Charge transfer between Si^{4+} ion and helium at electron-volt energies

Z. Fang and Victor H. S. Kwong
Department of Physics, University of Nevada, Las Vegas, 4505 Maryland Parkway, Las Vegas, Nevada 89154
(Received 6 July 1998)

The charge-transfer rate coefficient for the reaction $Si^{4+}+He \rightarrow$products was measured at an equivalent temperature of 4.6×10^3 K using a laser-induced plasma ion source and ion storage. The rate coefficient is $4.54(0.48)\times10^{-12}$ $cm^3\,s^{-1}$ and is at least an order of magnitude smaller than the available theoretical values. [S1050-2947(99)03401-0]

PACS number(s): 34.70.+e, 32.80.Pj, 52.50.Jm, 95.30.Dr

The charge-transfer reaction $Si^{4+}+He \rightarrow$products has been considered one of the major mechanisms for the depletion of Si^{4+} ions in astrophysical plasmas. The reaction $Si^{4+}+He \rightarrow Si^{3+}+He^+$ in particular has generated considerable interest as a potential mechanism for the formation of excited state Si^{3+} $(1s^2 2s^2 2p^6 3p)$ resulting in the emission at 1400 Å in a wide variety of astrophysical plasmas [1,2]. This radiation has been observed and has been used in the diagnostic of helium rich astrophysical plasmas [3]. Several calculations have been made in the past using techniques ranging from the Landau-Zener approximation [4] to full quantal calculations [5–7]. However, discrepancies exist among all four calculations and increase below 10 eV. Furthermore, no measurement has yet been made to test these values. The accuracy of these calculations and the role of this reaction in low-temperature, helium-rich, astrophysical plasmas clearly needs further confirmation experimentally.

The experimental techniques developed in our laboratory, recently used to measure the thermal-energy charge-transfer rate coefficient of O^{2+} with He [8], and Si^{3+} with He [9] can be used to test these calculations if we assume that the single-electron transfer channel $Si^{4+}+He \rightarrow Si^{3+}+He^+$, is the dominant process. With this technique, ions are directly produced by laser ablation of solid targets. The laser-produced ions are stored in a radio-frequency ion trap where charge transfer with neutral atoms of interest occurs. Since no carrier gas is involved in the ion production, the reaction between ions and the carrier gas that can be the major source of systematic error is completely eliminated. The mass selectivity of the trap enables us to store a specific ion group for study with no other concomitant ions present.

We have described the facilities in our earlier publications [10–12] and will not elaborate here. Si^{4+} ions are produced by laser ablation of 99.95% pure solid tungsten disilicide (WSi_2) targets. Tungsten disilicide targets give a more stable ion signal than pure silicon targets. The distinct difference in the mass-to-charge ratio between the low-charge-state tungsten ions (e.g., W^{3+}, $m/q=61.3$) and silicon ions Si^{4+} $(m/q=7)$ enables us to separate the Si^{4+} ions from the heavier W^{q+} ions. The amount of energy at 532 nm used in the ion production is about 3 mJ. At this laser energy, higher charge states of tungsten and silicon with $q>4$ were not observed. The ion trap parameters were chosen to optimize the storage of Si^{4+} ions. Figure 1 shows the time-of-flight mass spectrum of the laser produced Si^{4+} ions stored in the trap. For calibration purposes, the time-of-flight (TOF) spectra of stored N^{2+}, C^{2+}, C^+, and O^{2+} ions produced by electron impact ionization on ultrahigh-purity gases of N_2 and CO are also shown.

A cylindrical radio-frequency quadrupole ion trap was used to store laser-ablated ions. The trapping parameters (radio frequency $f=1.44$ MHz, amplitude $V_0=350$ V, and dc bias $U_0=32$ V) were chosen to optimize the storage of Si^{4+} ions. The axial well depth was $D_z=11.3$ V and the radial well depth was $D_r=18.8$ V. The heavier tungsten ions and the lower-charge-state silicon ions were excluded from the trap since they were outside the stable region of the trap. All the stored ions were extracted from the trap for mass analysis

