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IONIZATION OF LONG-LIVED HIGHLY EXCITED STATES OF HYDROGEN AND DEUTERIUM ATOMS BY COLLISION WITH WATER MOLECULES

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Long-lived highly excited Rydberg states of hydrogen (deuterium) atoms, H** or D**, were produced by impact of 80 eV electrons on H_2O or D_2O molecules. The ratio of the ionization cross sections forming protons and deuterons, $\sigma(D^{**}+D_2O \rightarrow D^+ + D_2O + e)/\sigma(H^{**}+D_2O \rightarrow H^+ + D_2O + e)$, was estimated from the dependence of the ion intensities on the target gas pressures to be 1.35±0.15. This ratio is in close agreement with a theoretical estimate, 1.38, based on Matsuzawa's theory predicting the transfer of the rotational energy of a polar target to the Rydberg electron when the excited atom is ionized.

Introduction

Since the presence of long-lived highly excited Rydberg states of atoms was first observed by Čermák,[1] a number of experiments have been made on the reactions of such states with molecules.[2-10] Cross sections of the processes in which highly excited atoms are ionized by collisions with molecules were calculated by Matsuzawa[11-13] with the impulse approximation. He proposed in his first paper[11] the following model,

$$A^{**} + B' \longrightarrow A^+ + B'' + e \qquad (1)$$

where a loosely bound Rydberg electron in a highly excited atom, A**, is given the rotational energy difference between the upper (B') and lower (B'') states of a symmetric polar molecule B. The cross sections he estimated were of the same order of magnitude as the experimental cross sections measured by Hotop and Niehaus.[2] According to Matsuzawa's theory,[11] the cross section σ, expressed in atomic units in terms of the reduced mass μ and the relative kinetic energy E, is

$$\sigma = 11.7(\mu/E)^{\frac{1}{2}}D^2[J/(2J+1)](n_0/n)^8 \qquad (2)$$

where D, J, n and n_0 denote, respectively, the dipole moment and the rotational quantum number of the upper rotational state of B, the principal quantum number of the Rydberg electron in A**, and the quantum number of the lowest level that can be ionized by this collision. Hence, n_0 is related to J as

$$(2n_0^2)^{-1} = 2BJ \qquad (3)$$

where B is the rotational constant. Thus the cross section should be inversely proportional to $(E/\mu)^{\frac{1}{2}}$, or the relative velocity, v, if the other variables in Eq. (2) remain unchanged. Therefore, Eq. (2) can be applied to estimate the isotopic dependence of σ.

As reported by Kupriyanov,[7] long-lived highly excited states of the hydrogen atom, H**, are produced by impact of slow electrons on H_2O, and H** species are ionized by collision with polar molecules. If the species H** and D** produced by electron impact on a mixture of H_2O and D_2O have similar distributions of kinetic energy and principal quantum number, the cross sections σ_H and σ_D for H** and D** forming H^+ and D^+, respectively, by collision with polar molecules should exhibit

