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Pulse Radiolysis Studies of Collisional Deexcitation of $Ne(^3P_1)$ by H_2

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ABSTRACT

The cross sections for the deexcitation of $Ne(^3P_1)$ by H_2 have been measured as a function of the mean collisional energy in the range of 17.3-37.9 meV or in the temperature range from 134 K to 293 K using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy. The deexcitation cross sections are in the range of 2.1- 5.6 $Å^2$ for $Ne(^3P_1)$ and nearly constant or increase slightly with increasing the collisional energy.

Key words: Pulse radiolysis method, deexcitation cross sections, resonant atoms, collisional energy

INTRODUCTION

The lowest excited atoms are divided as short-lived resonant atoms and long-lived metastable atoms. Deexcitation of excited rare gas atoms in metastable states has been studied extensively (Hatano 1991, Hotop & Niehaus 1969, Siska 1993, Ukai & Hatano 1991). Because of experimental difficulties, however, the reported cross sections for the deexcitation of resonant helium, neon and argon atoms by various atoms and molecules are still limited (Khadka *et al.* 1997, Kitajima *et al.* 1994, Yokoyama *et al.* 1980, Yoshida *et al.* 1991, Yoshida *et al.* 1992).

The rate constants or the cross sections for the deexcitation processes have been measured by several methods such as a flowing afterglow technique, a beam method, and a pulse radiolysis method. A few measurements of the rate constants or cross sections for the deexcitation of excited neon atoms have been studied in comparison with the excited helium atoms (Brunetti & Vecchiocattivi 1993, Fukuzawa *et al.* 2003, Hatano 1989, Hatano 1991, Hatano 1992, Hotop & Niehaus 1969, Khadka *et al.* 1997, Kitajima *et al.* 1994, Siska 1993, Ukai & Hatano 1991).

In this investigation, the cross sections for the deexcitation of $Ne(^3P_1)$ by H_2 have been measured as a function of the mean collisional energy in the range of 17.3-37.9 meV or in the temperature range from 134 K to 293 K using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy.

MATERIALS AND METHODS

Experiment

Sample gases used were all research grade. The Ne, H_2, and SF_6 and have purities of 99.99%, 99.9999% and 99.8% and mixture of (SF_6/Ne = 0.000747). The SF_6 was used after freeze pumping purification under 77 K.

A pulse radiolysis method, which has the advantage of measuring absolute deexcitation cross sections, is employed in this experiment. The experimental apparatus and experimental procedure have been described in detail previously (Fukuzawa *et al.* 2003, Hatano 1989, Hatano 1991, Hatano 1992, Khadka *et al.* 1997, Khadka *et al.* 1998-99, Kitajima *et al.* 1994, Ukai & Hatano 1991). The excitation source is a single nanosecond electron beam pulse (the maximum electron energy: □ 600 keV, a peak current: □ 7 kA) from a Febetron 706. The optical detection system is composed of an Ushio 450 W xenon flash lamp, a JASCO CT-100 1m grating monochromator and a Hamamatsu Photonics R-928 photomultiplier tube. The signal is stored in a transient digital memory, which is connected with a microcomputer. The time resolution of the signal detection system is 10 ns which are mainly due to the time width of each resolved channel of transient digital memory.

The sample cell is a 65 mm long, 30 mm internal diameter cylinder of Pyrex glass or quartz which has two optical windows perpendicular to the direction of the excitation electron beam. The front end of the cylinder is sealed with 80 μm thick aluminum foils which is the target window for the excitation beam by Arraldite cement and the near end is closed. The cell, which is set in a copper holder for homogeneous cooling, is put in a Dewar vessel for the measurements at low temperatures. The Dewar vessel is 500 mm tall and 90 mm internal diameter and has a 20 mm internal diameter aperture on the side for the excitation beam, which is sealed with polymer film from both inside and outside of the vessel for thermal insulation.

Temperature control is carried out by the rate of cold N_2 gas flow to Dewar vessel. The flow rate of cold N_2 gas is

regulated by electric current through a heater in a liquid N_2 container and the current is controlled by a copper-constantan thermocouple attached to the cell holder and by a thermo controller and a thyristor (Oyo-Denshi U-1326-2A and U-1111). The temperature of the cell is monitored at two points on the outside of it. Accuracy of temperature control is within ±2 deg. The time- resolved optical absorption of [Ne($^3P_1$) : $1s_4$ ® $2p_3$] at 607.43 nm was measured, thereby, the time dependent variation of the density of Ne($^3P_1$) was obtained. Artifacts such as collisional mixing and cascade optical emission followed by recombination, which are due to thermal electrons, are almost completely removed by the addition of SF_6 as a thermal electron scavenger.