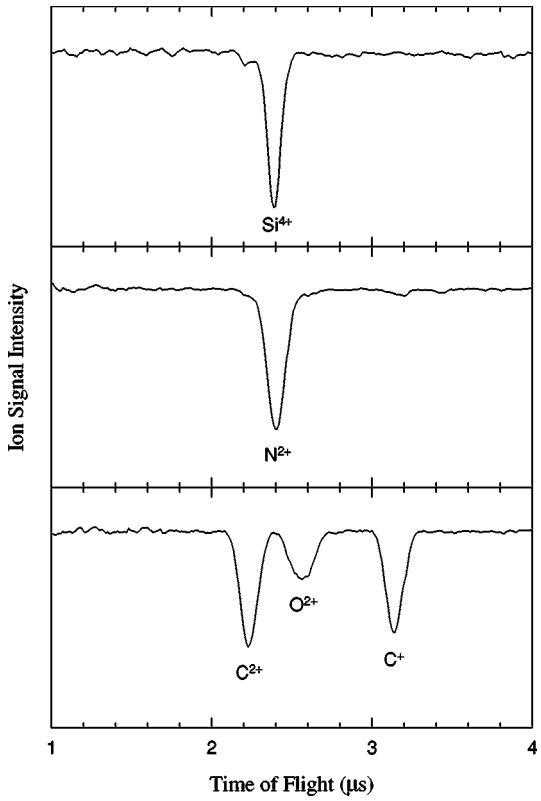

FIG. 1. Time-of-flight mass spectrum for laser-produced Si^{4+} ions stored in the trap under the trap conditions: rf frequency $f=1.44$ MHz, rf amplitude $V_0=350$ V, and dc bias $U_0=32$ V. For calibration purpose, also shown are the mass spectra of N^{2+} ions and of C^{2+}, O^{2+}, and C^+ ions produced by electron bombardment on N_2 gas and CO gas, respectively.

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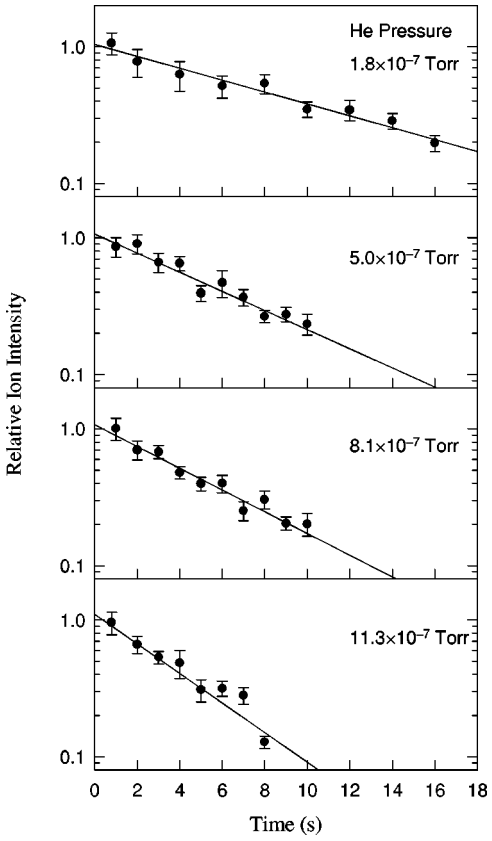

FIG. 2. Decay curves of normalized relative intensity of Si^{4+} ion vs storage time for different helium pressures.

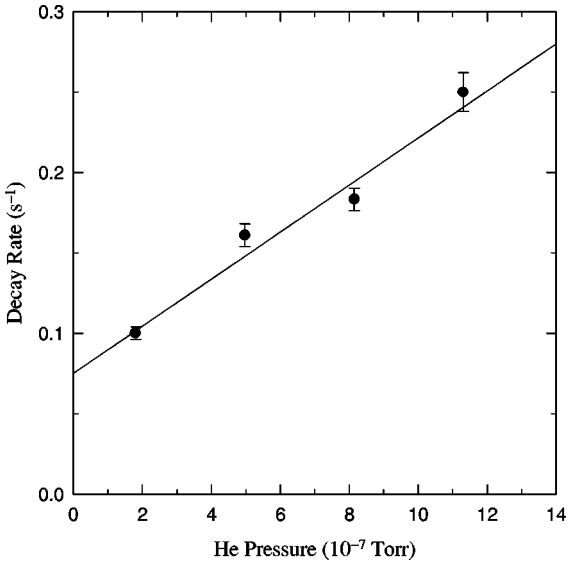

FIG. 3. Si^{4+} decay rate vs helium pressure. Each error bar represents the statistical uncertainty of 1σ. The slope of the straight line fit gives the charge-transfer rate coefficient of the Si^{4+} ion with He.

