ATOMIC AND MOLECULAR PROCESSES IN IONIZED GASES AS STUDIED BY A PULSE RADIOLYSIS METHOD

Y. Hatano, K. Shinsaka, M. Toriumi, H. Koizumi,
M. Ukai, E. Suzuki, and Y. Tanaka
Department of Chemistry, Tokyo Institute of Technology,
Meguro-ku, Tokyo 152

Abstract

The absolute rate constants or cross sections for the de-excitation of excited rare gas atoms have been measured and compared with theories. Thermal electron attachment to O_2 and van der Waals molecules ($O_2 \cdot M$) have been also studied.

1. Introduction

Investigation of atomic processes in ionized gases has been of great importance for understanding and substantiating more the interaction of high energy radiation with matter and various phenomena occurring in electrical discharges, gas lasers, plasmas, and in the upper atmosphere or interplanetary space.

The research described herein has been in progress with the following purposes: 1) To establish the pulse radiolysis method as a useful means for atomic collision research to which it has been difficult to apply other methods such as beam methods, flowing afterglow methods, pulse discharge methods, etc. 2) To get valuable information and idea for substantiating more the fundamental processes of various phenomena in ionized gases.

2. Experimental

A pulse radiolysis method usually comprises the time-resolved measurement of the number density of electrons, ions, excited atoms and molecules, or free radicals formed by irradiation of high intensity pulsed electron beams upon target gases. The experimental apparatuses for measuring signals with fast response and high sensitivity, which are corresponding to the number density of a particular species, are composed of the following two parts: 1) The apparatus for time-resolved optical emission and absorption spectroscopy (Fig.1). This is used for the measurement of ions, free radicals, and excited atoms and molecules. 2) The apparatus for time-resolved microwave cavity technique (Fig.2). This is used for the measurement of electrons.

3. Results and Discussion

3.1. De-excitation of Excited Rare Gas Atoms

There have been few measurements of the de-excitation rate constants or the cross sections for neon 1s states although those for argon, krypton and xenon 1s states and for He(2^3S) have been extensively studied. Therefore we have measured the de-excitation rate constants for Ne($^3P_2$, $^3P_1$, and $^3P_0$) individually by various atoms and molecules.[1,2] This is an extension of our previous work on He(2^3S) de-excitation,[3,4] which was the first attempt of the application of a pulse radiolysis method to Penning ionization.

The temperature dependence of the de-excitation rate con-

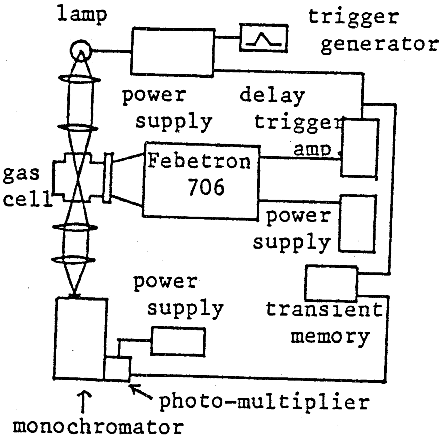

Fig.1 Experimental apparatus for time-resolved optical emission and absorption spectroscopy.

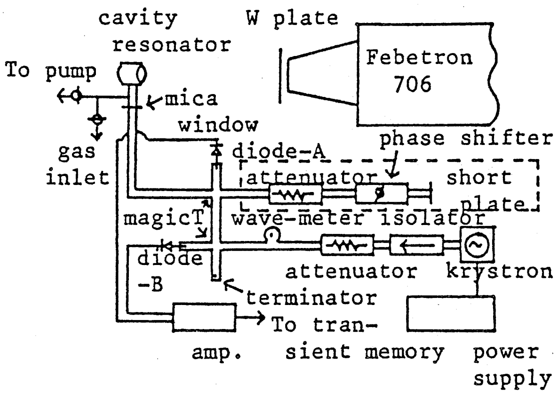

Fig.2 Experimental apparatus for time-resolved microwave cavity technique.

stants has been also measured in expectation of getting the collision energy dependence of the cross sections for both metastable and radiative atoms.[5]

In conclusion, the pulse radiolysis method has definitely various advantages as compared with other methods for determining the absolute de-excitation rate constants or cross sections of excited rare gas atoms.

