PHYSICAL REVIEW A VOLUME 55, NUMBER 1 JANUARY 1997

Charge transfer between ground-state N^{2+} and H_2, N_2, and CO at electron-volt energies

Z. Fang and Victor H. S. Kwong
Department of Physics, University of Nevada, 4505 Maryland Parkway, Las Vegas, Nevada 89154

(Received 19 August 1996)

The charge-transfer rate coefficients for reactions of $N^{2+}(2s^2 2p\ ^2P^o)$ with H_2, N_2, and CO are measured using ion storage. A cylindrical rf ion trap was used to store N^{2+} ions produced by laser ablation of a solid titanium nitride target. The rate coefficients were derived from the decay rate of the ion signal. The rate coefficients for the above three reactions are $3.38(0.35)\times10^{-11}$ cm^3 s^{-1} at $T_{\mathrm{equiv}}=2.9\times10^3$ K, $2.10(0.18)\times10^{-9}$ cm^3 s^{-1} at $T_{\mathrm{equiv}}=1.3\times10^4$ K, and $3.37(0.29)\times10^{-9}$ cm^3 s^{-1} at $T_{\mathrm{equiv}}=1.3\times10^4$ K, respectively. No theoretical or other experimental values are available at this energy range. [S1050-2947(97)08401-1]

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

I. INTRODUCTION

Charge transfer at electron-volt energies between multiply charged atomic ions and neutral atoms and molecules is of considerable importance in astrophysics, plasma physics, and, in particular, fusion plasmas. This process can determine the ionization equilibrium in these plasmas. Despite its importance, however, only a few experimental studies have been made at this energy range [1–4]. Moreover, theoretical treatments on these low energy collisions are far from complete. Furthermore, only a few theoretical studies have been made on reactions with molecules [5,6]. This may be due, in part, to the complicated electronic, vibrational, and rotational structures of the molecules and the availability and the accuracy of the position and orientation sensitive potentials of the pseudomolecule formed during the collision. Most of these calculations have not been tested. The experimental study of these processes is therefore particularly useful, not only to explain the ionization structures in these plasmas but also to verify the theoretical treatments at this energy range.

N^{2+} is of particular interest since it is present in significant abundance in astrophysical nebulas, nova shells, and interstellar molecular clouds [7,8]. These ions may play an important role in the production of excited state N^+. Furthermore, molecules such as nitrogen may be present as impurities at the edge of the fusion reactors and inside the diverter of the future International Thermonuclear Experimental Reactor (ITER). Since N^{2+} is only 44 eV above its neutral ground state, it can easily be produced by a variety of mechanisms, such as electron impact ionization, dielectronic recombination, photoionization, and charge transfer. Their electron-transfer collisions with helium, atomic and molecular hydrogen, nitrogen, carbon monoxide, and other molecules at mean collision energies of a few electron-volts can play an interesting role in regulating the energy and therefore the characteristics of the plasmas in these regions.

Our laser ablation ion source and ion storage facilities are primarily designed to study these charge-transfer reactions involving multiply charged atomic ions and a variety of neutral atoms and molecules at electron-volt energies. While our measured rate coefficient for O^{2+} with helium [1,9] is orders of magnitude different from the full quantal calculation of Gargaud *et al.* [10] and Kimura *et al.* [11] and the Landau-Zener approximation of Butler *et al.* [12], our recent charge-transfer measurement of N^{2+} with helium [13] is in good agreement with the calculation of Sun *et al.* [7]. These measurements may provide valuable information for the understanding of the collisional process and perhaps may inspire improvements in both experimental and theoretical approaches. In this paper, we will present charge-transfer results of ground state $(2s^2 2p\ ^2P^o)$ N^{2+} and H_2, N_2, and CO at electron-volt energies.

II. EXPERIMENTAL METHOD

The techniques of the laser ablation ion source and ion storage have been described in detail in previous publications [9,13–15]. The N^{2+} ions were produced by laser ablation of solid titanium nitride (TiN) targets. We chose titanium nitride as the target material because of the distinct difference of the mass-to-charge ratio between N^{2+} $(m/q=7)$ and other low-charge state ions that could be produced simultaneously during laser ablation. These ions include N^+ $(m/q=14)$, Ti^+ $(m/q=48)$, Ti^{2+} $(m/q=24)$, and Ti^{3+} $(m/q=16)$, and will be the focus of other experiments in the future. We used approximately 1 mJ of the second harmonic (532 nm) output emission of a pulsed Nd:YAG laser as the ablation source. The power density of the laser at the ablation target surface was estimated to be about 10^8 W cm^{-2}. The use of low laser power density eliminated the formation of higher charge state ions of titanium and nitrogen.

