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Measurement of Deexcitation Cross Sections of Ne($^3P_1$) by CH_4 Using a Pulse Radiolysis Method

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Abstract

The cross sections for the deexcitation of Ne($^3P_1$) by CH_4 have been measured as a function of the mean collisional energy in the range of 17.2-36.8 meV or in the temperature range from 134 K to 285 K using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy. The deexcitation cross sections are in the range of 10- 24 Å^2 for Ne($^3P_1$) by CH_4. The behavior of the collisional energy dependence cross sections are increase slightly with increasing the collisional energy. The results are interpreted in terms of an electron –exchange interaction.

Keywords: Pulse radiolysis method, resonance atoms, collisional energy, electron-exchange interaction and 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].

Collisional deexcitation processes of excited neon atoms have not been extensively studied in comparison with those of excited helium atoms[1-13]. On the other hand, there are limited data for resonance atoms. A major part of the deexcitation of the lowest excited neon and helium atoms by atoms and molecules, M, is ascribed to the collisional ionization of M[1-7]. Previous studies of the collisional deexcitation of excited rare gas atoms have shown that a pulse radiolysis method combined with the time-resolved optical emission and absorption spectroscopy has a clear advantage over the others methods such as flowing afterglow and beam methods to obtain absolute rate constants or the cross sections for the deexcitation of excited rare gas atoms not only in metastable states but also in resonant states[2, 3-6]. There have been several research works published [14-22] and the present author has also been reported the collisional energy dependence of the cross sections for deexcitation of the resonance and metastable states[8-11].

In this paper, the cross sections for the deexcitation of Ne($^3P_1$) by CH_4 have been measured as a function of the mean collisional energy in the range of 17.2-36.8 meV or in the temperature range from 134 K to 285 K using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy.

Material and Methods

For measuring the deexcitation cross sections a pulse radiolysis method is employed. The experimental apparatus and experimental procedure have been described in detail previously[3-6,7-11,23]. Briefly, after an irradiation by an intense electron beam pulse onto a mixture of Ne with a trace amount of SF_6 and M (M = CH_4) in a gas cell, the time- resolved optical absorption of [Ne($^3P_1$) : $1s_4 \rightarrow 2p_3$ 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. The temperature of a sample gas, which corresponds to a mean collisional energy, is controlled by introducing cold N_2 vapor onto the gas cell. The cell was kept temperature range from room temperature to 134 K within the error limit of ± 2 degree. Sample gases used were research grade. Pure Ne (99.99%), and mixture of Ne-CH_4 (CH_4/Ne = 0.0201) and (SF_6/Ne = 0.000747), where the values in the parentheses are the stated purity.

Results and Discussion

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[3-6, 8-11, 23].

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

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

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

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 CH_4. The value of k_{SF6} was obtained previously[24]. The total deexcitation rate of $Ne(^3P_1)$, 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. $[CH_4]$ plots in figure 1 at constant $[SF_6]$.

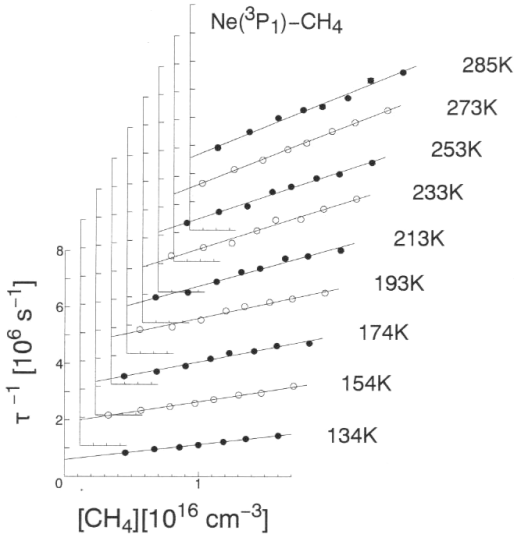

Figure-1
Kinetic plots for deexcitation rates τ^{-1} versus number densities of CH_4 for $Ne(^3P_1)$

In figure 2 a typical decay curve is shown for $Ne(^3P_1)$ by CH_4. 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 CH_4, respectively.

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 CH_4 using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy. The obtained experimental cross sections for the deexcitation of $Ne(^3P_1)$ by CH_4 as a function of the mean collisional energy are shown in figure 3. The deexcitation cross sections are in the range of 10-24 $Å^2$ for Ne($^3P_1$) by CH_4. The behavior of the collisional energy dependence cross sections are increase slightly with increasing the collisional energy. The experimental cross sections and their collisional energy dependence are compared with the Watanabe and Katsuura (WK) theoretical ones in figure 4. The absolute values of the experimental cross sections are in the same order of magnitude as the theoretical cross sections (σ_{WK}). Strictly speaking, however, the experimental cross sections are smaller for CH_4 than those by σ_{WK}. The energy dependence of the present cross sections is not correctly explained by σ_{WK}. Previously it was concluded that the WK formula does not reproduced well, even qualitatively, the deexcitation cross sections of $Ne(^3P_1)$ in collisions with rare gas atoms[8] due the rectilinear-trajectory approximation and the assumption of the only dominating dipole-dipole interaction. I pointed out the importance of bent trajectories and an electron exchange interaction. The difference between σ_{WK} and present experimental cross sections for $Ne(^3P_1)$ by CH_4 can be explained in the same manner.