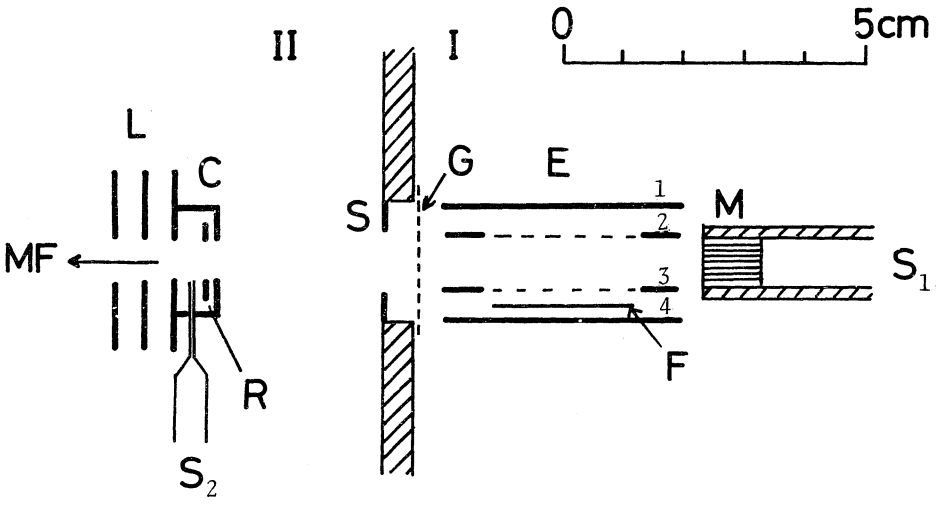

Fig. 1 Apparatus composed of Section I for producing long-lived excited atoms by electron impact and Section II, where a collision chamber C and a mass filter MF are installed. I: S_1, source of reactant molecules (a mixture of H_2O and D_2O in the present study); M, multichannel slit; E, electron gun; F, tungsten filament; 1, electron trapping electrode; 2 and 3, exciting region; 4, repeller electrode; G, grid; S, slit. II: S_2, source of target molecules (D_2O in the present study); R, ion repeller electrode; L, ion lens system. The apparatus of Section I is shown to scale but Section II is only schematic.

an isotopic dependence,

$$\sigma_D/\sigma_H = (\mu_D/\mu_H)^{\frac{1}{2}} = 1.38 \quad (4)$$

Experimental

The apparatus described in a previous paper[14] was evacuated to 2×10^{-6} Torr. A mixture of H_2O and D_2O vapors was introduced into the excitation region (Fig. 1) through a multichannel slit M and was subject to electron impact. The total pressure of the vapor at the source S_1 was about 0.4 Torr. The accelerating voltage was about 80 V, and the trap current measured at electrode 1 was about 400 μA. The excited neutral species were separated from accompanying ions by electrostatic potentials and were allowed to collide with the target D_2O molecules in the collision chamber C. The pressure of the target D_2O measured at the source S_2 was about 1 Torr. The protons or deuterons as well as other ions produced by the collision were measured by a quadrupole mass filter. The sample pressures were measured by oil manometers and Pirani gauges.

Results

Since the present study is concerned only with the ionization of H** and D** forming H^+ and D^+, the rest of the ions observed, D_2O^+ etc., were not analyzed in detail. A relevant portion of the mass spectrogram is shown in Fig. 2.

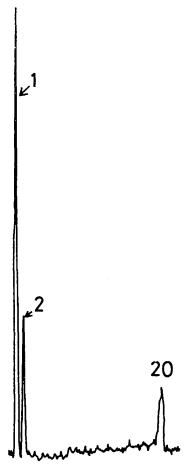

Fig. 2 Mass spectrogram of the ions produced by collisions of long-lived excited species obtained from H_2O and D_2O. Accelerating voltage of electrons: 80 V, trap current of electrons measured at electrode 1: 400 μA, pressure of the mixture of H_2O and D_2O at S_1: 0.4 Torr, pressure of D_2O at S_2: 1.3 Torr. The intensity of the ion with mass number 1 was approximately 5×10^{-10} A when 3 kV was applied to the electron multiplier.

The intensities of H^+ and D^+, I, were found to be proportional to the electron current and were dependent on the source pressure at S_1, p_s, as

$$I \propto p_s \exp(-c_s p_s) \quad (5)$$

where c_s is a constant. As discussed in Ref. 14, this dependence of I on p_s may be accounted for as a result of the attenuation of H** or D** by ionizing collisions with the source gas inside or in the vicinity of the excitation region. The ion intensities had a similar dependence on the target pressure, p, as shown in Fig. 3,

$$I \propto p \exp(-cp) \quad (6)$$

In terms of the effective density ρ of the target vapor in the collision chamber, which is proportional to p, the effective path length L of the excited species, and the effective cross section σ_a of the attenuation of the excited species by collision with the target, Eq. (6) can be rewritten as