and ion counting 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 TOF mass spectrometer and the ions were detected by a multichannel plate. 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. The number of Si^{4+} ions was estimated to be about 10^2. The storage time $(1/e)$ was in excess of 10 s at the base pressure of 4×10^{-10} Torr. The residual gas in the stainless-steel chamber is primarily of H_2, H_2O, and CO.

The charge-transfer rates were obtained by measuring the relative number of Si^{4+} remaining in the trap as a function of time, in the presence of ultrahigh purity (99.999%) helium of known density [11]. 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 signal was measured, alternately, at a delay time t and at the shortest delay time $t_0=0.4$ s. Each pair of measurements consisted of four laser shots. More than 100 such pairs of measurements were made for each time t. The intensity ratio $I_r=I_t/I_{t_0}$ was computed to obtain a normalized relative intensity. The storage time t was then scanned with a delay time increment Δt to obtain an ion decay curve. Figure 2 is a plot of the ion signal intensities versus delay time t, after laser ablation for four helium pressures. The scatter on the data points is due to the fluctuation of the ion signals. Each solid line is a least-squares fit of the data by a single-exponential decay function. The slopes of the fitted lines in Fig. 2 give the charge-transfer rates at the given helium pressures. The plot of the decay rate of the stored Si^{4+} ions versus helium pressure is shown in Fig. 3. The slope in the figure is obtained by the weighted least-squares fit by a linear function. The rate coefficient for Si^{4+} and helium obtained from the slope of Fig. 3 is 4.54×10^{-12} $cm^3\,s^{-1}$. The total uncertainty on the measurement is about $\pm10.5\%$ and this uncertainty is the result of the quadratic sum of the statistical fluctuation of ion signals $(\pm6.8\%)$, the uncertainty in the estimation on the helium density $(\pm8\%)$, and the nonlinearity of the detector and electronics $(\pm1\%)$.

Since N^{2+} ions have the same m/q as Si^{4+} ions, it is important to confirm that the stored Si^{4+} ions are not contaminated with N^{2+} ions generated by gas desorption from the target surface. However, our previous measurement on the charge-transfer reaction $N^{2+}+He\rightarrow$products indicates that the rate coefficient is 8.67×10^{-11} $cm^3\,s^{-1}$ [13], a factor of 20 larger than the current measurement, suggesting that N^{2+} ions are not present in the trap. In fact, the surface of the targets was cleaned by running the ablation laser at 10 Hz for a few seconds to remove any contaminants that physically or chemically absorbed on the surface of the targets when the targets were installed.

The mean energy of the stored Si^{4+} ions is about 4.5 eV [14–16]. This mean energy corresponds to an ion temperature of about 3.5×10^4 K, which can be calculated by using the relation that the mean energy $\overline{E}$ and the temperature T are related by $\overline{E}=\frac{3}{2}kT$ since the velocity distribution of the ions in a rf trap is nearly thermal [15]. Because the temperature of the neutral reactant gas is at room temperature (300 K), an equivalent temperature T_{equiv} is introduced that corresponds to the mean relative velocity of the Si^{4+} and the reactant atomic gas [17]. This equivalent temperature of the collisional system is given by

$$\frac{T_{\text{equiv}}}{\mu} = \frac{T_i}{m_i} + \frac{T_n}{m_n},$$

where the ion temperature is T_i, the reactant gas temperature is T_n, m_i and m_n are the masses of the ion and the neutral atom, respectively, and μ is their reduced mass. The estimated equivalent temperature for the current measurement is 4.6×10^3 K.