The laser produced ions were selectively stored in an rf quadrupole trap by choosing the following trap parameters: rf $f=1.44$ MHz, ac amplitude $V_0=350$ V, and dc bias $U_0=29$ V. The characteristics of the trap can be found in a previous publication [14]. These parameters generated a pseudopotential well for N^{2+} with an axial well depth $D_z=26.6$ eV and a radial well depth $D_r=35.6$ eV. At these trap parameters, the low charge state of titanium ions and the singly-charged nitrogen ions were excluded from the trap.

The stored ions in the trap were analyzed by extracting all the ions from the trap by two push-pull voltage pulses (+190 V and −200 V) applied simultaneously at the end caps of the trap. The extracted ions were then injected into a 0.3-m time-of-flight (TOF) mass spectrometer. They were collected and detected by a 1-in.-diam microchannel plate. The TOF mass spectrum was recorded by a transient digitizer and stored for later analysis. While the time of flight of the ion signal was used to identify the type of ions, the amplitude of the ion signal was used to measure the N^{2+} population stored in the trap prior to their extraction. The TOF mass spectrum confirmed that only N^{2+} ions were stored in the trap. We estimated that the number of N^{2+} ions stored in the trap was about 10^3. The storage time $(1/e)$ was in excess of 10 s at the base pressure of 4×10^{-10} Torr.

To measure the relative number of N^{2+} ions remaining in the trap, as a function of time after laser ablation, we measured the ion signal intensity alternately at a delay time t and at the shortest delay time $t_0=0.4$ s. More than a hundred such laser-ablation detection cycles for each delay time were carried out. The mean relative intensity $I_r(t)=(1/N)\Sigma_{n=1}^{N}[I(t)/I(t_0)]_n$, and its statistical uncertainty were computed. This averaging procedure enables us to minimize the measurement error due to the short-term fluctuation and the long-term drift of the ion signal caused by the random change of the laser power and the gradual change of the surface conditions of the target as the ablation laser drills into the target. The storage time is then scanned at a later time t with a time increment δt. To obtain an ion decay curve, we measured the relative intensity of the ion signal at more than ten different storage times over one decade of the initial value at the shortest delay.

The charge-transfer rate coefficients were obtained by measuring the decay rates of the stored ions in the presence of a reactant gas of known density (see Sec. III). Measurements obtained from four different gas pressures were usually adequate to derive accurately the rate coefficient. Since the laser ablation ion source uses a solid target in the ion production, the complexities and uncertainties caused by the interaction between the ions and their parent gas, as in some conventional ion source, are totally eliminated. In all the measurements, ultrahigh-purity (UHP) grade or research grade reactant gases were used. These gases include H_2 (Alphagaz, UHP, 99.999%), N_2 (Airco, UHP, 99.999%), and CO (Alphagaz, research, 99.97%). The reactant 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 [9]. The purity of the neutral reactant gas in the reaction chamber was further confirmed by a Vacuum Generator DX100 quadrupole residual gas analyzer.

III. DATA ANALYSIS AND RESULTS

The ground state of N^{2+} is 44 eV above its neutral ground state. The reaction channels with both single and double electron capture from reactant molecular gas are energetically possible, for example,

$$N^{2+}+H_2\rightarrow\begin{cases}N^{+}+H_2{}^{+}+E_{1a} & \text{with } E_{1a}\leqslant 14.2\ \text{eV},\\ N^{+}+H+H^{+}+E_{1b} & \text{with } E_{1b}\leqslant 11.5\ \text{eV},\\ N+2H^{+}+E_{1c} & \text{with } E_{1c}\leqslant 12.5\ \text{eV},\end{cases}\tag{1}$$

$$N^{2+}+N_2\rightarrow\begin{cases}N^{+}+N_2{}^{+}+E_{2a} & \text{with } E_{2a}\leqslant 14\ \text{eV},\\ N+2N^{+}+E_{2b} & \text{with } E_{2b}\leqslant 5.3\ \text{eV},\end{cases}\tag{2}$$

