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Mutual recombination in slow $Si^+ + H^-$ collisions*

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This paper studies the process of mutual neutralization of Si^+ and H^- ions in slow collisions within the multi-channel Landau–Zener model. All important ionic-covalent couplings in this collision system are included in the collision dynamics. The cross sections for population of specific final states of product Si atom are calculated in the CM energy range 0.05 eV/u–5 keV/u. Both singlet and triplet states are considered. At collision energies below ∼10 eV/u, the most populated singlet state is Si(3p4p, $^1S_0$), while for energies above ∼150 eV/u it is the Si(3p, 4p, $^1P_1$) state. In the case of triplet states, the mixed 3p4p($^3S_1$+$^3P_0$) states are the most populated in the entire collision energy range investigated. The total cross section exhibits a broad maximum around 200–300 eV/u and for $E_{\rm CM} \leq 10$ eV/u it monotonically increases with decreasing the collision energy, reaching a value of 8×10^{-13} cm^2 at $E_{\rm CM} = 0.05$ eV/u. The ion-pair formation process in Si($3p^2\ ^3P_J$)+H(1s) collisions has also been considered and its cross section in the considered energy range is very small (smaller than 10^{-20} cm^2 in the energy region below 1 keV/u).

Keywords: multi-channel Landau–Zener model, slow collision, mutual neutralization

PACC: 5220H, 3400, 9530E, 3490

1. Introduction

To the best of our knowledge, the process of mutual neutralization of Si^+ and H^- ions

$$Si^+(3s^2, 3p|^2p_{1/2} + H^-(1s^2|^1S_0) \rightarrow S(3s^2, 3pnl|^{1,3}\Lambda_5) + H(1s|^2S_0) \quad (1)$$

has never been studied either theoretically or experimentally. On general theoretical grounds, however, and in analogy with the existing studies of this process in other ion–ion collision systems,[1−5] it can be expected that the total cross section of reaction (1) at low collision energies ($E_{\rm CM} \leq 10$ keV/u) should be large. The process (1) may play an important role in silane-based plasma processing applications (such as in integrated circuit technology and logic devices[6−8]), in certain astrophysical environments (planetary atmospheres, hydrogen rich gaseous nebulae, etc.[9]) and in the edge plasmas of fusion devices having plasma facing components that contain Si as admixture.[10]

A specific feature of ion–ion mutual neutralization process is that the transferred electron from the negative to the positive ion populates predominantly excited states of the formed atom. The radiation from these states represents an energy loss for the plasma in which the ion pair exists, but it can also be used for diagnostic purposes.

In the present paper we shall study the reaction (1) within the semi-classical multi-channel Landau–Zener (MCLZ) model for the collision dynamics (see, e.g. Refs.[11] and [12]). This model has been successfully applied in the past to reactions with many ionic-covalent couplings, such as the ones appearing in alkali ion – H^- mutual recombination[5] or in the electron capture from H atom to highly charged ions.[12] In Section 2 we shall give a brief description of MCLZ model together with the determination of ionic-covalent couplings. In Section 3 we shall present the result of cross section calculations for different channels in reaction (1), and in Section 4 we shall briefly consider the ion-pair formation in Si + H slow collisions. Finally, in Section 5 we shall give some concluding remarks.

Atomic units will be used throughout this article, unless otherwise explicitly indicated.

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2. Description of collision dynamics

The electron capture in reaction (1) takes place due to the coupling of initial ionic molecular state $Si^+(3p^2P_{1/2}) + H^-(1s^2S_0)$ with a series of covalent molecular states $Si(3pnl|^{1,3}\Lambda_J) + H(1s^2S_0)$ corresponding to the ground multiplet ($3p^2\ ^3P_0, ^1D_2, ^1S_0$), and excited ($3pnl^{1,3}\Lambda_J$) states of Si atom, and having the same symmetry with the initial ionic state. The coupling interaction of the ionic and covalent diabatic molecular states has been subject for numerous studies in the past (see, e.g., Refs.[13] and [14]). This interaction is strongest in the regions of internuclear distances between the colliding particles where the potential energy curves of ionic and covalent states cross each other.

