Charge transfer recombination of Si^{2+} ions from atomic hydrogen

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Abstract

Ab-initio potential energy curves and coupling matrix elements of the molecular states involved in the collision of the Si^{2+} multicharged ion on atomic hydrogen have been determined by means of configuration interaction methods. The total and partial electron capture cross sections have been determined using a semi-classical approach in the 0.1–1000 eV center-of-mass energy range. The results are in fair agreement with previous works and show the influence of radial, rotational as well as translational effects. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Low energy electron capture by multiply charged ions with atomic hydrogen and helium has been shown to be an important process in controlled thermonuclear fusion research [1,2] as well as in astrophysics [3,4] where such reactions have been recognized to be possible ionization sources [5]. The charge transfer recombination process with atomic hydrogen is indeed particularly significant in astrophysical plasmas for many doubly or triply charged ions whose emission lines are used to provide direct information on the ionization structure of astronomical objects. The intensity line ratios of Si^{2+} ions are used, for example, to deduce electron temperature and density in emissive regions [6]. Besides, the charge exchange recombination of Si^{2+} ions with atomic hydrogen

$$Si^{2+}(3s^2)\,^1S + H(1s)\,^2S \rightarrow Si^+(3s^2\,3p)\,^2P + H^+$$
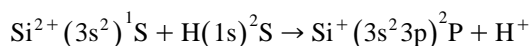
may lead directly to the formation of a ground state

and may thus induce a rapid ionization of Si^+ ions via the inverse charge transfer process. This ionization process has been shown to be essential in the determination of the abundance of Si^{2+} ions in coronal plasmas [5]. We have thus performed a complete ab-initio study of this reaction which may influence substantially the ionization balance of silicon ions. The process has been the subject of earlier investigations [7–9], in particular by means of the molecular approach using model potentials and couplings [8] and appears to be a good benchmark for ab-initio methods as it presents a relatively peaked, long range pseudo-crossing.

Our treatment involves an ab-initio molecular calculation of the potential energy curves and couplings followed by a collision dynamics taking account of translation effects. This approach has been shown to provide a quantitative interpretation of charge transfer processes [10–12], the use of ab-initio potentials allowing, in particular, to consider open-shell systems involving several outer electrons as low-charged

[10], or metastable multicharged ions [12]. Three states have to be taken into account in the calculation, the $^2\Sigma$ state correlated to the entry channel $\{Si^{2+}(3s^2)^1S + H(1s)^2S\}$, and the $^2\Sigma$ and $^2\Pi$ states correlated to the one-electron capture channel $\{Si^+(3s^23p)^2P + H^+\}$.

2. Molecular calculations

The potential energy curves have been determined in the 2–30 au internuclear distance range by means of MCSCF + CI calculations with configuration interaction based on the CIPSI algorithm [13]. A nonlocal pseudopotential [14] has been used to represent the core electrons of the silicon atom. The calculations have been performed with CI spaces lower than 400 determinants for the zeroth-order diagonalization with a threshold $\eta = 0.001$ for the perturbation con-

tribution providing a good description of the wavefunctions.

The basis of atomic functions used to represent silicon ions is an optimized 9s7p2d basis of Gaussian functions contracted to 5s4p2d, constructed from the basis sets of McLean and Chandler [15] and previously tested on the Si^{3+} + He collision system [16]. For hydrogen, we took the 5s3p basis optimized from Huzinaga [17] already used in the study of multicharged ion–hydrogen collisions [12].

