CHARGE TRANSFER RATE IN COLLISIONS OF H⁺ IONS WITH Si ATOMS

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ABSTRACT

Charge transfer in Si(^3P, ^1D) + H⁺ collisions is studied theoretically by using a semiclassical molecular representation with six molecular channels for the triplet manifold and four channels for the singlet manifold at collision energies above 30 eV, and by using a fully quantum mechanical approach with two molecular channels for both triplet and singlet manifolds below 30 eV. The ab initio potential curves and nonadiabatic coupling matrix elements for the HSi⁺ system are obtained from multireference single- and double-excitation configuration interaction (MRD-CI) calculations employing a relatively large basis set. The present rate coefficients for charge transfer to Si⁺(^4P) formation resulting from H⁺ + Si(^3P) collisions are found to be large with values from 1×10^{-10} cm³ s⁻¹ at 1000 K to 1×10^{-8} cm³ s⁻¹ at 100,000 K. The rate coefficient for Si⁺(^2P) formation, resulting from H⁺ + Si(^3P) collisions, is found to be much smaller because of a larger energy defect from the initial state. These calculated rates are much larger than those reported by Baliunas & Butler, who estimated a value of 10^{-11} cm³ s⁻¹ in their coronal plasma study. The present result may be relevant to the description of the silicon ionization equilibrium.
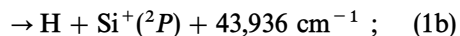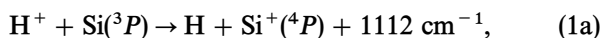
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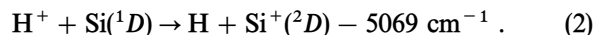
1. INTRODUCTION

Observation of the spectral lines of silicon has been used widely as a diagnostic of the physical conditions in astrophysical plasmas (Baliunas & Butler 1980), but all applications depend heavily on standard ionization equilibrium calculations for plasma parameters. Specifically, Baliunas & Butler examined the effect of charge transfer in conjunction with silicon spectral lines and estimated the value of the rate coefficient as 10^{-11} cm³ s⁻¹ for the charge transfer process in collisions of H⁺ ions with Si(^3P) ground-state atoms (Baliunas & Butler 1980) suggesting a possible importance of the process for the ionization of silicon atoms. Apart from this estimation, to the best of our knowledge, there is no theoretical or experimental determination of the charge transfer cross section for the system.

We have carried out a theoretical investigation for charge transfer in collisions of H⁺ ions with neutral Si atoms both in the ground and metastable states at collision energies from 10^{-3} eV to 10 keV, using molecular states for the SiH⁺ obtained earlier (Sannigrahi et al. 1995). The theoretical studies are based on a molecular orbital (MO) expansion method within a semiclassical or fully quantal formalism. The processes we have studied are as follows, with corresponding asymptotic energy defects:

1. Ground-state atoms:

$$H^+ + Si(^3P) \rightarrow H + Si^+(^4P) + 1112 \text{ cm}^{-1}, \quad (1a)$$

$$\rightarrow H + Si^+(^2P) + 43,936 \text{ cm}^{-1} ; \quad (1b)$$

2. Metastable atoms:

$$H^+ + Si(^1D) \rightarrow H + Si^+(^2D) - 5069 \text{ cm}^{-1} . \quad (2)$$

The metastable ^1D state in equation (2), which lies at 50,235 cm⁻¹ higher in energy than the [Si⁺(^2P) + H] state, is considered to compete in collision dynamics, at higher collision energies, with the ground state when the metastable ion is present in the environment. Hence, it is important to understand the charge transfer mechanisms of both the ground and metastable states and to determine each cross section accurately. Particularly, experimental beams produced by an electron-impact ionization and dissociation technique, for research relevant to fusion research, are often a mixture of unknown amount of ground and metastable states and hence, knowledge of their collision dynamics may be helpful for rigorous experimental analysis.

The present theoretical approach is basically the same as that used in earlier studies (Kimura et al. 1994a, 1994b, 1995), being based on the MO expansion method within a semiclassical formalism for collision energies above 30 eV and a fully quantal formalism below 30 eV.

2. THEORETICAL MODEL

The present SiH⁺ calculations are an extension of the earlier work on the SiH⁺ system reported (Sannigrahi et al. 1995) for determination of molecular electronic states. For collision dynamics, both semiclassical and quantal close-coupling methods have been used extensively by this groups (Kimura et al. 1994a, 1994b, 1995) and others (Butler, Heil, & Dalgarno), and hence, only a short summary of electronic-state and collision dynamics calculations is given here (Kimura & Lane 1989).