At large internuclear distances the potential energies of diabatic ionic and covalent states have the form

$$V_{\rm i}(R) \approx -\frac{1}{R} - E_{\rm H^-}, \quad V_{c\alpha} \approx -E_\alpha, \tag{2}$$

where $E_{\rm H^-} = 0.754\,{\rm eV}$ is the binding energy of loosely bound electron in H^- and E_α is the ionization energy of neutralized atom in its state $|\alpha\rangle$. The weak polarization and dispersion interaction energy terms in $V_{\rm i}(R)$ and $V_{c\alpha}(R)$ are neglected in Eq.(2). For the ground and first several excited state of Si atom (for symmetry reasons, only the even parity states are considered), the ionization energies E_α are given in Table 1.

Table 1. Electron binding energies, E_α, of low-lying $Si(3pnp,^{1,3}\Lambda_J)$ states, values of corresponding ionic-covalent curve-crossings R_x, and values of coupling interaction $H_{\rm ic}(R_x)$.

Atomic state	E_α/eV	R_x/a_0	$H_{\rm ic}(R_x)$/arb. units.
$(3p^2)^1D_2$	7.3707	4.111	0.08564
$(3p^2)^1S_0$	6.2430	4.955	0.07974
$(3p4p)^1P_1$	2.2892	17.717	3.462×10^{-3}
$(3p4p)^1D_2$	1.9290	23.149	1.411×10^{-3}
$(3p4p)^1S_0$	1.7526	27.238	7.101×10^{-4}
$(3p5p)^1P_0$	1.1118	76.0186	8.535×10^{-8}
$(3p^2)^3P_0$	8.1517	3.674	0.1567
$(3p4p)^3D_1$	2.1976	18.842	4.983×10^{-3}
$(3p4p)^3P_0$	2.07295	20.622	3.716×10^{-3}
$(3p4p)^3S_1$	2.0269	21.368	3.285×10^{-3}
$(3p5p)^3D_1$	1.0873	81.608	4.881×10^{-8}

In the same table the crossing points R_{x_α} of corresponding (Si + H) covalent potential energy curves with the potential energy curve of ($Si^+ + H^-$) ionic state are also given. The crossing points R_{x_α} are calculated from the condition $V_{\rm i}(R_{x_\alpha}) = V_{c\alpha}(R_{x_\alpha})$. The values of for the Si atom were taken from Ref.[15].

The analytic expression for the ionic-covalent coupling interaction $H_{\rm ic}(R)$ at large internuclear distances R has the form[13,14]

$$H_{\rm ic}(R) = \frac{1}{2}A_{\rm i}A_{\rm c}DR^{\frac{1}{\gamma}-1}{\rm e}^{-\gamma R}, \tag{3}$$

where $\gamma = (2E_\alpha)^{\frac{1}{2}}$, $A_{\rm i}$ and $A_{\rm c}$ are the normalization constants of the asymptotic radial wavefunctions of active electron in the initial (H^-) and final ($Si(nl\ ^{1,3}\Lambda_{\rm J})$) states respectively, and

$$D = [(2l+1)(2S+1)]^{\frac{1}{2}} \tag{4}$$

is a factor arising from the coupling of initial and final state electron angular and spin momenta.[14] As indicated in Table 1, the value of l in Eq.(4) is always $l = 1$, while $S = 0, 1$ for the singlet and triplet states respectively.

