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Pulse Radiolysis Studies of Collisional Deexcitation of $Ne(^3P_2)$ by N_2

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Abstract

The temperature dependence of the rate constants for the deexcitation of $Ne(^3P_2)$ by N_2 has been measured in the temperature range from 136 K to 294 K using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy and thus the collisional energy dependence of the deexcitation cross sections is obtained. The deexcitation cross sections are in the range of 6.1- 9.3 Å^2 for $Ne(^3P_2)$ and almost constant or increase slightly with increasing the collisional energy. The deexcitation cross sections are compared with those various reported methods. The results of $Ne(^3P_2)$ by N_2 has been also compared with the results of $Ne(^3P_1)$ by N_2. The comparison shows that more experimental and theoretical research works should be needed to clarify the deexcitation mechanism.

Keywords: Dewar vessel, pulse radiolysis method, metastable atoms, deexcitation cross sections.

Introduction

Collisional deexcitation of excited rare gas atoms by atoms and molecules is of great importance in both fundamental and applied sciences, which provides the essential features of chemical reactions, in particular, those including electronic energy transfer[1-4]. The collisional deexcitation is a key also to understand fundamental processes in the interaction of ionizing radiation with matter and the phenomena in ionized gases such as reactive plasmas and upper atmosphere[4-7].

The rate constants or the cross sections of these processes have been measured by various techniques such as flowing afterglow, beam, and pulse radiolysis methods. There have been several repots for the measurements of the rate constants or cross sections for the deexcitation of excited helium atoms in comparison with the excited neon atoms[1-11]. A number of theoretical investigations of these processes have been made[12-16] and the present author has also been reported the collisional energy dependence of the cross sections for deexcitation of the resonance and metastable states[8-10]. Recently several research works have also been published[17-20].

In the present investigation, the cross sections for the deexcitation of $Ne(^3P_2)$ by N_2 has been measured as a function of the mean collisional energy in the range of 17.5-37.9 meV or in the temperature range from 136 K to 294 K using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy. The measured deexcitation cross sections are in the range of 6.1- 9.3 Å^2 for $Ne(^3P_2)$ and almost constant or increase slightly with increasing the collisional energy. The results of $Ne(^3P_2)$ by N_2 has been also compared with the results of $Ne(^3P_1)$ by N_2. The comparison shows that more experimental and theoretical research works should be needed to clarify the deexcitation mechanism.

Material and Methods

Sample gases used were all research grade. The Ne (99.99%), N_2 (99.9999%), and SF_6 (99.8%) and mixture (SF_6/Ne = 0.000747), where the values in the parentheses are the stated purity. 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 for the measurement of time-resolved optical absorption by a pulse-radiolysis method is schematically shown in figure 1. 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 1 m 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.

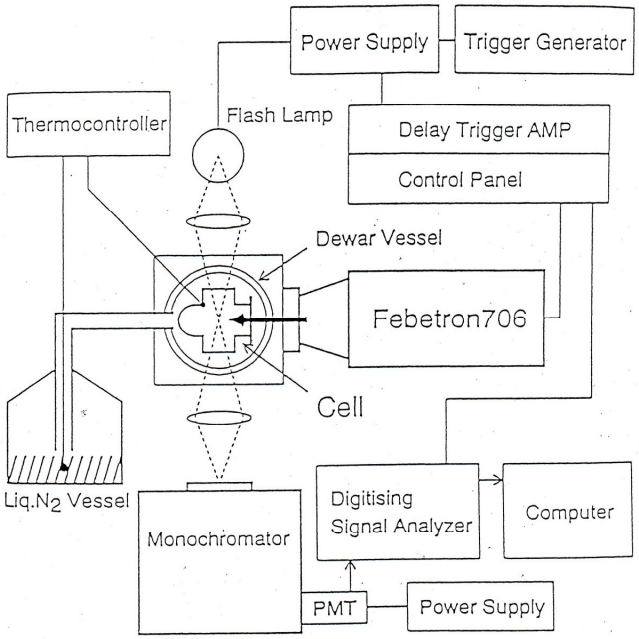

Figure-1
Experimental apparatus

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 $[Ne(^3P_2) : 1s_5 \rightarrow 2p_8]$ at 633.44 nm was measured, thereby, the time dependent variation of the density of $Ne(^3P_2)$ 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

The obtained time dependent density signals of Ne*, where Ne* is Ne ($^3P_2$), 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[3-6, 8-11].

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

$$Ne^* + SF_6 \xrightarrow{k_{SF6}} \text{Products}, \quad (2)$$

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

where τ_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 N_2. The value of k_{SF6} was obtained previously[21]. The total deexcitation rate of $Ne(^3P_2)$, τ^{-1}, at room temperature is given by

$$\tau^{-1} = \tau_0^{-1} + k_{SF6}[SF_6] + k_M[M], \quad (4)$$

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 τ^{-1} vs. $[N_2]$ plots in figure 2 at constant $[SF_6]$.