$$I \propto \rho \exp(-\rho L \sigma_a) \quad (7)$$

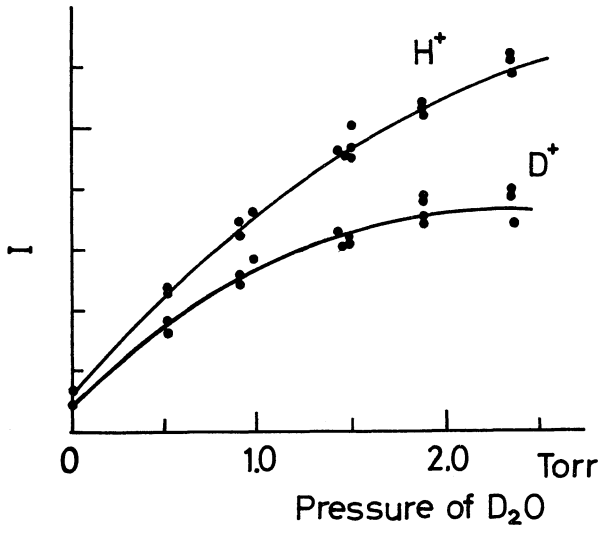

Fig. 3 Intensities of H^+ and D^+ plotted against the pressure of D_2O at S_2 (in Fig. 1). Accelerating voltage: 80 V, trap current at electrode 1: 400 μA, pressure of the mixture of H_2O and D_2O at S_1: 0.4 Torr.

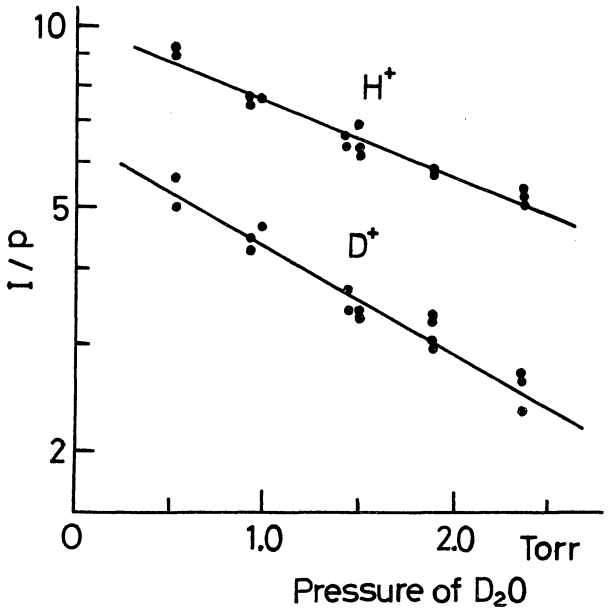

Fig. 4 Intensities of H^+ and D^+ displayed in Fig. 3 divided by the pressure p of D_2O at S_2 and plotted in a logarithmic scale against p.

Since ρ and L are common to H** and D**, the coefficient c in Eq. (6) should be proportional to σ_a. Plots of log(I/p) against p form nearly straight lines, as shown in Fig. 4, and the ratio of the cross sections, $\sigma_{a,D}/\sigma_{a,H}$, is estimated from the slopes to be 1.35±0.15. The ion intensities do not tend to zero in the absence of the target molecules, as shown in Fig. 3, since the excited species can be ionized not only by impact with the target but also with residual gases and/or the surface of the electrodes. This background has no significant effect on the ratio of the cross sections. The experimental ratio given above is obtained when the background is assumed to decrease rapidly with p, but it is essentially unchanged when the background is assumed to be independent of p. The error in the ratio from this origin is included in the estimated error limit, which is contributed mainly from the uncertainties in the slopes of log(I/p) and from the discrepancies among five independent experiments.

Discussion

The isotopic ratio of σ_a derived from the present experiment, 1.35±0.15, agrees with the theoretical ratio of σ estimated in Eq. (3), 1.38. This comparison is based on the assumptions that all the parameters in Eq. (2) besides μ are isotope invariant and that, as predicted by Matsuzawa,[11] the ionization by the transfer of rotational energy is dominant over all the other processes leading to the quenching of H** and D**. In spite of the following possibilities which can invalidate these assumptions, the good agreement does not seem to be simply fortuitous.

(a) The distributions of n for H** and D** may not be equal to each other, since there exist various complicated channels forming H** and D**, which may be isotope dependent.

(b) Inelastic processes of the excited species by the source gas, which take place inside or in the vicinity of the excitation region, can cause a change in the distributions of n and can alter the effective ratio of σ_a.

(c) The distribution of n at the collision chamber may have a different isotopic dependence because of spontaneous emission, since the flight time can be isotope dependent.

(d) Though most of the other quenching processes seem to have negligible cross sections, as demonstrated by Hotop and Niehaus[2] for the highly excited

states of rare gas atoms, elastic deflections of the excited species by the target may have an influence on the attenuation (possibly with a smaller isotopic dependence according to a simple classical estimation).

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