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2.1. *Molecular States and Couplings*

The adiabatic potential curves of SiH$^+$ are obtained by employing the ab initio multireference single- and double-excitation configuration interaction (MRD-CI) method (Buenker & Peyerimhoff 1974, 1975; Buenker 1986), with configuration selection at a threshold of $5.0 \times 10^{-6}E_h$ (where $E_h = 27.211$ eV) and energy extrapolation, using the Table CI algorithm (Buenker 1980, 1981; Buenker & Phillips 1985). The basis set used in the present study consists of $(16s10p5d3f)/[12s7p4d2f]$ and $(12s6p4d)/[8s4p2d]$ contracted Gaussian functions centered on the Si and H atoms, respectively. This basis set is the larger of the two employed by Matos et al. (1988) in their study of SiH$^+$. The nonadiabatic coupling matrix elements are calculated by using a finite-difference method (Hirsch et al. 1980). Further details of our ab initio MRD-CI calculations are presented in our previous paper on the spectrum of SiH$^+$ (Sannigrahi et al. 1995). Note that there are two different tabulated experimental energy values for the energy difference between quartet-P and doublet-P states of the Si$^+$ ion. One is the 44,080 cm^{-1} of Moore (1971), and the other is the 42,824 cm^{-1} of Bashkin & Stoner (1975). As a consequence, asymptotically, the channel [H + Si$^+$(^4P)] should be located 144 cm^{-1} higher above the channel [H$^+$ + Si(^3P)] according to Moore's table. On the other hand, channel [H + Si$^+$(^4P)] is 1112 cm^{-1} lower in energy than channel [H$^+$ + Si(^3P)] according to Bashkin & Stoner's value. Since Moore's value of the energy difference between the Si$^+$(^4P) and the Si$^+$(^2P) states was obtained indirectly, the value of Bashkin and Stoner is considered to be more reliable. Our calculated ordering of the states supports that of Bashkin & Stoner. Figure 1 displays the adiabatic potential curves for the ground and metastable initial [H$^+$ + Si] states and the charge transfer channels that lie close to the initial channels. From the bottom, they correspond asymptotically to atomic states [H + Si$^+$(^2P)], [H + Si$^+$(^4P)], and [H$^+$ + Si(^3P)] for the triplet manifold and [H$^+$ + Si(^1D)] and [H + Si$^+$(^2D)] for the singlet manifold. It should be noted that the $3^1\Sigma^+$ and $2^1\Sigma^+$ states have a sharp avoided crossing near internuclear separation $R = 5$ a.u. suggesting the Landau-Zener–type mechanism with a strong nonadiabatic coupling near this R region and therefore, a possible strong transition within the singlet manifold. On the other hand, for the triplet, there is no such strong avoided
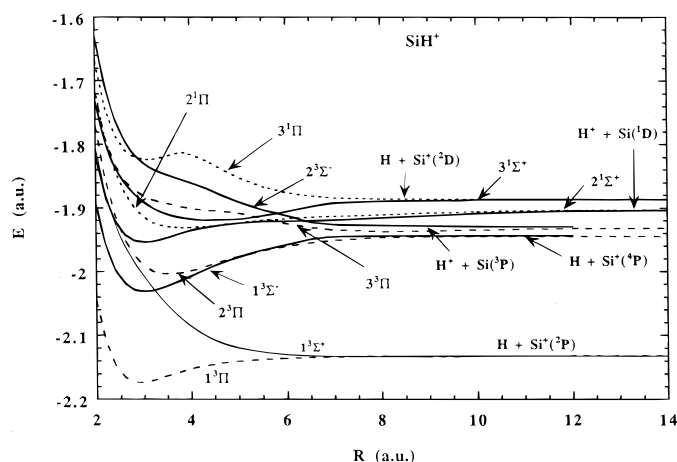

Fig. 1.—Adiabatic potentials of the SiH$^+$ system. All energies are given with respect to -287.0 a.u.

crossing, and the so-called Demkov-type mechanism dominates in the transition.

The corresponding nonadiabatic radial coupling matrix element for $2^1\Sigma^+$ and $3^1\Sigma^+$ has a large peak with the peak value of approximately 1.7 a.u. at $R = 5.3$ a.u., while that for $2^3\Pi$ and $3^3\Pi$ has a weak and broad peak with the value of 0.3 a.u. at $R = 7.5$ a.u., as shown in Figures 2a and 2b for the singlet and triplet manifolds, respectively. These features of the coupling are a manifestation of the Landau-Zener and Demkov type coupling schemes described above.

