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CHARGE TRANSFER BETWEEN GROUND-STATE Si^{3+} AND He AT ELECTRON-VOLT ENERGIES

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ABSTRACT

The charge-transfer rate coefficient for the reaction $Si^{3+}(3s\,^2S) + He \rightarrow$ products is measured by means of a combined technique of laser ablation and ion storage. A cylindrical radio-frequency ion trap was used to store Si^{3+} ions produced by laser ablation of solid silicon targets. The rate coefficient of the reaction was derived from the decay rate of the ion signal. The measured rate coefficient is $6.27^{+0.68}_{-0.52} \times 10^{-10}$ cm^3 s^{-1} at $T_{equiv} = 3.9 \times 10^3$ K. This value is about 30% higher than the Landau-Zener calculation of Butler & Dalgarno and is larger by about a factor of 3 than the recent full quantal calculation of Honvault et al.

Subject headings: atomic data — atomic processes

1. INTRODUCTION

Silicon is commonly found in a variety of astrophysical plasmas. The spectral lines of silicon ions have been observed in interstellar medium (Morton et al. 1973; Cohn & York 1977; McCray, Wright, & Hatchett 1977), circumstellar material (Steigman, Strittmatter, & Williams 1975), quasars, Seyfert galaxies (Boksenberg et al. 1978), the solar lower transition region (Dupree 1972; Dupree et al. 1973), and late-type stellar atmospheres (Doschek et al. 1978). These lines have been widely used as a diagnostic tool for the physical conditions in these low-temperature astrophysical plasmas. For example, the intensity ratios of C III 190.9 nm lines and Si III 189.2 nm lines have been used to determine the electron density of solar and stellar plasmas (Doschek et al. 1978). The emission- and absorption-line intensities, however, can be drastically affected by the shifting of the ionization equilibrium through charge-transfer collisions. Contribution by charge transfer of silicon ions and neutral hydrogen and helium has to be thoroughly investigated for the correct interpretation of these line emissions (Shull 1996).

Several important charge-transfer recombination reactions by multiply charged silicon ions have been suggested, and their effects on the ionization equilibrium have been discussed (Baliunas & Butler 1980; Butler & Dalgarno 1980; Dalgarno & Butler 1978; Bliman 1993):

$$Si^{3+}(3s\,^2S) + He \rightarrow Si^{2+}(3s^2\,^1S) + He^+ + 8.88\ eV\,, \quad (1a)$$

$$Si^{2+}(3s3p\,^3P) + He^+ + 2.3\ eV\,, \quad (1b)$$

$$Si^{4+}(2p^6\,^1S) + He \rightarrow Si^{3+}(2p^63s\,^2S) + He^+ + 20.55\ eV\,, \quad (2a)$$

$$Si^{3+}(2p^63p\,^2P^o) + He^+ + 11.7\ eV\,, \quad (2b)$$

$$Si^{2+}(3s^2\,^1S) + H \rightarrow Si^{+}(3s^23p\,^2P^o) + H^+ + 2.74\ eV\,, \quad (3)$$

$$Si^{3+}(3s\,^2S) + H \rightarrow Si^{2+}(3s3p\,^1P^o) + H^+ + 9.62\ eV\,, \quad (4a)$$

$$Si^{2+}(3p^2\,^1D) + H^+ + 4.74\ eV\,, \quad (4b)$$

$$Si^{2+}(3p^2\,^3P) + H^+ + 3.8\ eV\,, \quad (4c)$$

$$Si^{2+}(3s3d\,^3D) + H^+ + 2.17\ eV\,, \quad (4d)$$

$$Si^{4+}(2p^6\,^1S) + H \rightarrow Si^{3+}(2p^63d\,^2D) + H^+ + 11.7\ eV\,, \quad (5a)$$

