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Charge transfer of Ti^{4+} with Ar and N₂ at electron-volt energy ¹

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Abstract

The charge-transfer reactions of ground state Ti^{4+} (3p⁶, ¹S) with Ar and N₂ were studied in a quadrupole r.f. ion trap at the mean collision energy of 4.55 eV. The rate coefficients were measured to be 1.06(0.14) × 10⁻⁹ cm³/s for Ti⁴⁺ with Ar at an equilibrium temperature of 1.6×10^4 K and $7.45(0.38) \times 10^{-10}$ cm³/s for Ti⁴⁺ with N₂ at an equilibrium temperature of 1.3×10^4 K. Both results are comparable with the Langevin rate coefficients. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Charge transfer processes between multiply charged ions and neutrals are important atomic processes in many plasmas present in astrophysical objects (planetary nebulae, interstellar medium, etc.) and created in the laboratories for various purposes [1]. The experimental measurements of the charge transfer rate coefficients will help to understand plasma equilibrium which was strongly influenced by these processes and will also help to verify the basic theoretical treatment of these complicated quantum systems. Several experimental techniques have been developed for these studies, such as merged-beams [2], ion storage [3–6], and time-offlight mass spectrometers [7,8], but most of these experimental works have been carried out at keV collision energies, only a few have been made in the electronvolt energy range.

To gain some insight into the energy balance. charge- and excitation-state distribution and radiation power loss mechanisms of fusion plasmas due to the strong influence of the electron-capture processes, one has to study the charge transfer processes involving some specific multi-charged ions. The multicharged or even highly stripped complex ions of tungsten, molybdenum, titanium and iron can be originated and released from materials of the wall of some fusion plasma apparatus (the limiter and reactor, in the case of tokamaks) and be present as the major impurities of the plasma. The charge-transfer processes of these ions with neutral atoms and molecules may bring the most important practical implications [9]. Few experimental results have been reported for charge-transfer reactions of multicharged ions with electron-volt energy from these refractory elements which are present at the edge of the fusion plasma, only W^{2+} and Mo^{6+} have been

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studied by Kwong et al. [5,6] in their cylindrical r.f. trap. Here we report a measurement of charge transfer coefficients of Ti^{4+} (average energy of about 4.55 eV) with Ar and N₂. No theoretical and other experimental values are available for these reactions at electron-volt energy. Our experiment has been performed in a quadrupole r.f. ion trap, the low-energy Ti^{4+} has been created and then confined in the trap by laser ablation combined with the technique of crossed-beam cooling for ions introduced by Kwong et al. [4]. Due to the flexibility of these techniques this work can be extended to varieties of charge-transfer reactions of multi-charged ions with neutral atoms and molecules.

2. Experiments and results

The apparatus of our experiments consists of a quadrupole r.f. ion trap with a minimum radius of the ring electrode $r_0 = 0.99$ cm, and the minimum separation between two endcap electrodes $2 z_0 = 1.4$ cm. Two solid TiO₂ (99.9% purity) targets are held in position in the plane of the ring electrode and at the same fixed distance from its center. The arrangement of the apparatus and the method of laser ablation and crossed-beam cooling for creating low-energy multi-charged ions were similar to that demonstrated in Ref. [4]. Here we briefly describe the different approach of mass-selective confinement and rejection detection of the ions in our measurements.

The timing diagram for production, trapping and detection of the ions is shown in Fig. 1. The Ti⁴⁺



Fig. 1. Timing diagram for ion trap and laser ablation. The selective voltage of $V_{\rm AC}$ and $V_{\rm DC}$ are set for mass-selective storage of the Ti⁴⁺ ions. The delay time from the end of the selective-storage operation and the beginning of the analytical scan is changeable.