The Si^{4+} ion has a configuration $(1s^2 2s^2 2p^5 3s)$ that gives rise to the metastable $^3P_2$ and $^1P_0$ terms. These terms are about 104 eV above the ground configuration $(1s^2 2s^2 2p^6)$ [18]. Thompson and Gregory [18] and Pieksma *et al.* [19] estimated that the metastable state fraction in their fast Si^{4+} ion beam produced by an electron cyclotron resonance ion source is about 5%. However, the ions produced by laser ablation are cold. Our pulsed ion beam study of charge transfer between C^{2+} ions and H_2 using a laser ablation ion source and a reflection TOF mass spectrometer indicated no observable metastable state ions in the laser ablation ion beam [20]. This is consistent with our previous measurement of $O^{2+}+He\rightarrow$products using the ion trap [21,22]. The absence of the metastable state ions is primarily due to the rapid cooling of the laser-induced plasmas as the result of the self-similar expansion in vacuum [23]. We conclude that the Si^{4+} ions produced by laser ablation and stored in our trap are essentially Si^{4+} $(1s^2 2s^2 2p^6)$.

Since previous and recent calculations [5–7] indicate that the charge transfer rate coefficient can be as high as $\sim7\times10^{-10}$ $cm^3\,s^{-1}$ at 4.6×10^3 K, we carried out further tests to determine if the rapid charge-transfer rate coefficient exists for the $Si^{4+}+He$ reaction. If we assume such a rate coefficient, the mean charge-transfer collision time would be about 1.7 s at a helium pressure of 2.6×10^{-8} Torr and we should be able to detect a significant drop in the ion signal due to such a reaction rate. To eliminate the change in the ion signal caused by the residual gases in the vacuum chamber we compared the Si^{4+} ion signal intensities in the presence of 2.6×10^{-8} Torr of helium with that without helium at the delay time of 0.4, 1, 2, 3, and 4 s after the ions are stored in the trap. Figure 4 shows the invariance of the differential ion signals over 4 *s*. This indicates that a rapid charge-transfer rate with He does not exist. We conclude that the measured rate coefficient is at least an order of magnitude smaller than the calculated values for the $Si^{3+}+He^+$ product channel previously published [4–7,24].

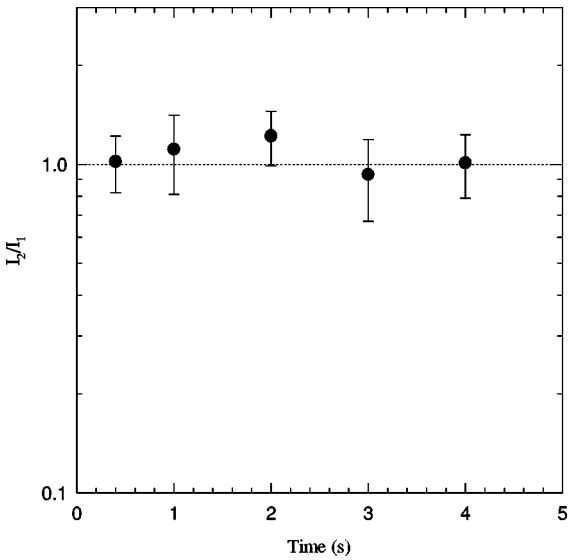

FIG. 4. Ratio of the Si^{4+} ion signal at 2.6×10^{-8} Torr, I_2, and the Si^{4+} ion signal with He pumped out of the vacuum chamber, I_1, at 0.4, 1, 2, 3, and 4 s. The horizontal dotted line indicates the intensity ratio of 1.

At such a slow rate, it is highly unlikely that charge transfer of Si^{4+} ions and helium plays a significant role in suppressing the abundance of Si^{4+} in helium-rich astrophysical plasmas. For the same reason, the discrepancies between the observed and the calculated intensity of the Si^{3+} 1400-Å emission in helium-rich astrophysical plasmas, such as the cataclysmic variable DQ Hercules [3], planetary nebula [1], and astrophysical shocks [2], cannot be explained by this relatively slow reaction alone. The role of this charge-transfer reaction in astrophysical plasmas needs to be reassessed.

This work was supported by NASA under Grant Nos. NAGW-4279 and NAG5-3917 to the University of Nevada, Las Vegas.

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