$$Si^{3+}(2p^64s\,^2S) + H^+ + 7.5\ eV\,. \quad (5b)$$

Each one of these reactions is capable of suppressing the abundance of highly charged states of silicon ions if the rate coefficient is large. This will result in an underestimation of the plasma temperature. On the other hand, for a system in which charge-transfer recombination populates the ground state of the product ions, such as the processes given by equations (1a), (2a), and (3), it is necessary to take into account the reverse process, charge-transfer ionization, at energies above the threshold of a few electron volts. The rate coefficient of charge-transfer ionization, $K_i(T)$, is related to the rate coefficient of charge-transfer recombination, $K_r(T)$, by $K_i(T) \sim K_r(T) \exp(-\Delta E/kT)$, where ΔE is the energy gain in the recombination reaction (Baliunas & Butler 1980; Gargaud, McCarroll, & Valiron 1982). For a plasma not in thermodynamic equilibrium, this reverse process will increase the population of higher charge state ions, which results in an overestimation of the plasma temperature. The calculation of Baliunas & Butler (1980) has indicated that reduction in plasma temperature by a factor of 2 can result when the charge transfer of silicon ions is incorporated in the plasma modeling. Butler & Raymond (1980) have also shown that these processes have significant effects on astrophysical shocks. The column densities, line intensities, and line ratios of the silicon are therefore substantially modified.

The rate coefficients related to the processes described by equations (1–5) have been calculated by McCarroll & Valiron (1976), Butler & Dalgarno (1980), Gargaud et al. (1982), Opradolce, McCarroll, & Valiron (1985), Gargaud & McCarroll (1988), Honvault et al. (1995), and Stancil et al. (1997). However, none of these results have been tested experimentally. We have recently measured the rate coefficients for $O^{2+} + He \rightarrow$ products (Kwong & Fang 1993; Fang & Kwong 1995) and $N^{2+} + He \rightarrow$ products (Fang & Kwong 1997). While our result for $N^{2+} + He$ agrees well with the calculated value (Sun et al. 1996), the result for $O^{2+} + He$ differs significantly from the calculated values (Butler, Heil, & Dalgarno 1980; Gargaud, Bacchus-Montabonel, & McCarroll 1993; Kimura et al. 1996). It is therefore very important that these calculated values be tested against the measurement. In this paper, we report the

first measurement of the total charge-transfer rate coefficient for the reactions given by equations (1a) and (1b), $Si^{3+} + He \rightarrow$ products. This measurement will help to clarify the role of this reaction in the determination of the ionization structures of astrophysical plasma.

2. EXPERIMENTAL METHOD

The measurement of the ground-state thermal energy charge-transfer rate coefficient between the Si^{3+} ion and helium is carried out with the technique of laser-ablation ion source and ion storage. We have described in detail this measurement technique in our previous publications (Kwong et al. 1990; Fang & Kwong 1994, 1995, 1997). We have demonstrated that this novel technique is applicable not only to ions from refractory elements such as iron, molybdenum, and tungsten but also to ions from gaseous elements such as oxygen and nitrogen.

Si^{3+} ions were produced by laser ablation of solid silicon targets (99.999% purity). We used the output of the second harmonic (532 nm) of a pulsed Nd:YAG laser as an ablation source. In this measurement, approximately 5 mJ of the second harmonic of the Nd:YAG laser was used. The increase in the ablation laser energy, about 5 times over previous measurements on O^{2+} and N^{2+}, was to ensure the optimal production of Si^{3+} ions.

A cylindrical radio-frequency quadrupole ion trap was used to store laser-ablation–produced ions. The trapping parameters (radio frequency: $f = 1.26$ MHz; amplitude: $V_0 = 360$ V; and DC bias: $U_0 = 38$ V) were chosen to selectively store Si^{3+} ions. The axial well depth was $D_z = 25.3$ V, and the radial well depth was $D_r = 12.7$ V. The lower charge-state ions, Si^+ and Si^{2+}, were excluded from the trap since they were outside the stable region of the trap at these trap parameters. The production of higher charge-state ions, Si^{q+} with $q > 3$, could be eliminated by keeping the low laser power density in the experiment. The stored ions were extracted from the trap for ion counting and mass analysis by two push-and-pull extraction pulses applied simultaneously to the upper and lower end caps of the trap, respectively. These ions were mass analyzed by a 0.3 m time-of-flight (TOF) mass spectrometer. The TOF mass spectrum was recorded by a transient digitizer and stored in a computer for later analysis. While the TOF signal was used to identify the ion species, the signal intensity served to measure the population of the ions stored in the trap prior to their extraction. Figure 1 shows a typical TOF mass spectrum of the laser-produced Si^{3+} ions stored in the trap under the above-mentioned trapping conditions. For the purpose of comparison, it also shows the TOF mass spectra of stored N^+, N^{2+}, C^+, C^{2+}, and O^{2+} ions produced by electron impact on ultra-high-purity gases N_2 and CO. The number of Si^{3+} ions stored in the trap was about 10^3. The storage time ($1/e$) was in excess of 7 s at a base pressure of 4×10^{-10} torr, which mainly consisted of H_2, H_2O, and CO.