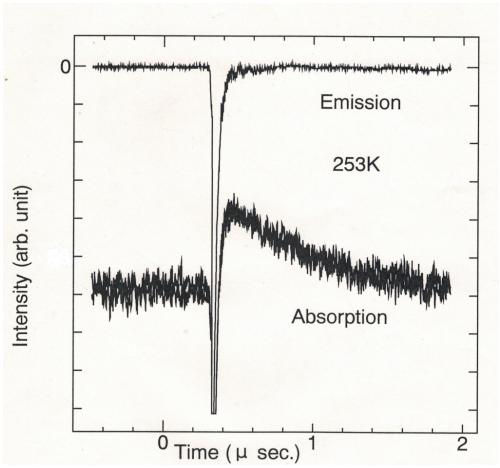

Figure-2
Decay curve for $Ne(^3P_1)$-CH_4 system. Ne (200 Torr), CH_4 (0.17 Torr) and SF_6 (0.18 Torr). λ = 607.43 nm; ($1s_4 \rightarrow 2p_3$)

The collisional energy dependence of the cross sections for the deexcitation of $Ne(^3P_1)$ by CH_4 is shown in figure 4 for comparison by plotting the experimental results together with both the results of optical model calculation and the results using the WK formula (σ_{WK}). The absolute values of the cross sections are in good agreement with the results of optical model calculation and explained reasonably well. Furthermore, there is obtained significant difference between the calculated cross sections with and without electron exchange interaction, namely, between σ_{diex} and σ_{di}, respectively, which shows predominant contribution of the electron exchange interaction to the deexcitation cross sections. There is also observed small difference between the calculated cross sections of σ_{diex} and σ_{di}. This is due to the contribution from the dipole-dipole interaction. The comparison between the obtained experimental results with theoretical ones confirms that the deexcitation for $Ne(^3P_1)$ by CH_4 is dominated by collisional ionization induced by an electron-exchange interaction. Further experimental

measurements of the cross section in an adequately wide collisional energy and theoretical investigations such as an *ab initio* calculation of the optical potentials are greatly needed for further understanding.

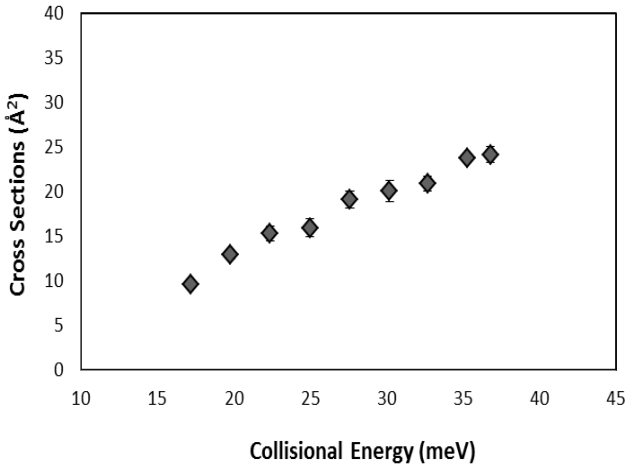

Figure-3
The experimental cross sections for the deexcitation of Ne($^3P_1$) by CH_4

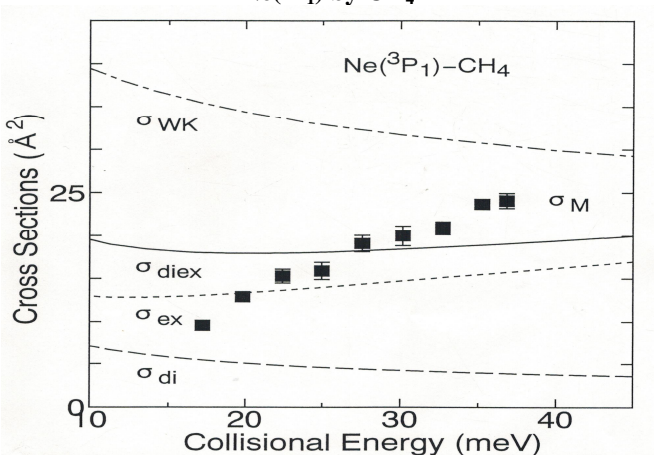

Figure-4
The experimental cross sections for the deexcitation of Ne($^3P_1$) by ■: CH_4. Theoretical total Penning ionization cross sections for Ne($^3P_1$) by an optical-model calculation of — — — , σ_{di}; - - - - -, σ_{ex} ; ————, σ_{diex}; considering the dipole-dipole interaction, the electron-exchange interaction, and both, respectively, and a semi-classical cross sections, — - — - —, σ_{WK}; are shown together

Conclusion

In this paper, the cross sections for the deexcitation of Ne($^3P_1$) by CH_4 have been measured as a function of the mean collisional energy in the range of 17.2-36.8 meV or in the temperature range from 134 K to 285 K using a pulse radiolysis method as combined with time-resolved optical absorption spectroscopy. The deexcitation cross sections are in the range of 10- 24 Å^2 for Ne($^3P_1$) by CH_4. The behavior of the collisional energy dependence cross sections are increase slightly with increasing the collisional energy. The results are interpreted in terms of an electron–exchange interaction.

For further understanding of the deexcitation mechanisms for the Ne($^3P_1$) by CH_4 cross sections in an adequately wide collisional energy and theoretical investigations such as an *ab initio* calculation of the optical potentials are greatly needed.

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