The potential energy curves of the $^2\Sigma$ and $^2\Pi$ states correlated to the entry channel $\{Si^{2+}(3s^2)^1S + H(1s)^2S\}$ are displayed in Fig. 1. In accordance with previous works [8,9,18], they show a sharp avoided crossing at $R = 10.5$ au between the $^2\Sigma$ $\{Si^{2+}(3s^2) + H(1s)\}$ and $\{Si^+(3s^23p) + H^+\}$ states. A deep potential well for the $X^2\Sigma^+$ ground state of the SiH^{2+} diatomic may be observed with a barrier of 1.04 eV, in quite good agreement with the MRD-CI and CASSCF calculations of Koch et al. [18] (respectively 1.06 and 1.07 eV). More generally, our calcu-
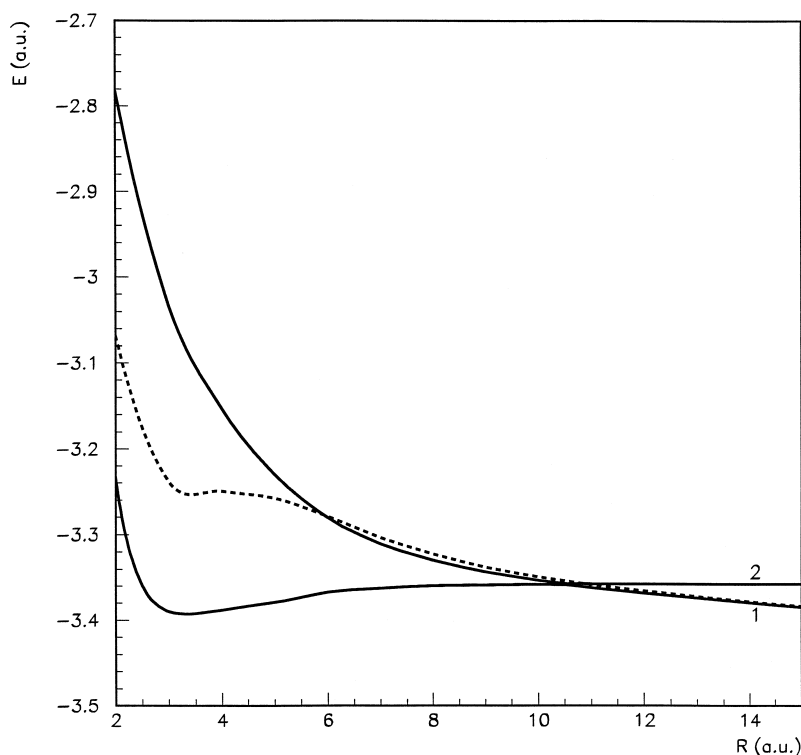

Fig. 1. Adiabatic potential energy curves for the $^2\Sigma$ and $^2\Pi$ states of SiH^{2+}. — $^2\Sigma$, - - - $^2\Pi$. 1: Σ, Π states dissociating to $\{Si^+(3s^23p)^2P + H^+\}$. 2: Σ state dissociating to $\{Si^{2+}(3s^2)^1S + H(1s)\}$.

Table 1
Spectroscopic constants (cm^{-1}) for the ground X$^2\Sigma^+$ state of SiH^{2+}

Calculation	R_e (au)	ω_e	$\omega_e \chi_e$	B_e	α_e	D_e (eV)	Barrier (eV)
This work	3.29	1037.0	9.2	5.711	0.558	−1.55	1.04
Hv [20]	3.20	1142.7	9.6	6.08	0.486	−1.47	1.12
MP4 [19]	3.10	1121				−1.54	0.89
CASSCF [18]	3.30	958.0	10.3	5.685		−1.41	1.06
MRD-CI [18]	3.30	965.2	8.7	5.685		−1.43	1.07
MOLPRO [22]	3.29	965					1.19

lated spectroscopic quantities presented in Table 1, compare positively with the most recent values obtained for SiH^{2+} [18–22].

The radial coupling matrix elements between all pairs of states of the same symmetry have been calculated by means of the finite difference technique :

$$g_{KL}(R) = \langle \Psi_K | \partial/\partial R | \Psi_L \rangle$$
$$= \lim_{\Delta \to 0} 1/\Delta \langle \Psi_K(R) | \Psi_L(R + \Delta) \rangle,$$

with the parameter $\Delta = 0.0012$ au as previously tested and using the silicon nucleus as origin of electronic coordinates. The radial coupling matrix element displayed in Fig. 2 presents the same features as exhibited by the potential energy curves with a sharp peak, 2.47 au high, corresponding to the crossing at $R = 10.5$ au. Our calculation has been performed for a very large number of interatomic distances in the avoided crossing region leading to a better description of the maximum of the radial coupling than in previous work [8]. A good agreement is observed with SCVB calculations [9].