The charge transfer rates were obtained by measuring the relative number of Si^{3+} ions remaining in the trap as a function of time, in the presence of helium gas of known density. To minimize both the short-term and the long-term ion signal fluctuation and drift caused by the variation of laser power and the changing surface condition of the target when the ablation laser gradually drills into the target surface, the ion signals were measured, alternately, at a delay time t and at the shortest delay time $t_0 = 0.4$ s. Each

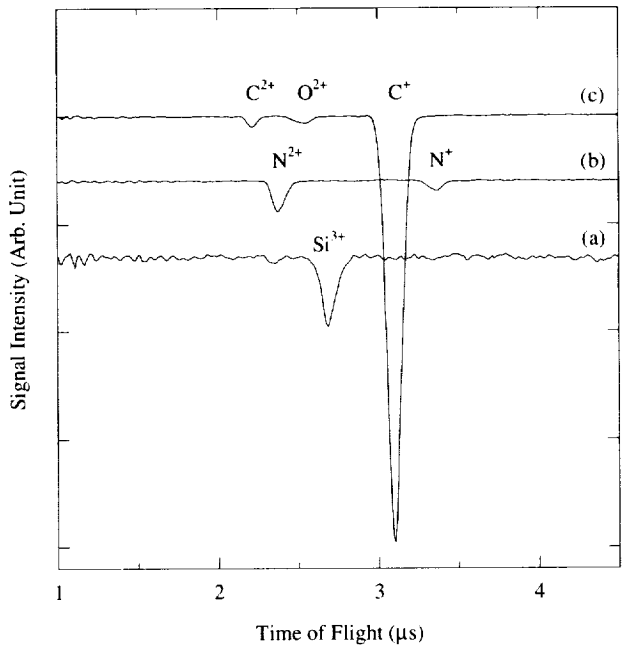

FIG. 1.—TOF mass spectrum of the laser-produced Si^{3+} ions stored in the trap (*a*), and TOF mass spectra of the stored ions produced by electron impact dissociative ionization of gases N_2 (*b*) and CO (*c*).

pair of measurements consisted of four laser shots. More than 50 such pairs of measurements were made for each time t. The intensity ratio, $I_r = I_t/I_{t_0}$, is computed to obtain a normalized relative intensity. The storage time, t, is then scanned with a delay time increment, δt, to obtain an ion decay curve.

Since the laser ablation ion source uses a solid target in the ion production, the complexities and uncertainties caused by the interaction between the stored ions and its parent gas, as in some conventional ion sources, are totally eliminated. Helium gas was introduced into the vacuum chamber through a stainless-steel gas-handling system. The procedure for the operation of the gas-handling system to minimize contamination was described earlier (Fang & Kwong 1995). The purity of the He gas in the vacuum chamber was confirmed by a Vacuum Generator DX100 quadrupole residual gas analyzer.

3. DATA ANALYSIS AND RESULTS

The Si^{3+} (sodium-like) ions can be in a variety of excited electronic states immediately after they are produced by laser ablation. They rapidly cascade to their ground state through allowed transitions and collisional de-excitation by plasma electrons. At the time we began the measurement (0.4 s after the ions were produced and trapped), all the stored Si^{3+} ions were expected to be in their ground state.

The Si^{3+} ions were stored in a 12.7 V potential well; the probability of the Si^{3+} ions being knocked out of the trap by elastic collision with He atoms at room temperature (0.04 eV) was negligible. The loss of Si^{3+} ions in the trap, therefore, was caused only by the single electron capture from He as described in equations (1a) and (1b).