2.2. *Collision Dynamics*

1. *Semiclassical approach.*—A semiclassical MO expansion method with a straight-line trajectory of the incident was employed to study the collision dynamics above 30 eV ion (Kimura & Lane 1989). In this approach, the relative motion of heavy particles is treated classically, while electronic motions are treated quantum mechanically. The total scattering wave function was expanded in terms of products of a molecular electronic state and atomic-type electron translation factors (ETFs), in which the inclusion of the ETF satisfies the correct scattering boundary condition. Substituting the total wave function into the time-
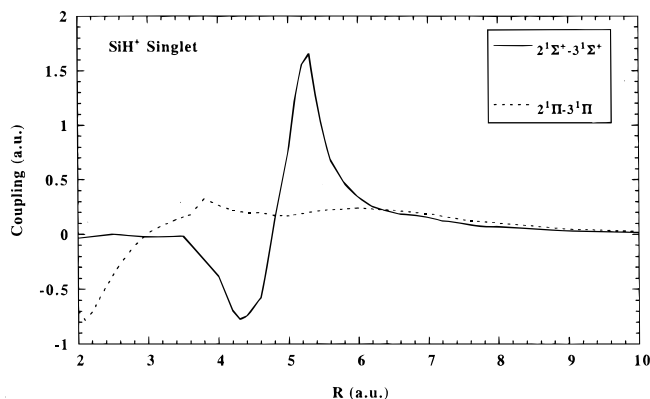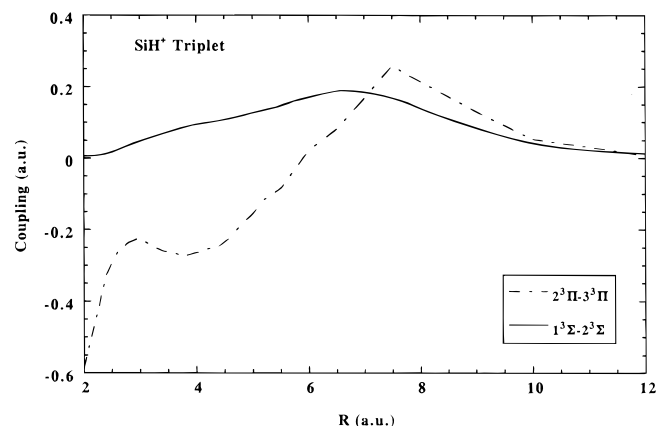

Fig. 2a

Fig. 2b

Fig. 2.—Representative radial coupling matrix elements for (a) the singlet and (b) the triplet
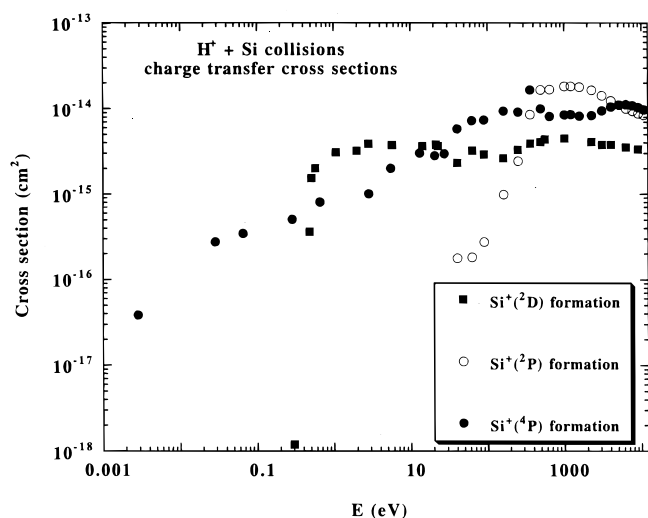
FIG. 3.—Charge transfer cross sections below 10 keV. *Filled circles:* Si$^+$(^4P) formation; *open circles:* Si$^+$(^2P) formation; *filled squares:* Si$^+$(^2D) formation.

dependent Schrödinger equation and retaining the ETF correction up to the first order in the relative velocity between the collision partners, we obtain a set of first-order equations in time t. Transitions between the molecular states are driven by nonadiabatic couplings. By solving the coupled equations numerically, we obtain the scattering amplitudes for transitions: the square of the amplitude gives the transition probability, and integration of the probability over the impact parameter gives the cross section. The molecular states included in the dynamical calculations are the two sets of states, shown in Figure 1, separating to [H$^+$ + Si(^3P)]($2^3\Sigma^-$, $3^3\Pi$), [H + Si$^+$(^4P)] ($1^3\Sigma^-$, $2^3\Pi$), [H + Si$^+$(^2P)]($1^3\Sigma^+$, $1^3\Pi$) for charge transfer from the initial ground state, and [H$^+$ + Si(^1D)]($2^1\Sigma^+$, $2^1\Pi$), [H + Si$^+$(^2D)]($3^1\Sigma^+$, $3^1\Pi$) for charge transfer from the initial metastable state.

