a_0$. The mutual neutralization cross section is compared with theoretical [6, 9] and experimental results [2, 6], as shown in Fig. 4. The present calculation is very comparable with the theoretical result by Launoy et al., although there is a slight difference at energies above 10 eV. The interest in the present work, for this system as well, is to increase the energy range to 1000 eV for systematic comparison with the other systems.

3.4. Mutual neutralization of $\text{Li}^+ + \text{Cl}^-$

The potential energy curves of alkali halides have been known to possess avoided crossing between low-lying adiabatic electronic states [11, 34, 35, 36]. The potential energy curves for the LiCl system that are relevant for mutual neutralization are reported by Kurosaki et al. [37]. The potential energy curve of the lowest lying state is pointing to a possibility of the formation of stable LiCl, although this process could be greatly hampered by the very high centrifugal barrier. The Lorentzian function is used to approximate the non-adiabatic coupling, with an optimized $\Gamma = 0.25$, to ensure a full diabatic transformation. The avoided crossing is at $R_x = 61.8 a_0$, while after performing the adiabatic-to-diabatic transformation, the electronic coupling, $H_{12} = 4.152 \times 10^{-3}$ Hartree. The diabatic potential energy curves, are shown in Fig. 5.

Fig. 6 shows the $\text{Li}^+ + \text{Cl}^-$ reaction cross section obtained in our model. To our knowledge, there are no results for the mutual neutralization cross section that have been previously reported. A comparison with previous results for $\text{Li}^+ + \text{F}^-$ [11], where a similar model was employed, has been done. Isotope effect is also studied for Cl^- .

3.5. Cross section comparison

The reaction cross section for reactions (1) - (4) are shown in Fig. 7. For the collisions between ions of metals and hydrogen, there is an observable trend, at collision energies below 10 eV. The reaction cross section from the heavier metal is larger than the reaction cross section formed from collisions between the hydrogen anion and a lighter metal cation species. At higher energies, it is difficult to conclude since this model seems to be breaking down, or neglecting some very important quantum effects.

4. Discussion and conclusion

Using the Landau-Zener model, we have carried out systematic mutual neutralization studies, investigating three metal-hydrides systems and isotope effect in an alkali-halide system. The Landau-Zener formula seems to work quite well for systems studied here. At low collision energies (below 10 eV), mutual neutralization reaction cross section results computed are comparable to other results. The mutual neutralization cross section for all species considered here are following the well-known Wigner-threshold law at low collision energies [38]. At collision energies above 10 eV, the cross section obtained using the Landau-Zener formula deviates from fully quantum and experimental studies.

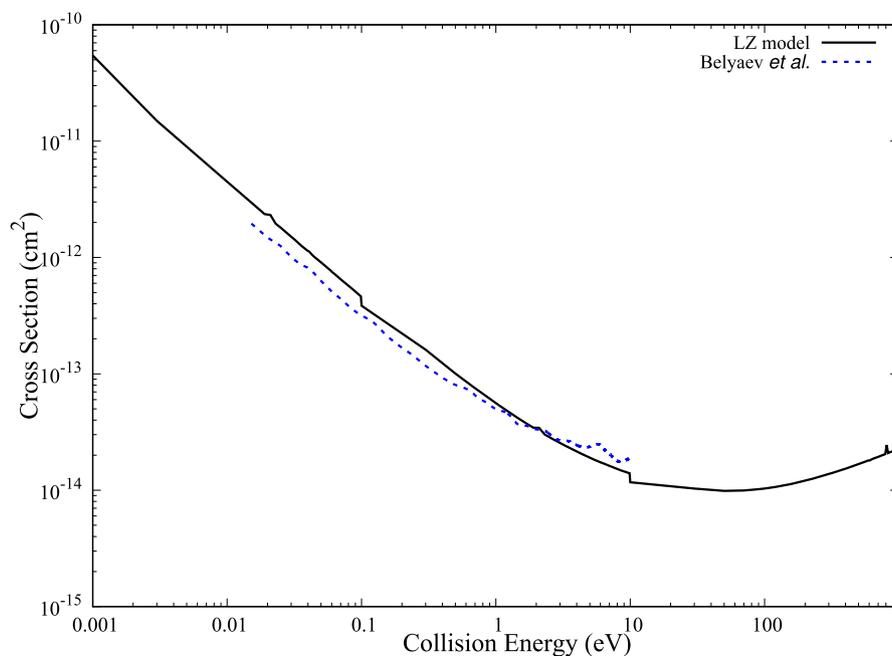


Fig. 2. Mutual neutralization cross section for $\text{Mg}^+ + \text{H}^-$, using the Landau-Zener method, compared with previous theoretical results [15].