The values of asymptotic constants $A_{\rm i}$ for H^- and $A_{\rm c}$ for the ground state of $Si(3p^2)$ are 1.12 and 1.10 respectively.[16] For the excited Si(3pnp) states, for the constant $A_{\rm c}$ one can adopt its Coulomb value[14]

$$A_{\rm c} = \gamma(2\gamma)^{\frac{1}{\gamma}}\left[\Gamma\left(\frac{1}{\gamma}+l+1\right)\Gamma\left(\frac{1}{\gamma}-l\right)\right]^{-\frac{1}{2}}, \quad l=1, \tag{5}$$

where $\Gamma(x)$ is the gamma function. The values of coupling interaction at the considered ionic-covalent curve-crossing points are also given in Table 1. It is to be noted from this table that at the crossing points corresponding to the final Si(3p5p, $^1P_1$) and Si(3p5p, $^3D_1$) states the coupling interaction $H_{\rm ic}(R_x)$ is too weak to induce an electron transition between them. Therefore, these couplings can be omitted when considering the collision dynamics in this system.

The MCLZ model requires that the strong coupling regions of any two coupled states are well separated (in time, or along the inter-nuclear distance R) from the neighbouring strong coupling regions. Only in that case the multi-state coupling dynamics can be reduced to a finite number of two-state close-coupling problems that are mutually isolated. From Eq.(3) it follows that the extension δR_x of the transition zone associated with the curve-crossing point R_x is $\delta R_x \approx \dfrac{1}{\gamma}$. δR_x should be smaller than the distance $\Delta R_{x,x+1} = |R_x - R_{x+1}|$ between two consecutive crossings R_x and R_{x+1}. From the data in Table 1, one can see that this condition is not fulfilled for the

transition zones associated with the crossing points of $Si(3p^2\,{}^1D_2)$ and $Si(3p^2\,{}^1S_0)$ states and for $Si(3p4p\,{}^3P_0)$ and $Si(3p4p\,{}^3S_0)$ states. Since the transition regions of such a pair of $|\alpha\rangle$ and $|\beta\rangle$ states are strongly mixed, we can represent them by an equivalent quasi-degenerate state that has an effective coupling interaction $H_{\rm ic}^{(\alpha,\beta)}$ with the ionic state equal to (in analogy with Ref.[1])

$$H_{\rm ic}^{(\alpha,\beta)} = \sqrt{H_{\rm ic}^{(\alpha)^2} + H_{\rm ic}^{(\beta)^2}}, \tag{6}$$

and a curve crossing with the ionic state at $R_x^{(\alpha,\beta)} = \frac{1}{2}(R_{x\alpha} + R_{x\beta})$.

For a system of N covalent states interacting with the ionic state at mutually well separated curve-crossing regions, for which the crossing points $R_{x,k}$ are ordered as $R_{x,1} > R_{x,2} > \cdots > R_{x,N}$ (see Fig.1), the probability P_n for population of a given exit

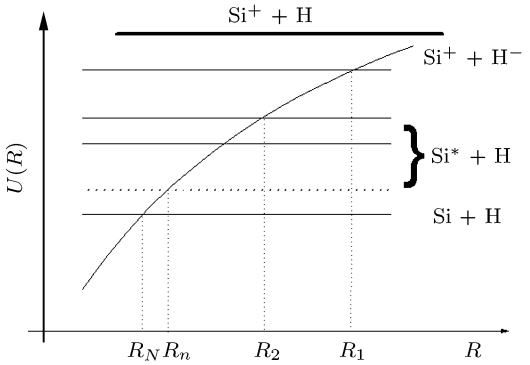


Fig.1. Schematic diagram of potential energies of ionic and covalent states involved in reaction (1).

covalent channel n within the quasi-classical approximation is[11,12]

$$\begin{aligned} P_n &= p_1 p_2 \cdots p_n(1-p_n)\Big\{1 + (p_{n+1}p_{n+2} \cdots p_N)^2 + (1-p_{n+1})^2 + [p_{n+1}(1-p_{n+2})]^2 \\ &\quad + [p_{n+1}p_{n+2}(1-p_{n+3})]^2 + \cdots + (p_{n+1}p_{n+2} \cdots p_{N-1})^2 (1-p_N)^2\Big\}, \quad n < N-1, \\ &= (p_1 p_2 \cdots p_{N-1})(1-p_{N-1})\left[1 + p_N^2 + (1-p_N)^2\right], \quad n = N-1, \\ &= 2p_1 p_2 \cdots p_{N-1}(1-p_N), \quad n = N, \end{aligned} \tag{7}$$