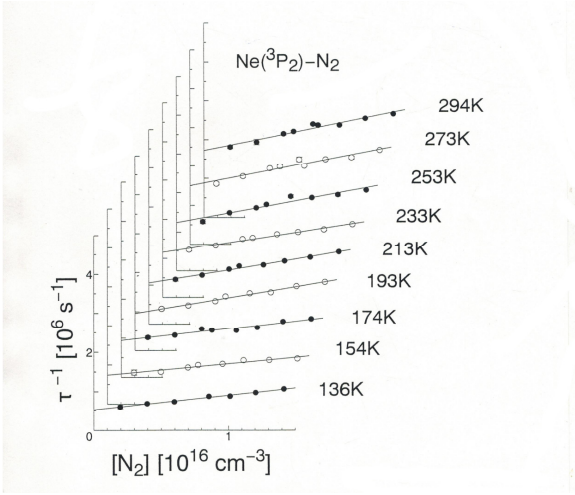

Figure-2
Kinetic plots for deexcitation rates τ^{-1} versus number densities of N_2 for $Ne(^3P_2)$

In figure 3 a typical decay curve is shown for $Ne(^3P_2)$ by N_2. A total deexcitation rate constant, k_M, at each temperature, T, is converted into a velocity averaged cross section, σ_M, at a mean collisional energy, $E = (3/2)\, k_B T$, following,

$$\sigma_M = k_M / (8k_B T/\pi\mu)^{1/2} \quad (5)$$

where k_B is the Boltzmann constant, T is the absolute temperature and μ is the reduced mass of Ne and N_2, respectively.

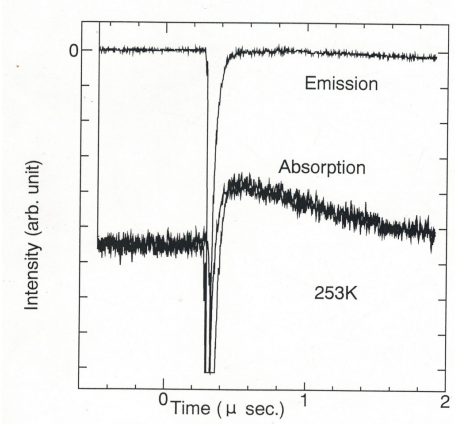

Figure – 3
Decay curve for $Ne(^3P_2)$-N_2 system. Ne (200 Torr), N_2 (0.265 Torr) and SF_6 (0.133 Torr). λ = 633.44 nm; ($1s_5 \rightarrow 2p_8$)

The obtained experimental cross sections for the deexcitation of $Ne(^3P_2)$ by N_2 as a function of the mean collisional energy are shown in figure 4. The deexcitation cross sections are in the range of 6.1- 9.3 $Å^2$ for $Ne(^3P_2)$ and almost constant or increase slightly with increasing the collisional energy. 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 $Ne(^3P_2)$ by N_2 using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy. Since electronic energy of the lowest excited $Ne(^3P_2)$ (16.62 eV) exceeds the ionization potentials of the N_2 (15.58 eV). Therefore the possibility of several ionization channels, in addition to Penning ionization and associative ionization can also occur. The reported results of West et al. show that the possible ion products for $Ne(^3P_{2,0})$ by N_2 are $N_2^+ : NeN_2^+$ which were determined to be in a 94.1:5.9 at a collisional energy around 45 meV[22]. Similar branching ratio might be expected for the deexcitation of $Ne(^3P_2)$ by N_2. The present cross sections at the mean collisional energy corresponding room temperature are in agreement with those by Yokoyama and Hatano using the pulse radiolysis method[23]. There have been limited data for the deexcitation of $Ne(^3P_2)$ by N_2 compared to those deexcitation of $Ne(^3P_2)$ by rare gas atoms. The obtained deexcitation cross sections of $Ne(^3P_2)$ by N_2 together with the reported data are shown in figure 5. The comparison shows that the collisional energy dependence of the cross sections has the same general behavior. The present cross sections are in good agreement within the experimental errors with those obtained by West et al., Yokoyama and Hatano and Broom et al. at room temperature[22-24]. The cross sections obtained by Baudon et al., van den Berg et al. and Aguilar et al. are larger than the present cross sections for $Ne(^3P_2)$ by N_2[25-27]. The present cross sections are velocity averaged, so I average the compiled results of velocity selected cross sections in Baudon et al. (—— in figure 5) with a Maxwellian velocity distribution to allow a more direct comparison[25]. However, such velocity averaged cross sections in figure 5 still have different cross sections as the unaveraged ones. Since the data for the metastable states have been obtained with quite different experimental methods, systematic experimental error could be involved in either or both sets of experiments. On the other hand, there is no results for $Ne(^3P_2)$ by N_2 in the investigated energy range by various methods. Thus it would be useful to compare the results to the cross sections for the same experimental method and collisional energy but so far there have not been determined. The reported deexcitation cross sections are in the range of 9.7- 16.3 $Å^2$ for $Ne(^3P_1)$ and the values are slightly larger than those of $Ne(^3P_2)$ by N_2[9]. The behavior of the collisional energy dependence are similar both of the metastable and resonant states. Experimental and theoretical results on the wide collisional energy dependence of the cross sections for deexcitation of the $Ne(^3P_2)$ by N_2 should be investigated by various research groups and methods.