RESULTS AND DISCUSSION

From the obtained time dependent density signals of Ne*, where Ne* is Ne ($^3P_1$), the deexcitation rate constants, and thus cross sections, are obtained. In the deexcitation of Ne* in the present condition of a Ne-SF_6-M system, the following reactions are exclusively dominant (Fukuzawa *et al.* 2003, Hatano 1991, Khadka *et al.* 1997, Khadka *et al.* 1998-99, Kitajima *et al.* 1994, Ukai & Hatano 1991).

$$\mathrm{Ne^*} \xrightarrow{\tau_0^{-1}} \mathrm{Ne\ (in\ pure\ Ne)}, \text{ ....} \quad (1)$$

$$\mathrm{Ne^* + SF6} \xrightarrow{k_{SF6}} \mathrm{Products}, \text{ ....} \quad (2)$$

$$\mathrm{Ne^* + M} \xrightarrow{k_M} \mathrm{Products}, \text{.... ....} \quad (3)$$

where t_0 is the effective lifetime of Ne* in pure Ne, k_{SF6} and k_M are the deexcitation rate constants of Ne* by SF_6 and H_2. The value of k_{SF6} was obtained previously (Yokoyama *et al.* 1980). The total deexcitation rate of Ne($^3P_1$), t^{-1}, at room temperature is given by

$$t^{-1} = t_0^{-1} + k_{SF6}[SF_6] + k_M[M], \text{ ....} (4)$$

where $[SF_6]$ and [M] are the number densities of SF_6 and M, respectively. The value of k_M is given by the slope of t^{-1} vs. $[H_2]$ plots in Fig. 1 at constant $[SF_6]$.

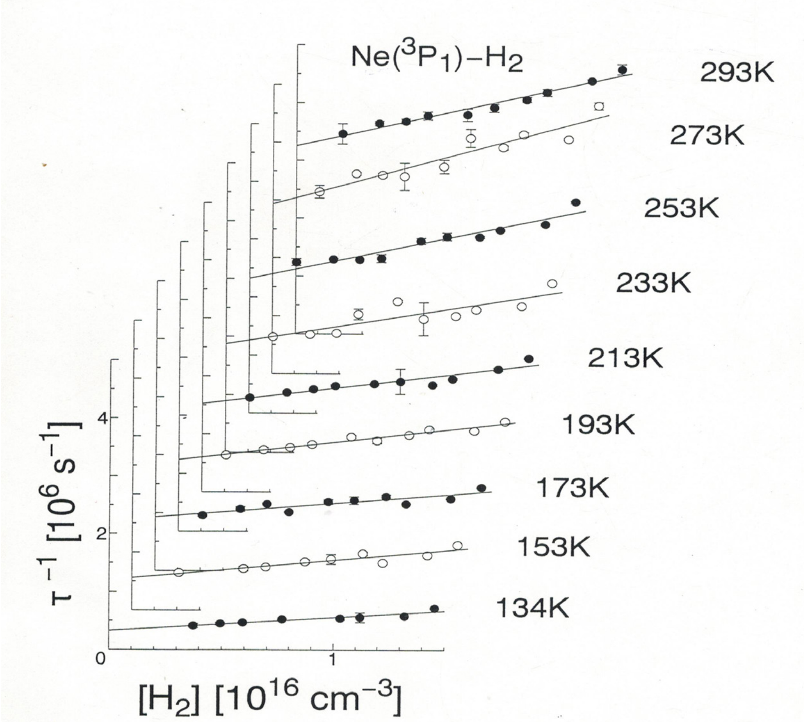

Fig. 1. Kinetic plots for deexcitation rates t^{-1} **versus number densities of H_2 for Ne($^3P_1$).**

In Fig. 2 a typical decay curve is shown for Ne($^3P_1$) by H_2. A total deexcitation rate constant, k_M, at each temperature, T, is converted into a velocity averaged cross section, s_M, at a mean collisional energy, E = (3/2) k_BT, following,

$$s_M = k_M / (8k_BT/pm)^{1/2} \quad (5)$$

where k_B is the Boltzmann constant, T is the absolute temperature and m is the reduced mass of Ne and H_2, respectively.