ions were created by laser ablation using the focused light (two lens with focus length of 45 cm were used) from the output of the second harmonic (532 nm) of a pulsed Nd:YAG laser. With the laser energy per pulse of approximately 5 mJ corresponding to the pulse power density above 1×10^9 W/cm² with laser pulse duration of about 15 ns, other charge-state ions such as Ti^{3+} (m/q = 16), Ti^{2+} (m/q = 24), Ti⁺ (m/q = 48), O⁺ (m/q = 16) and O^{2+} (m/q = 8) were produced with Ti⁴⁺ ions and may be confined in the trap. So operating the trap near the cross point of $\beta_r = 1$ and $\beta_r = 0$ of the first stability region (i.e. the operating point of $a_z = 0.15$, $q_{z} = 0.78$) was chosen for selective-storage of the specific ions. In our measurement for Ti⁴⁺ ions with the r.f. frequency of 1.1MHz the mass-selective-confinement operating voltage are about 115 V for r.f. voltage and 11 V for DC voltage. We can maintain an appropriate density of Ti⁴⁺ ions for measurement and eliminate all other charge state ions by keeping the trap working near this operation point for about several milliseconds. The ions were extracted for analysis from the trap axially due to the axial destability by scanning the r.f. voltage applied to the ring electrode, and the ions were ejected through a hole in the center of an endcap electrode to the surface of a channel electron-multiplier quite near the endcap electrode. With an appropriate r.f. voltage scanning rate (corresponding to a mass scanning rate about 2000 au/s) we can give the best mass resolution of $M/dM \ge 6$ at 12 au.

The experimental procedure for measuring the charge transfer rate coefficients is summarized as follows. A small amount (about 10⁻⁷ torr) of reactant gas Ar or N2 was introduced to the vacuum chamber through a variable leak valve. The Ti⁴⁺ ions and other ion species were created by laser ablation and cooled due to crossed-beam collision. The Ti⁴⁺ ions were selectively stored in the trap by the method mentioned above, and then extracted from the trap by scanning the r.f. voltage at a delay time $t_0 + \delta t$ (t_0 refers to the initial delay time of about 50 ms in our measurement) relative to the selective-confinement, and collected by the electron multiplier due to the influence of the negative potential (about -2500 V in our experiments) which is applied to the surface of the multiplier. The mass spectrum from the multiplier was amplified by a

narrow-banded DC amplifier and then transferred by a fast AD/DA converter, and finally recorded in the computer for later analysis. The storage time was increased from the initial delay time t_0 with a fixed increment δt until the ion signal intensity had dropped to one-tenth of that at the initial delay time. More than ten such time delay points were used to obtain the data. For each delay time more than five data points were acquired. Then we repeated such measurements by varying the storage time in the opposite direction. The average of the data in each time delay gave the mean relative ion density that remained in the trap and could minimize the measurement error due to the random change of the laser



Fig. 2. (a) The decay of relative ion intensity of Ti^{4+} vs. storage time in different Ar pressures. The solid lines are the least-square fits to a single exponential function. (b) Variations of the Ti^{4+} decay rate vs. Ar pressure. The slope of the straight line fit gives the charge-transfer rate coefficient.



Fig. 3. (a) The decay of relative ion intensity of Ti^{4+} vs. storage time in different N₂ pressures. The solid lines are the least-square fits to a single exponential function. (b) Variations of the Ti4+ decay rate vs. N₂ pressure. The slope of the straight line fit gives the charge-transfer rate coefficient.

power and the effects of changing conditions on the target surface. The approach was performed for five different Ar or N_2 pressures.

Data points with different shapes in Fig. 2a and Fig. 3a represents the results obtained under different gas pressures. Each set of data points denotes variations of the relative ion intensities versus storage time *t*. The solid line is a least-squares fit to the data by a single exponential decay function in natural logarithm scale. Its slope gives the charge transfer rate at a given Ar or N₂ pressure.

Fig. 2b plots the charge transfer rate between Ti^{4+} ions and Ar as a function of Ar pressure while Fig. 3b plots that between Ti^{4+} ions and N_2 . The

solid line in each figure is the least-squares fit to a linear function of the experimental data and its slope gives the charge transfer rate coefficient. For Ti⁴⁺ ions and Ar the value is deduced to be $1.06(0.14) \times 10^{-9}$ cm³/s, and for Ti⁴⁺ ions and N₂, $7.45(0.38) \times 10^{-10}$ cm³/s. The uncertainty presented here is due to the uncertainty of the gas pressure measurements and the uncertainty of the ion signal intensity results from the fluctuation of laser power and other nonlinear effects of the detection circuit. We neglected the ions escape loss and its uncertainty in our measurements.