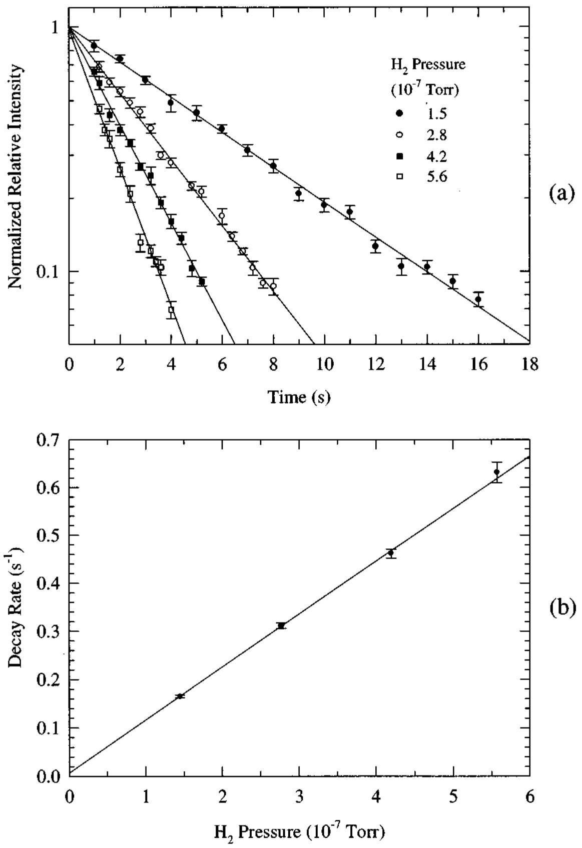

FIG. 1. (a) The normalized relative intensity of N^{2+} vs storage time at four different pressures of H_2. Solid lines are the least-squares fits to a single exponential function. (b) N^{2+} decay rate vs H_2 pressure.

$$N^{2+}+CO\rightarrow\begin{cases}N^{+}+CO^{+}+E_{3a} & \text{with } E_{3a}\leqslant 15.6\ \text{eV},\\ N^{+}+C^{+}+O+E_{3b} & \text{with } E_{3b}\leqslant 7.2\ \text{eV},\\ N+C^{+}+O^{+}+E_{3c} & \text{with } E_{3c}\leqslant 8.2\ \text{eV}.\end{cases}\tag{3}$$

However, the parameters of the ion trap were set only to store N^{2+}. Ions with m/q greater than 10 or smaller that 4 are outside the stable region of the trap and will not be stored. Low charge state titanium ions, N^{+} ions formed during laser ablation, and all product ions produced by single electron transfer and double electron transfer were also excluded from the trap. For this measurement, our present facility only allows us to measure the total charge transfer rate coefficient. Improvement on the facility to identify the energy state of the product ions is underway.

The N^{2+} ions were stored in a 27 eV potential well, the probability of N^{2+} being kicked out of the trap by elastic collisions with reactant gas at room temperature (0.04 eV) is very small. This loss mechanism could be ignored in the analysis.

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

$$I_r(t)=\exp[-R(t-t_0)],\tag{4}$$

with

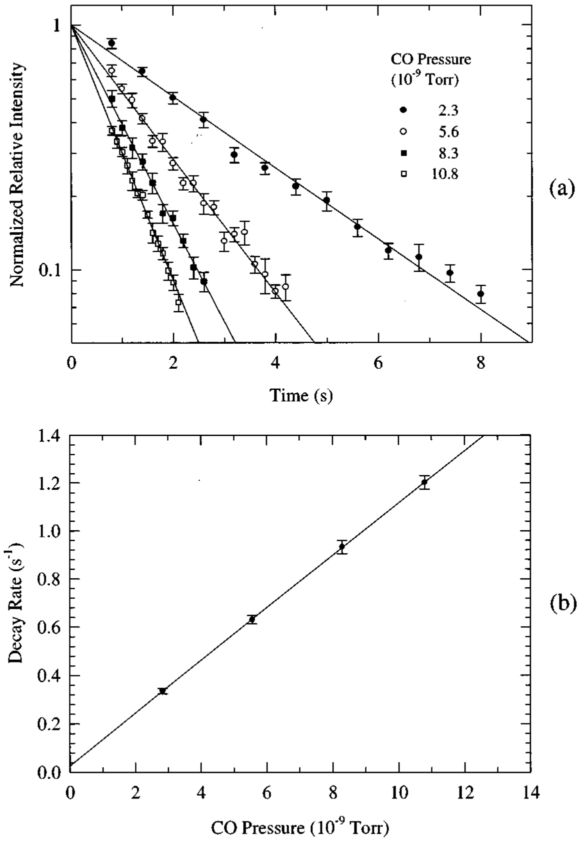

FIG. 2. (a) The normalized relative intensity of N^{2+} vs storage time at four different pressures of CO. (b) N^{2+} decay rate vs CO pressure.