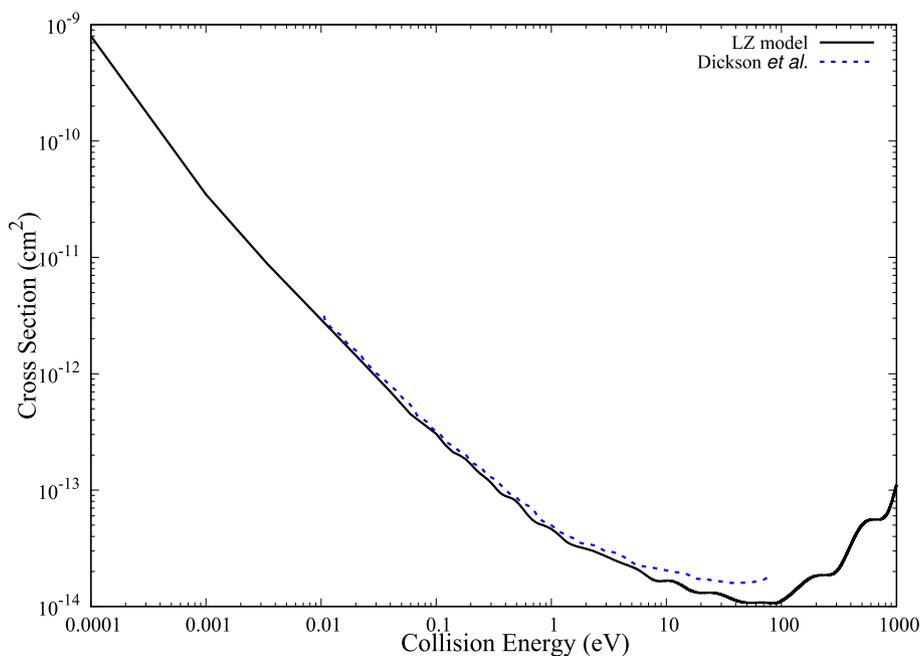


Fig. 3. Mutual neutralization cross section for $\text{Na}^+ + \text{H}^-$, using the Landau-Zener method, compared with previous theoretical results [10].

This could be due to the fact that this model treats coupling, at the curve crossing only. The neglected rotational and translational factors could also be contributing to the discrepancy. A discrepancy between the fully quantum study and the semi-classical model has recently been observed for the mutual neutralization of $\text{He}^+ + \text{H}^-$ process [21]. The treatment of the radial velocity, v_x , at the curve crossing classically leads to a wrong asymptotic dependence of the reaction cross section on $\frac{1}{v_x}$, rather than $\frac{1}{v_x^2}$ [7]. Thus the Landau-Zener model seems to be neglecting important effects at energies above 10 eV, which alters the magnitude of the mutual neutralization reaction cross section. A fully quantum study would be the most dependable in this energy range, however this is limited to the availability of high level electronic structure data. Rotational factors have previously been observed to play an

important role in altering the magnitude of the reaction cross section, for energies above 1 eV, as depicted in the study of mutual neutralization of $\text{He}^+ + \text{H}^-$ of Larson et al. [14].

In the metal-hydrides systems, the reaction cross section from involving a heavier metal cation species is larger than the reaction cross section from lighter metal cation species, at low collision energies. At energies above 10 eV the model breaks down by neglecting a lot of other factors, hence it is inconclusive on the cross section obtained in this collision energy range.