The time-dependent mean relative intensity, $I_r(t)$, of the stored Si^{3+} ions is related to the total charge-transfer rate coefficient, K, by a single-exponential function:

$$I_r(t) = e^{-R(t-t_0)}, \quad (6)$$

with

$$R = n_{He}\langle v_1 Q_1\rangle + n_b\langle v_2 Q_2\rangle \quad (7)$$

$$= n_{He} K + R_0 , \quad (8)$$

where n_{He} is the number density of the helium gas and n_b is the number density of the residual background gas in the ultra-high-vacuum (UHV) chamber. Q_1 and Q_2 are the charge-transfer cross sections for Si^{3+} with He and the residual gas, respectively, through all channels; v_1 and v_2 are the relative velocities of the Si^{3+} ions with He atoms and residual gas molecules, respectively; and R_0 is the decay rate of Si^{3+} in the UHV system with only residual background gas present. The data set containing the mean relative intensity, $I_r(t)$, was fitted to equation (6) with a weighted least-squares method. The weight for each point was determined by its statistical uncertainty. The decay rate R, as a parameter of the fitting, and its statistical uncertainty were determined from the fitting algorithm. The rate coefficient, K, was obtained by the weighted least-squares fits of the decay rates R at four different He densities n_{He} to equation (8).

The uncertainty of the rate coefficient was derived mainly from a quadratic sum of the statistical uncertainty derived from the data fitting and the uncertainty of the He gas density measurement. Absolute calibration of the ion gauge to measure the reactant gas density has been described in a previous publication (Kwong et al. 1990). A systematic error caused by a small quantity of the probable Si^{4+} contaminant in the ion trap was also considered. Because of the nonlinear power dependence of ion production by laser ablation and the power fluctuation of the laser from shot to shot, such a contaminant could be randomly produced. With the data collected at the shortest delay time of 0.4 s, the average ratio for Si^{4+} to Si^{3+} was less than 2.5%. The higher charge states of silicon were not observed. We modeled the effect on the decay of the total Si^{3+} ions in the trap assuming a 2.5% contamination of Si^{4+} ions. We also assumed that the kinetic energy of the product ions, Si^{3+}, from the charge-transfer process described by equations (2a) and (2b) was smaller than the potential energy of the trap

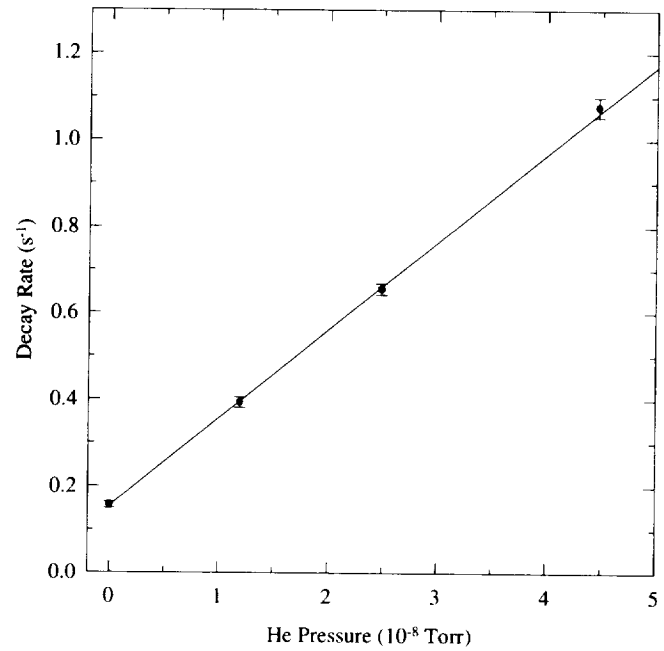

FIG. 3.—Si^{3+} ion decay rate versus He pressure. Each error bar represents the statistical uncertainty of 1 σ. The slope of the straight line fit gives the charge transfer rate coefficient of the Si^{3+} ion with He.