where p_k is the transition probability at the curve-crossing $R_{x,k}$. Equation (7) assumes that the electron transition takes place in a narrow region around $R_{x,k}$, and that the system evolves adiabatically between two consecutive transition regions. Moreover, the accumulated adiabatic energy phases along the potential energy curves of covalent states are assumed to be large and are averaged over in Eq.(7).

The transition probability p_k in the Landau–Zener two-state close-coupling model is given by[11,12]

$$p_k = \exp\left[-\frac{2\pi H_{\rm ic}^2(R)}{v_R|\Delta F(R)|}\right]_{R=R_{x,k}}, \tag{8}$$

where $\Delta F(R) = R^{-2}$ is the difference of the slopes of ionic and covalent potential energy curves (the latter assumed to be constant at the distances $R \sim R_{x,k}$), and v_R is the radial collision velocity, given by

$$v_R = v\left[1 + \frac{1}{R_x E} - \left(\frac{b}{R_x}\right)^2\right]^{\frac{1}{2}}, \tag{9}$$

where $E = \frac{1}{2}\mu v^2$, μ is reduced mass of colliding particles v is the collision velocity and b is the impact parameter. The cross section for the nth exit reaction channel is then

$$\sigma_n = 2\pi \int_0^{b_{x,n}} P_n(b) b \mathrm{d}b, \quad b_{x,n} = R_{x,n}\left[1 + \frac{1}{R_{x,n}E}\right]^{\frac{1}{2}}. \tag{10}$$

In the electron capture reaction (1), the electron transitions to the singlet and triplet final states are mutually decoupled and, therefore, the cross section calculations for these two systems of states can be performed separately. The total cross section for the mutual neutralization is obtained by summing all the channel cross sections.

3. Results of cross section calculations

By using Eqs.(7)–(10) and the data for $H_{\rm ic}(R_x)$ from Table 1, and keeping in mind the 'quasi-degeneracy' of reaction channels associated with the $Si[(3p^2)^1D_2,\ {}^1S_0]$ + H(1s) and $Si[(3p4p)^3P_0,\ {}^3S_1]$ + H(1s) covalent states, we have performed the channel cross section calculations σ_n for the singlet and triplet

systems of states in the energy range from 0.05 eV/u to 5 keV/u. The energy restriction from below is connected with the classical description of relative nuclear motion, while for energies above 5 keV/u the neglected electron momentum transfer effects in the Landau–Zener formula (8) may lead to significant overestimation of calculated cross sections. The neglected rotational couplings within the MCLZ model may also affect the electron capture cross sections at these relatively high energies.

The cross sections for population of $3p^2(^1D_2 + {}^1S_0)$, $(3p4p)^1P_1$, $^1D_2$, $^1S_0$ states of Si are presented in Fig.2.

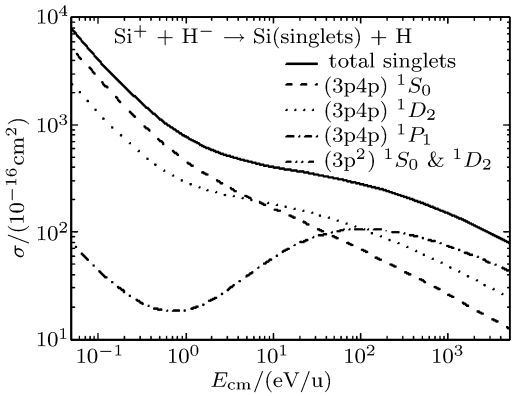


Fig.2. Cross section for population of singlet states in reaction (1).