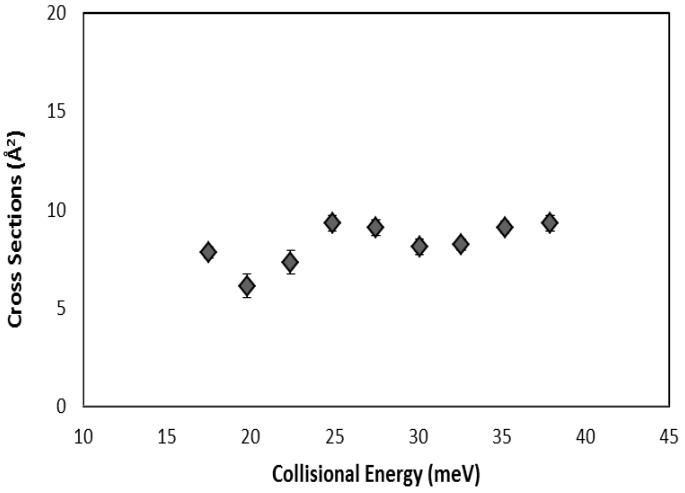

Figure-4
The experimental cross sections for deexcitation of $Ne(^3P_2)$ by N_2

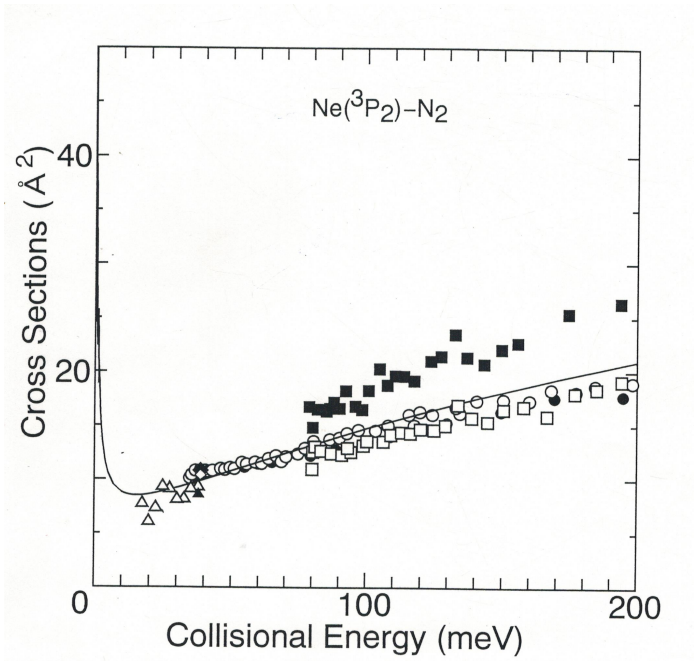

Figure-5
A comparison of the cross sections for deexcitation of $Ne(^3P_2)$ and $Ne(^3P_{2,0})$ by N_2 with those different experiments. Δ: represent the present results

Conclusion

In the present research work, the cross sections for the deexcitation of $Ne(^3P_2)$ by N_2 has been measured as a function of the mean collisional energy in the range of 17.5-37.9 meV or in the temperature range from 136 K to 294 K using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy. The measured deexcitation cross sections are in the range of 6.1- 9.3 $Å^2$ for $Ne(^3P_2)$ and almost

constant or increase slightly with increasing the collisional energy. The results of $Ne(^3P_2)$ by N_2 has been also compared with the results of $Ne(^3P_1)$ by N_2.

A better understanding of the deexcitation mechanisms for the $Ne(^3P_2)$ by N_2 can be achieved by considering information on different observations such as crossed beam results and flowing afterglow results in a wide collisional energy. Theoretical investigations such as an *ab initio* calculation of the optical potentials are greatly needed for further understanding.

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