2. *Quantum approach.*—A fully quantum mechanical representation of the MO expansion method was employed for

TABLE 1

RATE COEFFICIENTS FOR ELECTRON CAPTURE[a]

TEMPERATURE (K)	PROCESSES	
	H$^+$ + Si(^3P) → H + Si$^+$(^4P)	H$^+$ + Si(^1D) → H + Si$^+$(^2D)
200	5.26×10^{-11}	$< 10^{-20}$
400	9.28×10^{-11}	6.21×10^{-15}
600	1.26×10^{-10}	4.69×10^{-13}
800	1.57×10^{-10}	4.21×10^{-12}
1,000	1.90×10^{-10}	2.20×10^{-11}
2,000	3.61×10^{-10}	2.63×10^{-10}
4,000	6.90×10^{-10}	1.40×10^{-9}
6,000	9.67×10^{-10}	2.41×10^{-9}
8,000	1.21×10^{-9}	3.46×10^{-9}
10,000	1.45×10^{-9}	4.14×10^{-9}
20,000	2.87×10^{-9}	7.07×10^{-9}
40,000	6.03×10^{-9}	1.04×10^{-8}
60,000	8.75×10^{-9}	1.22×10^{-8}
80,000	1.13×10^{-8}	1.44×10^{-8}
100,000	1.40×10^{-8}	1.57×10^{-8}
200,000	2.93×10^{-8}	2.73×10^{-8}

[a] In units of cm^3 s^{-1}.

collision energies below 30 eV. In this energy region, transitions are also driven by nonadiabatic coupling. The total scattering wave function is expanded as a sum of products of molecular electronic wave functions and nuclear wave functions. The coupled equations in R that the nuclear wave functions satisfy are obtained from the time-independent Schrödinger equation (Kimura & Lane 1989). The coupled equations are solved numerically, after partial wave decomposition, to obtain the scattering matrix. The molecular states included are two sets of channels: (1) [Si$^+$(^4P) + H]($2^3\Pi$) and [Si(^3P) + H$^+$]($3^3\Pi$) and (2) [Si$^+$(^2D) + H]($3^1\Pi$) and [Si(^1D) + H$^+$]($2^1\Pi$).

3. RESULTS

3.1. *Charge Transfer from the Ground-State* Si(^3P) *Atoms*

The calculated charge transfer cross sections are illustrated in Figure 3. The cross section for Si$^+$(^4P) formation is large, with a magnitude of 4×10^{-17} cm^2 at 0.0025 eV, and it increases to nearly 10^{-14} cm^2 around 30 eV, with its energy dependence being weak, while that for Si$^+$(^2P) formation is similar in magnitude to the Si$^+$(^4P) cross section above 300 eV but drops rather sharply below this energy due to a larger energy defect for the charge transfer in equation (1b) than that for equation (1a). Oscillatory structures seen in the cross sections are due to multichannel interferences.

3.2. *Charge Transfer from the Metastable* Si(^1D) *Atoms*

The charge transfer cross section from the metastable Si(^1D) atoms by H$^+$ impact is also included in Figure 3. Due to a combination of a small energy defect and effectiveness of the coupling between the initial and charge transfer channels, the cross section is found to be as large as a magnitude of 10^{-15} cm^2, except in the near-threshold region, despite the endothermic reaction (see eq. [2]).

3.3. *Rate Coefficients*

The rate coefficients for charge transfer from the ground-state Si(^3P) and metastable Si(^1D) atoms are listed in Table 1. The values for the ground-state atoms increase from 10^{-10} cm^3 s^{-1} at 1000 K to 10^{-8} cm^3 s^{-1} at 80,000 K, while those for the metastable atoms vary from 10^{-11} cm^3 s^{-1} to 10^{-8} cm^3 s^{-1}. The large charge transfer rate from the metastable state, which is even larger than that from the ground state except at low temperatures, may become important for applications at higher temperatures.

4. CONCLUSION

We have studied charge transfer in collisions of Si(^3P) with H$^+$ below 10 keV and found that the cross sections for Si$^+$(^4P, ^2P) formations are as large as $\sim 10^{-14}$ cm^2 above 300 eV. We also investigated charge transfer from metastable Si(^1D) atoms by H$^+$ ion impact in the same energy range and found that, although the magnitude of the cross section is comparable to that for the ground-state atom above 1 eV and is nearly flat in a wide range of energy, it decreases rapidly in the threshold region and becomes less than 10^{-18} cm^2 below 0.1 eV. Our rate coefficient for charge transfer from the ground-state atom is larger than 10^{-9} cm^3 s^{-1} above 6000 K, much larger than that estimated earlier as 10^{-11} cm^2 by Baliunas & Butler (1980). The rate coefficient for charge transfer from the metastable Si(^1D) atom is also

larger than 10^{-9} cm^3 s^{-1} above 4000 K, although its value drops rather sharply below this temperature.

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