

PULSE RADIOLYSIS STUDIES OF THE DE-EXCITATION
 PROCESSES OF EXCITED RARE GAS ATOMS

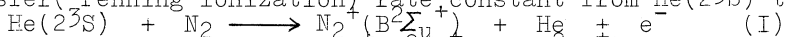
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Recently there have been increased interests in the de-excitation processes of rare gas excited atoms in many fields such as radiation chemistry, astrophysics, and gaseous electronics. The rate constants or the cross sections of these processes have been measured using a flowing afterglow technique, a crossed molecular beam method, a pulsed discharge method, etc.

We have recently investigated energy transfer processes from some excited rare gas atoms to many kinds of molecules using a pulse radiolysis technique combined with optical emission spectroscopy and microwave cavity technique. The experimental apparatus is sketched in fig.1. A Febetron 706, which produces a several nsec pulse of 600 kev electrons, was used as the electron pulse source²⁾.

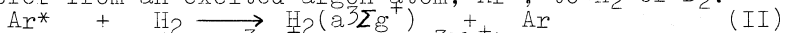
We have presented the first attempt of the application of the pulse radiolysis technique to the determination of the energy transfer (Penning ionization) rate constant from He(2^3S) to N_2^+ .



The emission decay rate of $N_2^+(B^2\Sigma_u^+ \longrightarrow X^2\Sigma_g^+)$ varies as a function of He or N_2 pressures. From the kinetic plots of the data, the rate constant of the process (I) is obtained to be $(6.8 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. The addition of other atoms or molecules, M, to He- N_2 mixtures changes the decay rate of the optical emission of $N_2^+(B^2\Sigma_u^+ \longrightarrow X^2\Sigma_g^+)$. From the kinetic plots of the data, the rate constants for He(2^3S) de-excitation by M are obtained (Table I)⁴⁾. The de-excitation cross section, σ , calculated by dividing the measured rate constant, k, by the relative velocity of the reacting particles in thermal equilibrium has been correlated with some physical constants for M. For example, the σ 's are plotted as a function of polarizability, α , in fig.2.

The time resolved measurement⁵⁾ of the concentration of electrons produced by Penning ionization in He- N_2 mixtures has been carried out using the microwave cavity technique combined with pulse radiolysis⁶⁾. The kinetic analysis of the increase in the concentration of electrons gives the rate constant of Penning ionization, which is compared with that obtained above by the optical emission spectroscopy.

The time resolved optical emissions of $H_2(a^3\Sigma_g^+ \longrightarrow b^3\Sigma_u^+)$ and $D_2(a^3\Sigma_g^+ \longrightarrow b^3\Sigma_u^+)$ have been observed in Ar- H_2 and Ar- D_2 mixtures, respectively⁷⁾. These emissions are induced by energy transfer from an excited argon atom, Ar^* , to H_2 or D_2 .



The precursor of $H_2(a^3\Sigma_g^+)$ or $D_2(a^3\Sigma_g^+)$ is not the lowest metastable argon atom or $Ar(^1P_1)$. From the kinetic plots of the data, the energy transfer rate constants in each mixtures are obtained to be $k(Ar^* + H_2) = (8.2 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ and $k(Ar^* + D_2) = (6.8 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. The optical emissions of $N_2(C^3\Pi_u \longrightarrow B^3\Pi_g)$ and $(B^3\Pi_g \longrightarrow A^3\Sigma_u^+)$ have also been observed in Ar- N_2 mixtures. These emissions are induced by energy transfer from the lowest metastable states of argon, $Ar(^3P_{0,2})$, to N_2 , whose rate constant is obtained to be $k(Ar(^3P_{0,2}) + N_2) = (2.3 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$.

We are also carrying out the time resolved measurements of optical absorption of excited rare gas atoms in order to determine their de-excitation rate constants and to compare with the results obtained by optical emission spectroscopy and microwave cavity technique. The experimental apparatus is sketched in fig. 3.

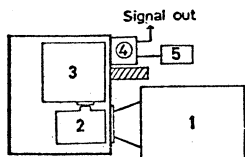


Fig. 1. Experimental apparatus for optical emission spectroscopy. (1)Electron gun,(2)gas cell,(3)monochromator,(4)photo-multiplier,(5)power supply.

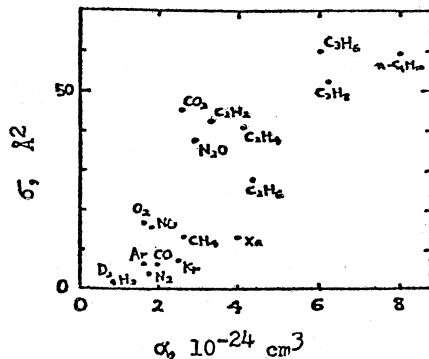


Fig. 2. Variation of He(2^3S) de-excitation cross sections with polarizability.

Table I. He(2^3S) de-excitation rate constants and cross sections.

	k ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)	σ (\AA^2)
Ar	8.9 ± 0.5	6.8
Kr	10.0 ± 0.5	7.8
Xe	17.2 ± 1.0	14
H ₂	4.2 ± 0.6	1.9
D ₂	3.7 ± 0.4	2.1
N ₂	6.8 ± 0.4	5.1
CO	9.2 ± 1.0	6.9
NO	21.4 ± 4.2	16
O ₂	22.8 ± 2.0	17
N ₂ O	50.0 ± 4.0	38
CO ₂	59.0 ± 4.0	45
CH ₄	19.2 ± 1.6	14
C ₂ H ₆	37.5 ± 2.5	28
C ₂ H ₄	55.5 ± 6.5	41
C ₂ H ₂	57.5 ± 6.2	43
C ₃ H ₂	68.5 ± 7.5	52
C ₃ H ₈	80 ± 8	61
C ₃ H ₆	80 ± 8	61
n-C ₄ H ₁₀	78 ± 10	60

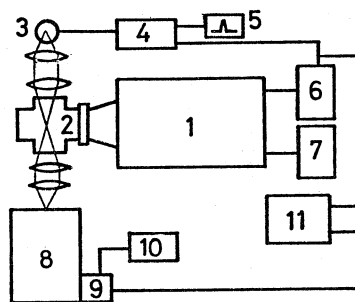


Fig. 3. Experimental apparatus for optical absorption spectroscopy. (1)electron gun,(2)gas sell,(3) flash lamp,(4)power supply,(5) trigger generator,(6)delay trigger amp,(7)power supply,(8)monochromator,(9)photomultiplier,(10)power supply,(11)oscilloscope.

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