3. Discussion

The argon-like Ti⁴⁺ ion has no low-lying metastable state. If the ions produced by laser ablation were in a variety of excited electronic states, they will rapidly cascade to their ground state through allowed transitions and collisional deexcitations by plasma electrons. After the selective-confinement and a given initial delay time of about 50 ms, the stored Ti⁴⁺ ion should be in its $3p^{6}(^{1}S)$ ground state. With 91 eV above its neutral ground state the Ti⁴⁺ in ground state can undergo charge transfer reaction in following possible exothermic channels with Ar or N₂,

$$Ti^{4+} + Ar \rightarrow \begin{cases} Ti^{3+} + Ar^{+} + \Delta E & (\Delta E \le 27.49 \text{ eV}) \\ Ti^{2+} + Ar^{2+} + \Delta E & (\Delta E \le 27.34 \text{ eV}) \end{cases}$$
(1)
$$Ti^{4+} + N_2 \rightarrow \begin{cases} Ti^{3+} + N_2^{+} + \Delta E & (\Delta E \le 27.66 \text{ eV}) \\ Ti^{3+} + N + N^{+} + \Delta E & (\Delta E \le 19.05 \text{ eV}) \\ Ti^{3+} + 2N^{+} + e + \Delta E & (\Delta E \le 4.52 \text{ eV}) \\ Ti^{2+} + 2N^{+} + \Delta E & (\Delta E \le 31.99 \text{ eV}) \end{cases}$$
(2)

For $Ti^{4+} + Ar$, two channels are possible with similar exothermicity. The first one is a single electron transfer process but the second is a double electrons transfer reaction. For $Ti^{4+} + N_2$, four channels stated above are possible with different exothermicity. Since we did not measure the product ion signal for different channels in the experiment, the values we gave were the total charge-transfer rate coefficients of all these reaction channels.

With the AC voltage of 114 V and no DC bias after the selective-storage the axial potential well

depth for Ti⁴⁺ was about 45.5 eV. We estimate that the mean energy of the stored Ti^{4+} ions is 4.55 eV which is approximately a tenth of the potential well [10]. This mean energy corresponds to a nearly thermal distribution of ion temperature of about 3.52 $\times 10^4$ K. A equilibrium temperature of Ti⁴⁺ ions with corresponding room temperature reaction gas could be obtained. For Ti⁴⁺ ions and Ar this temperature is about 1.6×10^4 K and that of Ti⁴⁺ with N₂ is about 1.3×10^4 K. From these data we could derive the mean relative velocity of the Ti⁴⁺ and the reactant gas Ar or N₂ according to $\frac{1}{2}mv^2 = \frac{3}{2}k_BT_{eq}$ $(k_B \text{ is the Boltzman constant, } T_{eq} \text{ is the equilibrium}$ temperature for each collision reaction), the corresponding values are 9.1×10^3 m/s and 8.2×10^3 m/s. respectively.

Since there is no available theoretical value at this energy range for charge transfer of Ti⁴⁺ with neutral atoms or molecules, we may compare the measured results with the Langevin cross sections [11]. The static average electric dipole polarizability for Ar and N₂ is 1.64×10^{-24} cm³ and 1.74×10^{-24} cm³, respectively [12]. The corresponding Langevin charge-transfer rate coefficients for Ti^{4+} + Ar can be estimated to be 5.43×10^{-9} cm³/s and that for $Ti^{4+} + N_2$ to be 5.59×10^{-9} cm³/s. These values are about five and seven times larger than our measurements, respectively, and can be considered as to be comparable with the measured results. Since the Langevin model is based on the classical kinetic theory, there always exists a discrepancy between the charge-transfer rate coefficients and corresponding experimental values [6,13]. More precise theoretical calculations need complex guantal models which are still under development for the treatment of these charge-transfer collisions at electron-volt energies [14 - 16].

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