From this figure it can be seen that for energies below ∼7 – 8 eV/u the population of $(3p4p,{}^1S_0)$ state of Si is dominant, while for energies above ∼150 eV/u dominantly populated state of Si is $(3p4p, {}^1P_1)$. The population of the ground state sub-levels $(3p^2\ {}^1D_2,{}^1S_0)$ is negligible in the considered energy range in comparison with the population of excited singlet states.

In Fig.3 we give the cross sections for population of triplet states of Si in reaction (1). The population of the quasi-degenerate $(3p4p, {}^3P_0, {}^3S_1)$ states dominates for collision energies below ∼100 eV/u, and only at energies above ∼500 eV/u the electron capture to $(3p4p^3D_1)$ state starts to compete. The electron capture to the ground $(3p^2\ {}^3P_0)$ state is negligible in the considered energy range compared with the capture to the excited triplet states.

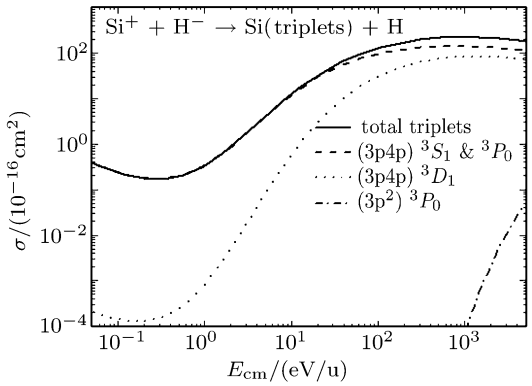


Fig.3. Cross section for population of triplet states in reaction (1).

The total cross section for reaction (1) is shown in Fig.4, together with the total cross sections for population of singlet and triplet systems of states. The total cross section shows a broad maximum at energies around 200–300 eV/u where the total singlet and triplet cross sections are comparable. Below ∼10–20 eV/u, however, the total cross section of reaction (1) is determined by electron capture to the singlet states only, and it monotonically increases with decreasing the energy in this energy region. This is a consequence of the strong ion–ion attractive interaction in the initial reaction channel.

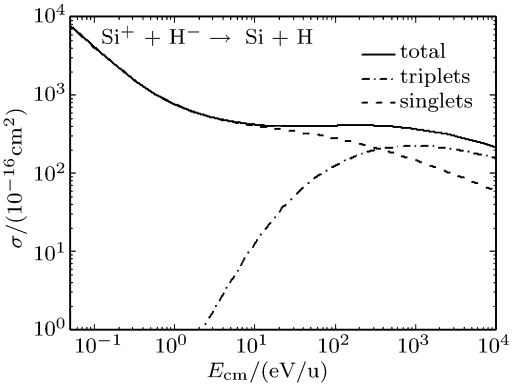


Fig.4. Total cross section for reaction (1).

4. Ion-pair formation in $Si(3p^2, {}^3P_J)$ + H(1s) collisions

The process of ion-pair formation

$$Si(3p^2,\ {}^3P_J) + H(1s,\ {}^2S_0) \rightarrow Si^+(3p,\ {}^2P_{1/2}) + H^-(1s^2,\ {}^2S_0) \qquad (11)$$

is inverse to the reaction channel in Eq.(1) producing a Si atom in its ground state. The energy level of this state has three fine-structure components corresponding to $J = 0, 1$ and 3. The $J = 1$ and $J = 2$ sub-levels lie above the $J = 0$ sub-level by 9.56×10^{-3} eV and 2.768×10^{-2} eV respectively,[15] and within a MCLZ treatment of dynamics of reaction (11) they can be considered as degenerate. Considering also the Si[(3p4p)$^3P_0$, $^3S_1$] + H(1s) as quasi-degenerate (as in the previous section), we can write the probability $P_{\rm ip}$ for the ion-pair formation process (11) as (in the notation of Fig.1)

$$P_{\rm ip} = 2p_3(1 - p_3)p_2p_1, \qquad (12)$$

where p_3, p_2 and p_1 are the Landau–Zener transition probabilities at the crossing points corresponding to the atomic states (3p^2, $^3P_{\rm J}$), (3p4p, $^3D_1$) and (3p4p, $^3P_0 + ^3S_1$).