The Lorentzian function can fully mimic the non-adiabatic coupling elements for a two-state system. The alkali-halide systems considered here are exhibiting a larger cross section for lighter species. This is the case even when considering isotope effects, as seen in the case of colli-

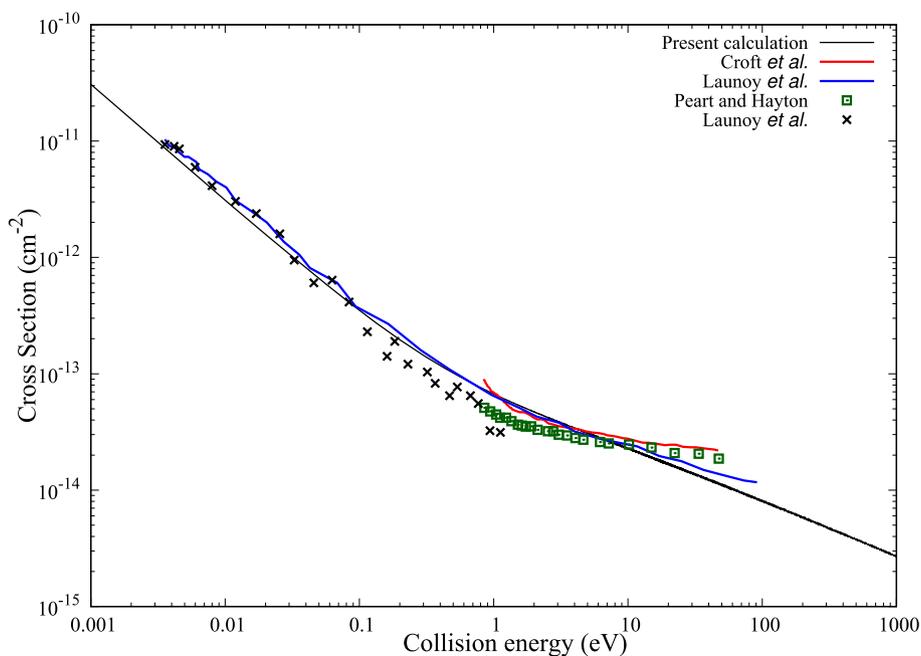


Fig. 4. Mutual neutralization cross section for $\text{Li}^+ + \text{H}^-$, using the Landau-Zener method, compared with previous theoretical (points) and experimental results (lines).

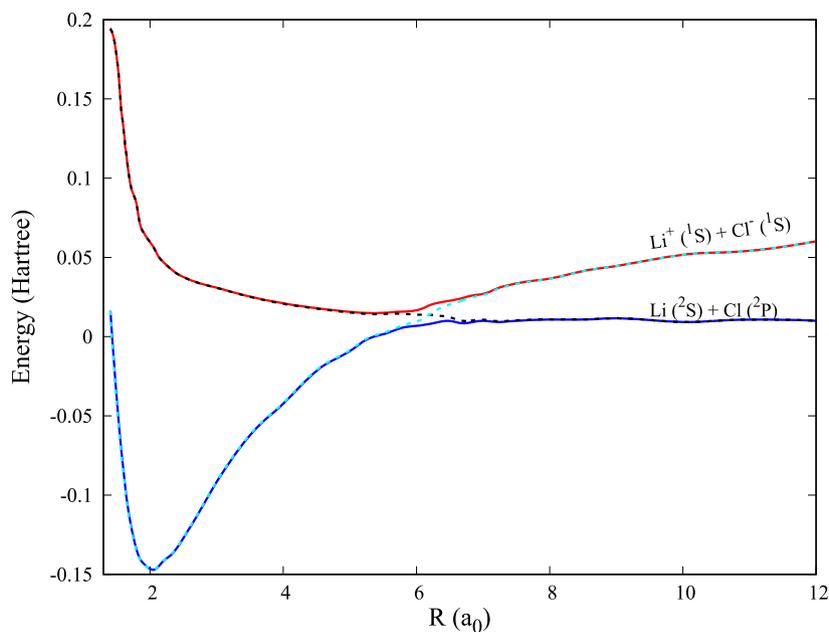


Fig. 5. Adiabatic (solid lines) and diabatic (dashed lines) potential energy curves for the two electronic states involved in the $\text{Li}^+ + \text{Cl}^-$ mutual neutralization process.

sions between Li^+ and $^{35}\text{Cl}^- / ^{37}\text{Cl}^-$. The heavier isotope exhibits a lower reaction cross section at low collision energies. Olson et al. [7] observed a similar trend for collisions involving isotopologues of H^+ and H^- . This method could be extended to mutual neutralization collisions involving heavier ions, although much caution has to be taken into incorporating spin-orbit coupling and relativistic effects.

Declarations

Author contribution statement

Sifiso M. Nkambule: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Oscar N. Mabuza: Performed the experiments; Analyzed and interpreted the data.

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Data availability statement

Data included in article/supp. material/referenced in article.