The rotational coupling matrix elements $\langle \Psi_K | iL_y | \Psi_L \rangle$ between $^2\Sigma^+$–$^2\Pi$ and $^2\Pi$–$^2\Delta$ molecu-
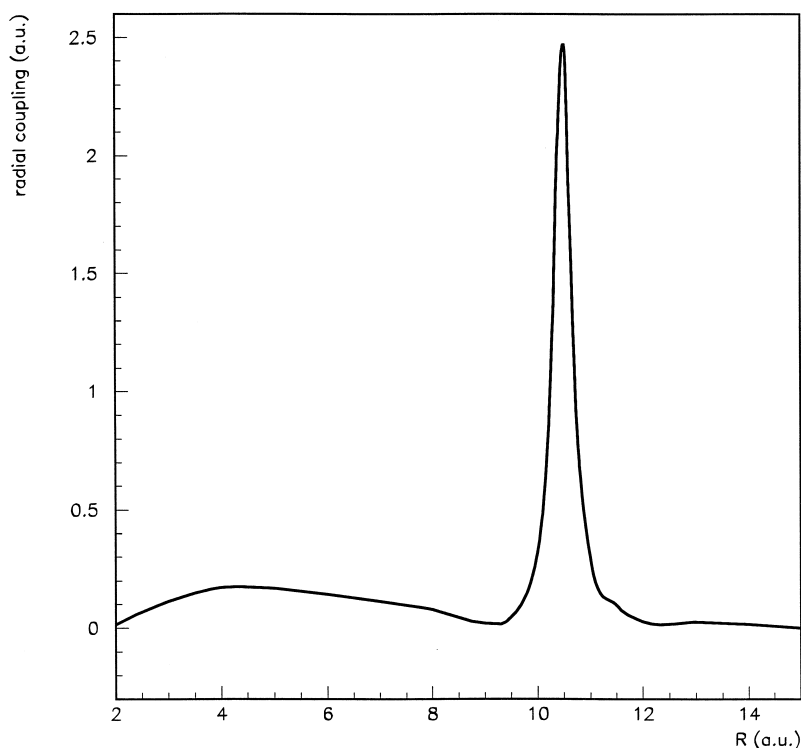

Fig. 2. Non-adiabatic radial coupling matrix element between $^2\Sigma$ states.
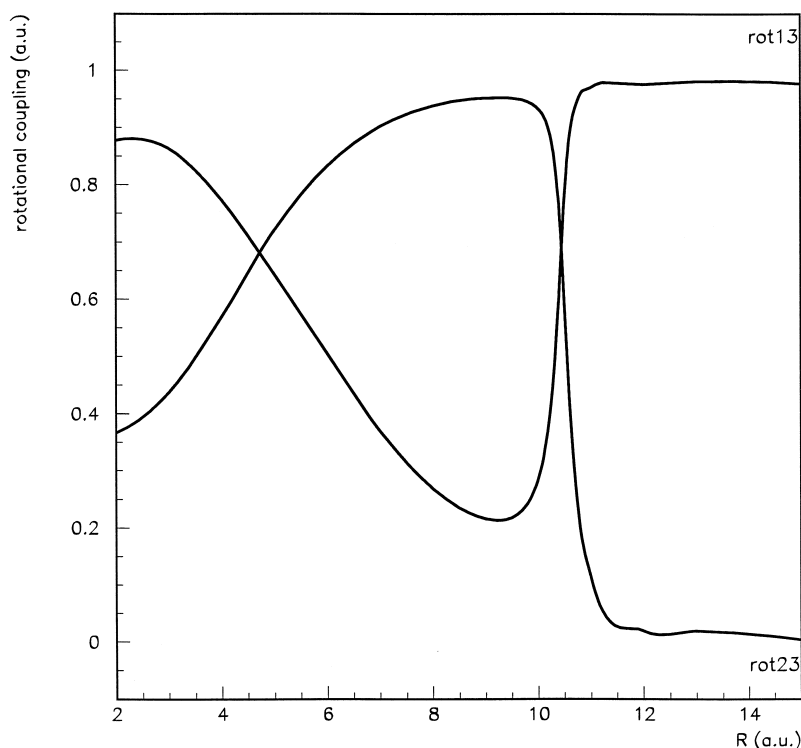
Fig. 3. Rotational coupling matrix elements between $^2\Sigma$ and $^2\Pi$ states. 1: Σ state dissociating to $\{Si^+(3s^23p)^2P + H^+\}$. 2: Σ state dissociating to $\{Si^{2+}(3s^2)^1S + H(1s)\}$. 3: Π state dissociating to $\{Si^+(3s^23p)^2P + H^+\}$.

lar states have been determined directly from the quadrupole moment tensor [23]. The coupling matrix elements are presented in Fig. 3 and show clearly the changes of the wavefunctions in the neighbourhood of the avoided crossing.