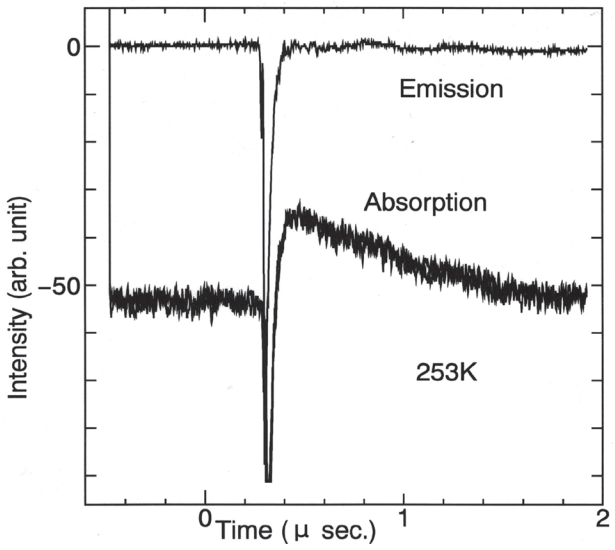

Fig. 2. Decay curve for Ne($^3P_1$)-H_2 system. Ne(200 Torr), H_2 (0.128 Torr) and SF_6 (0.136 Torr). λ = 607.43 nm; ($1s_4$ ® $2p_3$).

To the best of my knowledge, this is the first measurement of the temperature dependence rate constants or the collisional energy dependence of the deexcitation cross sections of Ne($^3P_1$) by H_2. The obtained experimental cross sections for the deexcitation of Ne($^3P_1$) by H_2 as a function of the mean collisional energy are shown in Fig. 3. The deexcitation cross sections are in the range of 2.1-5.6 Å^2 for Ne($^3P_1$) and nearly constant or increase slightly with increasing the collisional energy.

The present cross sections at the mean collisional energy corresponding room temperature are in agreement with those by Yokoyama & Hatano using the pulse radiolysis method. The excitation energy of the resonance atom Ne($^3P_1$) exceeds the ionization potentials of the H_2. Thus, the initial state of the collision complex is imbedded in a continuum and is subject to rapid auto-ionization. In the present case, the possibility of several ionization channels, in addition to Penning ionization and associative ionization, molecular ion decomposition or rearrangement ionization can also occur. Based on the reported results of West *et al.* 1975, the possible ion products for Ne($^3P_{2,0}$) by H_2 are $H_2^+ : NeH^+ : NeH_2^+$ which were determined to be in a 78:20:2 at a collisional energy around 45 meV. Similar branching ratio might be expected for the deexcitation of Ne($^3P_1$) by H_2. These branching's are not due to the different process but by the transfer of excitation energy. Further experimental and theoretical results on the wide collisional energy dependence of the cross sections for deexcitation of the Ne($^3P_1$) by H_2 should be done by various researchh groups.

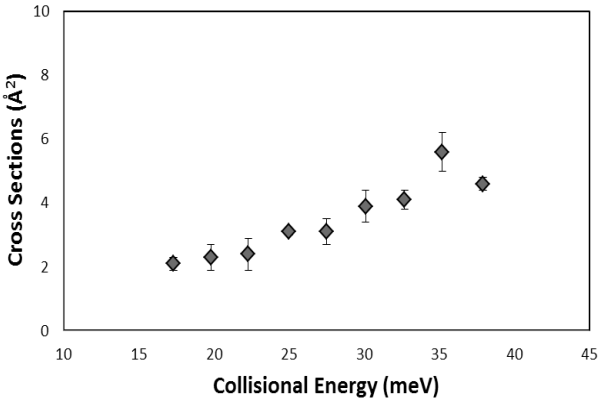

Fig. 3. The experimental Cross sections for deexcitation of Ne($^3P_1$) by H_2

CONCLUSIONS

In this research work, the cross sections for the deexcitation of Ne($^3P_1$) by H_2 have been measured as a function of the mean collisional energy in the range of 17.3-37.9 meV or in the temperature range from 134 K to 293 K using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy. The deexcitation cross sections are in the range of 2.1- 5.6 Å^2 for Ne($^3P_1$) and nearly constant or increase slightly with increasing the collisional energy. Theoretical and experimental works on the wide collisional energy dependence of the cross sections for deexcitation of the Ne($^3P_1$) by H_2 should be investigated by various research groups.

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