3.2 Electron Attachment to O_2 and van der Waals Molecules

The low energy electron attachment in O_2 and O_2-M mixtures, where M is a third-body molecule, proceeds via a two-stage three-body process being called the Bloch-Bradbury mechanism:

$$O_2(X^3\Sigma_g^-,\ v=0) + e^- \rightleftarrows O_2^{-*}(X^2\Pi_g,\ v'=4),$$
$$O_2^{-*}(X^2\Pi_g,\ v'=4) + M \longrightarrow O_2^-(X^2\Pi_g,\ v'\leqq 3) + M.$$

We previously investigated[6-8] thermal electron attachment in O_2 and O_2-M mixtures and showed the electron attachment to O_2 could be explained by the Bloch-Bradbury mechanism in many binary gas mixtures, and determined the initial electron attachment rate constant, the lifetime of $O_2^{-*}(X^2\Pi_g,\ v'=4)$, and the overall three-body rate constant for each stabilizing partner M.

We have recently applied this method to measuring electron attachment in dense gases and found an anomalous electron attachment to van der Waals molecules $(O_2 \cdot M)$.[9-14] The rate constant of the initial electron attachment to $(O_2 \cdot M)$ is found to be at least two orders of magnitude larger than that for O_2 itself. An ordinary electron attachment to an isolated single oxygen molecule is highly affected by the presence of surrounding molecules, which probably makes a decrease in the resonance energy with an increase in the resonance width. In conclusion, the pulse radiolysis-microwave cavity technique has definitely various advantages as compared with other methods such as beam method, DC swarm method, ecr method, etc., for investigating low energy electron attachment to molecules.

This method has been recently shown useful also for studying Penning ionization[15] and the energy relaxation of subexcitation electrons.[16]

References

1) A. Yokoyama, S. Takao, T. Ueno and Y. Hatano, Chem. Phys., 45, 439 (1980).
2) A. Yokoyama and Y. Hatano, Chem. Phys., 63, 59 (1981).
3) T. Ueno and Y. Hatano, Chem. Phys. Lett., 40, 283 (1976).
4) T. Ueno, A. Yokoyama, S. Takao and Y. Hatano, Chem. Phys., 45, 261 (1980).
5) H. Koizumi, M. Ukai, K. Shinsaka and Y. Hatano, Chem. Phys., to be published.
6) H. Shimamori and Y. Hatano, Chem. Phys. Lett., 38, 242 (1976).
7) H. Shimamori and Y. Hatano, Chem. Phys., 12, 439 (1976).
8) H. Shimamori and Y. Hatano, Chem. Phys., 21, 187 (1977).
9) Y. Kokaku, Y. Hatano, H. Shimamori and R. W. Fessenden, J. Chem. Phys., 71, 4883 (1979).
10) Y. Kokaku, M. Toriumi and Y. Hatano, J. Chem. Phys., 73, 6167 (1980).
11) H. Shimamori and R. W. Fessenden, J. Chem. Phys., 74, 453 (1981).
12) M. Toriumi and Y. Hatano, J. Chem. Phys., to be published.
13) H. Shimamori and R. W. Fessenden, J. Chem. Phys., 71, 3009 (1979).
14) Y. Hatano and H. Shimamori, "Electron Attachment in Dense Gases" in "Electron and Ion Swarms" ed. by L. G. Christophorou, Pergamon Press (1981), p. 103.
15) Y. Hatano, Y. Kimizuka and H. Shimamori, Radiat. Phys. Chem., 19, 255 (1982).
16) Y. Kokaku, A. Nishikawa and Y. Hatano, to be published.