$$R = n_m \langle v_1 q_1 \rangle + n_b \langle v_2 q_2 \rangle = n_m K + R_b, \tag{5}$$

where n_m is the density of the reactant gas, n_b is the density of the residual background gas in the ultrahigh vacuum chamber, $I_r(t)$ is proportional to the number of N^{2+} ions at time t, q_1 and q_2 are the charge-transfer cross sections to all channels including single and multiple electron transfer with the reactant molecular gas and with residual gas, respectively, and v_1 and v_2 are the relative velocities of the interacting multiply charged ions with reactant gas molecules and the residual gas molecules, respectively. R_b is the decay rate of N^{2+} in the ultrahigh vacuum system with only residual background gas present. The data set containing the mean relative intensity $I_r(t)$ (cf. Sec. II) was fitted to Eq. (4) using the weighted least-squares method. The weight for each point is determined from 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 each reactant molecular gas density n_m to Eq. (5). The uncertainty of the rate coefficient was a quadratic sum of the statistical uncertainty derived from the data fitting and the uncertainty of the reactant gas density measurement. Absolute calibration of the ion gauge to measure the reactant gas density has been described in a previous publication [14] and will not be elaborated here.

The data and their fitting curves for the reaction $N^{2+} + H_2 \rightarrow$ products are shown in Figs. 1(a) and 1(b). Figure 1(a) shows the decay of the relative N^{2+} intensities at four different H_2 pressures. The solid lines represent the result of the weighted least-squares fit. Figure 1(b) plots the decay rates as a function of H_2 pressure. The slope of the solid line gives the charge transfer rate coefficient of $3.38(0.35) \times 10^{-11}$ cm^3 s^{-1}. In a similar way, Figs. 2(a) and 2(b) show the results of the reaction $N^{2+} + CO \rightarrow$ products. The rate coefficient of N^{2+} with CO is $3.37(0.29) \times 10^{-9}$ cm^3 s^{-1}.

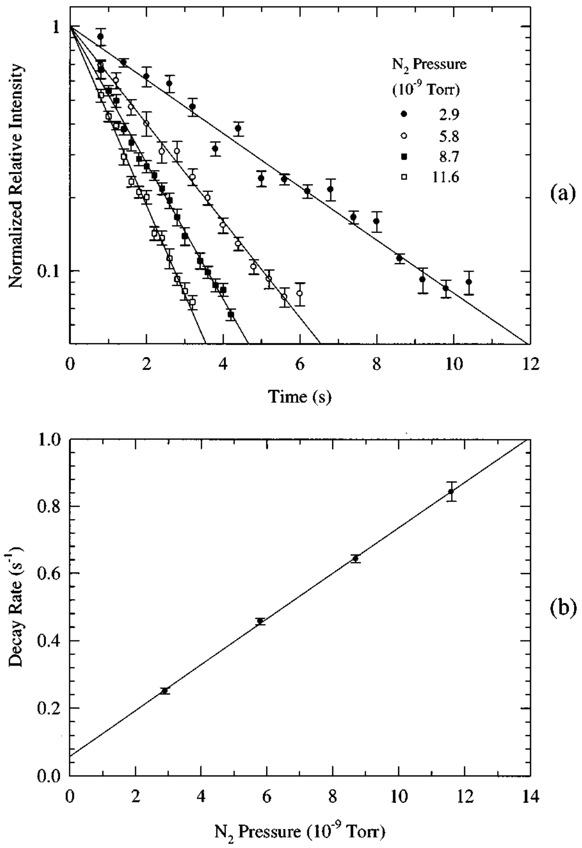

FIG. 3. (a) The normalized relative intensity of N^{2+} vs storage time at four different pressures of N_2. (b) N^{2+} decay rate vs N_2 pressure.

The N^{2+} with N_2 measurement was carried out with two different ion sources: (a) laser ablation ion source as was described in Sec. II and (b) the electron impact ionization ion source with N_2 as the parent gas. The results of these two measurements are consistent: $2.10(0.18) \times 10^{-9}$ cm^3 s^{-1} for the laser ablation method, and $2.0(0.2) \times 10^{-9}$ cm^3 s^{-1} for the electron impact ionization method. These results are also consistent with our previous result of $1.73(0.18) \times 10^{-9}$ cm^3 s^{-1} [14]. Both measured results are in agreement with that obtained by Church and Holzscheiter [16]. Figures 3(a) and 3(b) show the results using the laser ablation method.