3. Collision dynamics

The capture cross sections have been calculated by a semi-classical method using the EIKONXS program [24] in the 0.1–1000 eV center-of-mass energy range. The translation effects have been taken into account by introducing common translation factors as proposed by Errea et al. [25]. As expected, the translation effects are quite negligible at low collision energies, until about $E_{CM} = 40$ eV (Fig. 4). They appear to be more important, and from lower collision energies, for the capture on the $^2\Sigma$ $\{Si^+ + H^+\}$ level populated by means of radial coupling

than for the corresponding $^2\Pi$ state correlated by rotational coupling. All the calculated values of the cross sections, including translation effects, are reported in Table 2. They show a quite important rotational effect, the cross sections being as important on the Π level as on the Σ level for energies up to 40 eV.

Our treatment may be compared to the previous work of Gargaud et al. [8] using a quantum collision dynamics within a model potential molecular approach (Fig. 5). Both calculations are in excellent agreement for collision center-of-mass energies up to about 20 eV. For lower energies, the use of a semi-classical collision method in our calculation leads to somewhat underestimated values for the capture cross sections as trajectory effects have to be taken into account, in particular for the capture on the $^2\Sigma$ level. On the contrary, for higher energies from about 20 eV to keV center-of-mass energies, a semi-classical collision dynamics is quite accurate
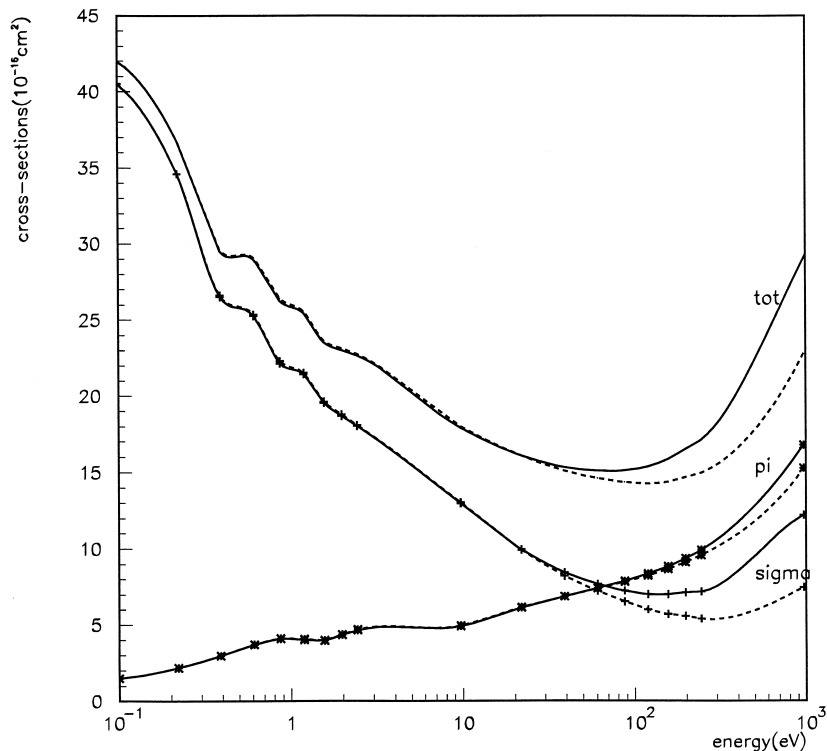
Fig. 4. Total and partial cross-sections on the $\{Si^+(3s^2 3p) + H^+\}$ levels with respect to center-of-mass energies. — with translation effect, - - - without translation effect. $+$ capture to the $^2\Sigma$ state, $*$ capture to the $^2\Pi$ state.