In the calculation of the cross section of ion-pair formation process one should take into account that in the initial channel the interaction of colliding particles at large distances R is very weak (van der Waals interaction). This is in contrast to the strong Coulomb attraction of colliding particles in the ion–ion recombination reaction (1). Therefore, the use of the straight-line trajectory approximation for description of nuclear motion in reaction (11) is appropriate, which leads to the replacement of $b_{x,n}$ in Eq.(10) by $R_{x,n}(= R_{x,3})$.

The calculated ion-pair formation cross section for the reaction (11) is shown in Fig.5 in the energy range 1 keV/u–30 keV/u. In comparison with the ion–ion recombination cross sections, the ion-pair formation cross section is very small and reaches values of the order of 10^{-16} cm^2 only at ∼20–30 keV/u energies where the application of LZ-model is not quite well justified. The small value of this cross section in the entire energy region below ∼20 keV/u is due to the small value of $R_{x,3}$ and the large value of energy splitting $\Delta E = 2H_{\rm ic}$ of ionic and covalent states at the curve-crossing $R_{x,3}$. Significant part of the ion-pair flux evolving along the ionic potential energy curve during the receding stage of the collision is lost at the strong coupling regions around $R_{x,2}$ and $R_{x,1}$ on the expense of population of (3p4p,$^3D_1$), (3p4p,$^3S_1$) and (3p4p,$^3P_0$) excited states of Si.

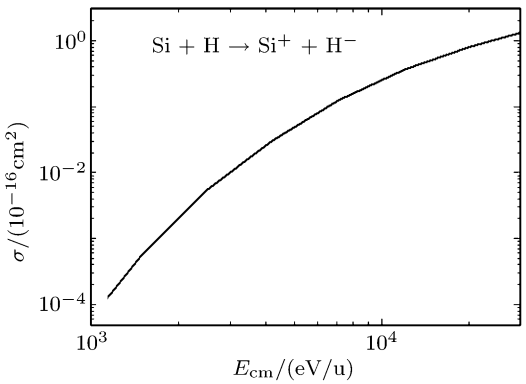


Fig.5. Total cross section for reaction (11).

5. Concluding remarks

In the present article we have studied the mutual neutralization of Si^+ and H^- ions within the MCLZ model of collision dynamics for the process. The cross section for population of specific states of Si atom with even symmetry was calculated in the energy range 0.05 eV/u–5 keV/u, where the applied MCLZ model is expected to be applicable, at least from the point of view of its energetic constraints (classical nuclear motion and neglect of electron translational factors). The neglect of rotational couplings within the MCLZ model should not affect significantly the calculated cross sections in the considered energy range.

The effects of the interference of adiabatic energy phases, accumulated during the evolution of the system along the covalent potential energy curves in the $R < R_{x,k}$ region, cannot be *a priori* estimated. In general, for the covalent states with large $R_{x,k}$, the adiabatic energy phases should be large enough to allow an efficient averaging (and, consequently, negligible phase interference effects). The agreement of the cross section results for the $H^+ + H^-$ system, performed within the MCLZ model[1] and by the molecular orbital close-coupling method (with quantum-mechanical description of nuclear motion)[17] in the energy region below 20 eV/u fully supports the above assertion. Except for the ionic-covalent curve-crossings corresponding to the ground-state sublevels of Si, the values of all other curve-crossing points are in the same range of internuclear distances as the ionic-covalent curve crossings in the H^+–H^- system. This circumstance may be taken as an indication that the phase interference effects should not play a significant role in the Si^+–H^- collision system as well, at least for the channels that give the main contribution to the total cross section.

The calculated ion-pair formation cross section in slow Si + H collision is very small in the energy region below $\sim$1 keV/u (below 10^{-20} cm^2) and exponentially decreases with decreasing the energy.

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