IV. DISCUSSION

The N^{2+} ions produced by laser ablation can be in a variety of excited electronic states immediately after they are produced. They rapidly cascade to their ground state and low lying metastable states through allowed transitions and collisional deexcitations by plasma electrons. We have shown in previous measurements that the ions stored in the trap produced by low laser power are in their ground state [1,9,15]. Furthermore, N^{2+} has only one low lying $2s2p^2(\,^4P)$ metastable state with three fine structure levels. Their lifetimes are: 0.98 ms, 13.4 ms, and 3.2 ms for the ^4P_j with $j=\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$, respectively [17]. At the time we start to measure the ion intensity (0.4 s after the laser ablation), the stored metastable N^{2+} ions, if there are any, should have decayed to the $2s^22p(\,^2P^o)$ ground state.

The mean energy of the stored N^{2+} ions is about 2.7 eV [1,18]. This mean energy corresponds to an ion temperature of about 2.1×10^4 K, which can be calculated by using the relation that the mean energy $\overline{E}$ and the temperature T is related by $\overline{E}=\frac{3}{2}kT$ since the velocity distribution of the ions in an rf trap is nearly thermal [18]. Because the temperature of the neutral reactant gas is at room temperature (300 K), we introduce an equivalent temperature corresponding to the mean relative velocity of the N^{2+} and the reactant gas molecules [19]. This equivalent temperature T_{equiv} of the colli--sional 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 and the reactant gas temperature is T_n. m_i and m_n are the masses of the ion and the neutral, respectively, and μ is their reduced mass. Using this relation, the equivalent temperatures for each measurement are estimated to be 2.9×10^3 K for N^{2+} with H_2, 1.3×10^4 K for N^{2+} with CO and N_2.

The above data show that the charge transfer reaction for N^{2+} with H_2 is slower by two orders of magnitude than that for N^{2+} with CO and N_2, even though all three reactant molecules have similar ionization potentials. Furthermore, the charge transfer reaction with H_2 is slower than that with He [13]. This could presumably be due to the sparsity of low-lying electronic states of ${H_2}^+$.

ACKNOWLEDGMENTS

We acknowledge the technical assistance of Heinz Knocke. Helpful discussions with Phillip Stancil are appreciated. This work is supported by FY 95 Nevada EPSCoR Laser Physics Program and NASA Grant No. NAGW-4279 to UNLV.

---

[1] V. H. S. Kwong and Z. Fang, Phys. Rev. Lett. **71**, 4127 (1993).
[2] M. Pieksma, M. Gargaud, R. McCarroll, and C. C. Havener, Phys. Rev. A **54**, R13 (1996).
[3] B. R. Beck, J. Steiger, G. Weinberg, D. A. Church, J. McDonald, and D. Schneider, Phys. Rev. Lett. **77**, 1735 (1996).
[4] D. A. Church, Phys. Rep. **228**, 253 (1993).
[5] M. Gargaud and R. McCarroll, J. Phys. B **18**, 463 (1985).
[6] M. Kimura and N. F. Lane, Phys. Rev. A **35**, 70 (1987).
[7] Y. Sun, H. R. Sadeghpour, K. Kirby, and A. Dalgarno, Int. Rev. Phys. Chem. **15**, 53 (1996).
[8] A. Dalgarno, Nucl. Instrum. Methods B **9**, 655 (1985).
[9] Z. Fang and V. H. S. Kwong, Phys. Rev. A **51**, 1321 (1995).
[10] M. Gargaud, M. C. Bacchus-Montabonel, and R. McCarroll, J. Chem. Phys. **99**, 4495 (1993).
[11] M. Kimura, J. P. Gu, G. Hirsch, and R. J. Buenker, Phys. Rev. A **53**, 4164 (1996).
[12] S. E. Butler, T. G. Heil, and A. Dalgarno, Astrophys. J. **241**, 442 (1980).
[13] Z. Fang and V. H. S. Kwong, Astrophys. J (to be published).
[14] V. H. S. Kwong, T. T. Gibbons, Z. Fang, J. Jiang, H. Knocke, Y. Jiang, B. Rugar, S. Huang, E. Braganza, and W. Clark, Rev. Sci. Instrum. **61**, 1931 (1990).
[15] Z. Fang and V. H. S. Kwong, Rev. Sci. Instrum. **65**, 2143 (1994).
[16] D. A. Church and H. M. Holzscheiter, Chem. Phys. Lett. **76**, 109 (1980).
[17] Z. Fang, V. H. S. Kwong, and W. H. Parkinson, Astrophys. J. **413**, L141 (1993).
[18] R. D. Knight and M. H. Prior, J. Appl. Phys. **50**, 3044 (1979).
[19] A. S. Dickinson (private communication).