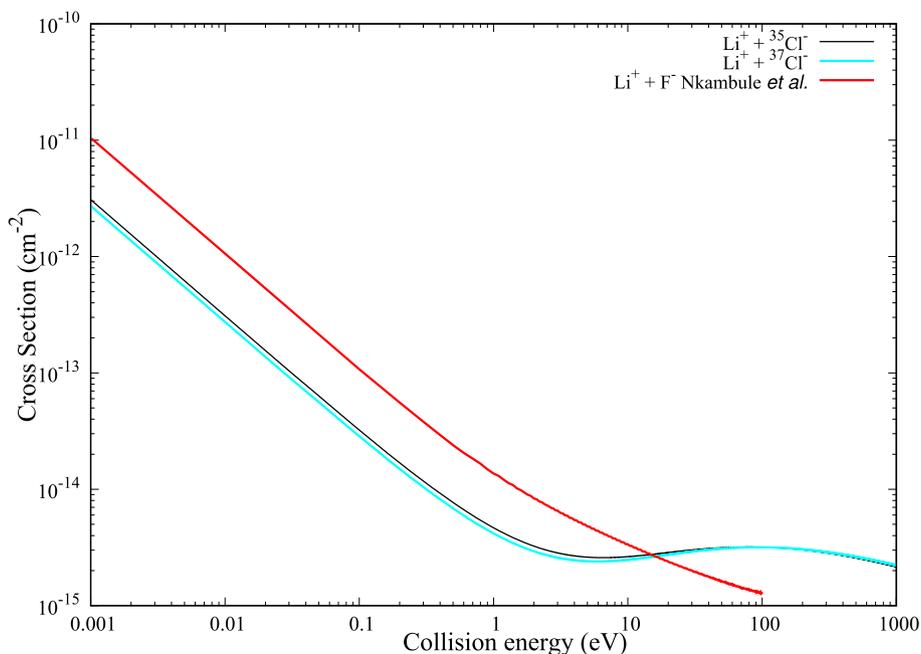


Fig. 6. Mutual neutralization cross section for $\text{Li}^+ + \text{Cl}^-$, using the Landau-Zener method, compared with previous results for $\text{Li}^+ + \text{F}^-$ [11], using a similar method.

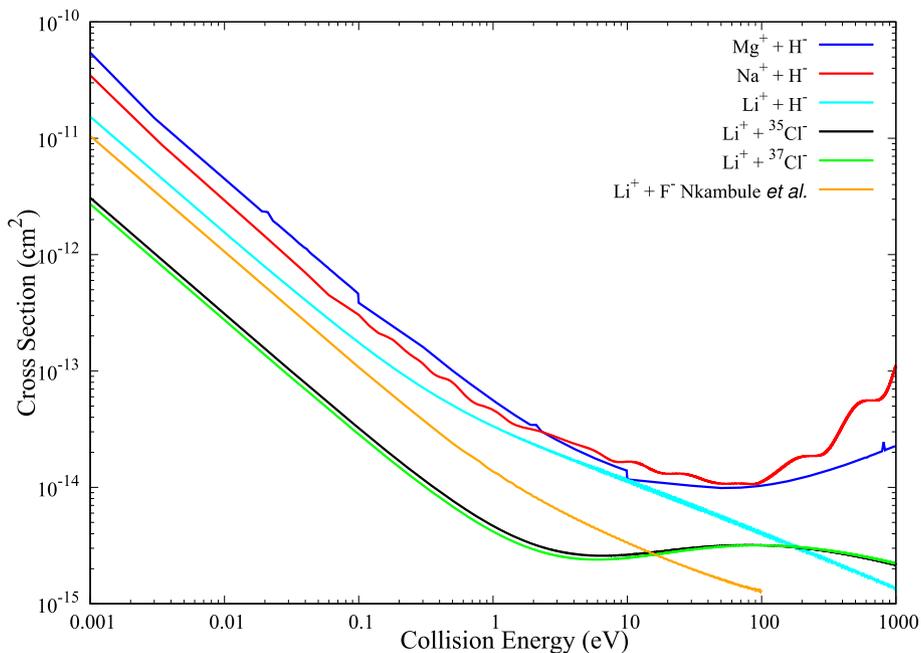


Fig. 7. Mutual neutralization cross section for different species using the Landau-Zener method. Here are compared with previous results for $\text{Li}^+ + \text{F}^-$ [11], using a similar method.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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