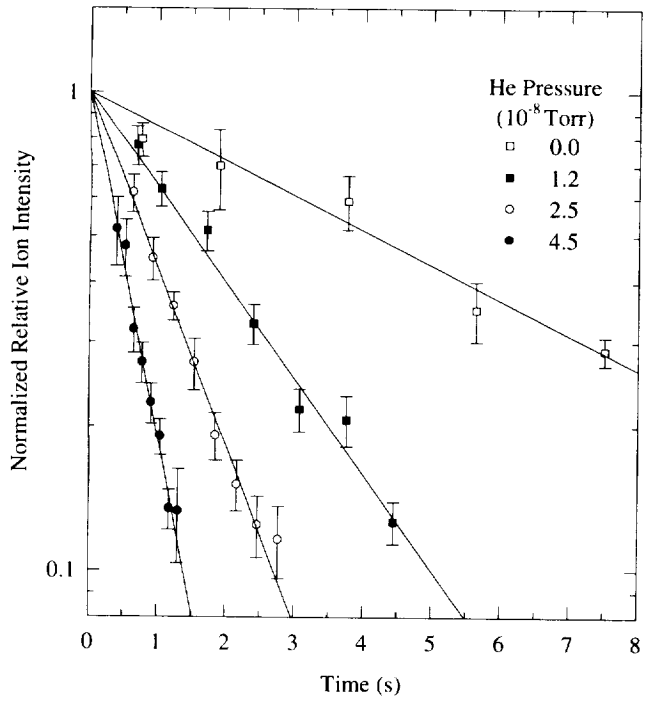

FIG. 2.—Decay curves of normalized relative intensity of Si^{3+} ions versus storage time at four different pressures of He. The uncertainty (1 σ) is due to the statistical fluctuation of the ion signal. Solid lines indicate the least-squares fits to a single exponential function.

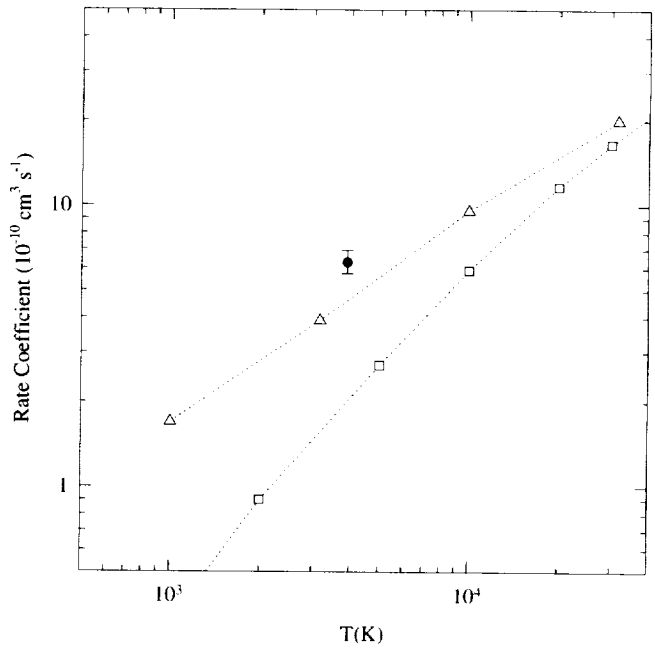

FIG. 4.—Total rate coefficients of charge transfer between Si^{3+} ($3s^2S$) and He. The filled circle represents the present work. The calculated values are from (*open triangles*) Butler & Dalgarno (1980) and (*open squares*) Honvault et al. (1995). The dotted lines joining the calculated values are visual aids only.

and that these ions remained in the trap. Our simulation indicates that the rate coefficient for the charge-transfer reaction, $Si^{3+} + He \rightarrow$ products, can be underestimated by, at most, 2.45%. The underestimate reaches this maximum value when the total rate coefficient for the charge-transfer process described by equations (1a) and (2b) has the same value as that described by equations (2a) and (2b). The total estimated error for the measurement will reflect this systematic uncertainty.

The data and their fitting curves for the reactions given by equations (1a) and (1b), $Si^{3+} + He \rightarrow$ products, at four different He pressures are shown in Figure 2. The solid lines represent the result of the weighted least-squares fit. Figure 3 plots the decay rates as a function of He pressure. The slope of the solid line gives the charge-transfer recombination rate coefficient of $6.27^{+0.68}_{-0.52} \times 10^{-10}$ cm^3 s^{-1}. The equivalent temperature for the measurement is estimated to be 3.9×10^3 K (Fang & Kwong 1997; Dickinson 1995). Figure 4 is a plot of the calculated rate coefficients by Butler & Dalgarno (1980) that uses the Landau-Zener method and a plot of the full quantal calculation of Honvault et al. (1995). Our measured rate coefficient, at 3.9×10^3 K, is about 30% larger than that of the Landau-Zener estimation and is higher by about a factor of 3 than the full quantal calculation. We should also mention that the reaction given by equations (5a) and (5b) on deuterium has recently been calculated and measured (Pieksma et al. 1996).

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