Table 2
Partial and total cross sections for the $Si^{2+} + H \rightarrow Si^+ + H^+$ process (in 10^{-16} cm^2)

E_{CM} (eV)	σ_Σ	σ_Π	σ_{tot}
0.1	40.482	1.488	41.970
0.22	34.584	2.173	36.757
0.39	26.510	2.965	29.475
0.61	25.258	3.693	28.951
0.87	22.149	4.074	26.223
1.19	21.426	4.009	25.435
1.56	19.545	3.960	23.505
1.97	18.676	4.338	23.014
2.43	18.014	4.640	22.654
9.72	12.990	4.912	17.902
21.87	9.952	6.120	16.072
38.89	8.440	6.862	15.302
60.76	7.670	7.407	15.077
87.50	7.231	7.877	15.108
119.10	7.017	8.343	15.360
155.55	7.009	8.840	15.849
196.87	7.132	9.359	16.491
243.05	7.200	9.916	17.116
972.21	12.207	16.753	28.960
2187.5	13.771	23.175	36.946

and allows us to extend the results of Gargaud et al. [8], our approach taking into account translation effects.

4. Concluding remarks

This work provides a complete ab-initio treatment of the $Si^{2+} + H$ charge transfer recombination process. Both radial and rotational couplings have been shown to be necessary in a fair description of the process, as well as translation effects for higher collision energies.

In the whole energy range of interest, spin orbit and other relativistic effects have been considered as negligible, allowing a treatment involving only spin doublet Σ and Π states. This assumption, generally accepted in ion-atom collisions, seems reasonable for the $Si^{2+} + H$ process as fine structure splitting of $Si^+(^2P)$ (0.036 eV) is relatively small with regard to the interaction energies in the vicinity of the avoided crossing. The consideration of spin orbit interaction
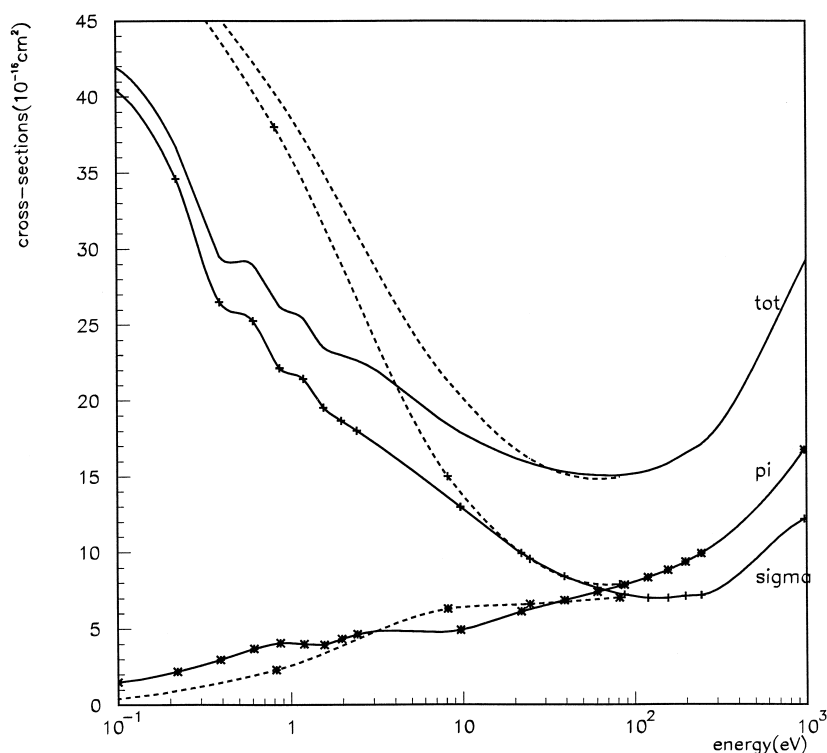
Fig. 5. Comparison of total and partial cross-sections on the $\{Si^+(3s^23p) + H^+\}$ levels with other theoretical work. — this work, - - - Gargaud et al. [8]. + capture to the $^2\Sigma$ state, * capture to the $^2\Pi$ state.

should not affect markedly the radial coupling mechanism, however, the lift of degeneracy for $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ levels should intervene through rotational coupling. A complete treatment of spin orbit effects is now in progress

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