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TRANSLATIONAL ENERGIES OF THE EXCITED HYDROGEN AND DEUTERIUM ATOMS PRODUCED BY CONTROLLED ELECTRON IMPACT (300 eV) ON WATER AND HEAVY WATER

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The emission spectra of four Balmer lines (α,β,γ,δ) by electron impact on H_2O and D_2O were measured. The translational energies (*E*) of the excited H and D atoms were determined by their Doppler widths.

	α	β	γ	δ
E_H/eV	1.9±0.3	2.3±0.2	2.3±0.3	2.1±0.3
E_D/eV	2.6±0.3	2.7±0.3	2.9±0.4	3.1±0.4

The excited hydrogen atom produced by electron impact has been presumed to have a large translational energy, since the proton produced by electron impact was found to have a large translational energy[1,2] and since the analysis of the product of the radiation-induced reaction revealed the importance of a "hot" hydrogen atom.[3] The emission spectra by controlled electron impact have been found to be a powerful method to investigate the excited species produced in an electron-molecule collision.[4,5] The measurement of the spectral line shape would clarify the motion of the excited hydrogen atom produced by electron impact.

The Doppler widths of the Balmer β lines by electron impact on H_2O and D_2O have been reported before.[6] However, since the photographic method was insensitive and the collision chamber was made of glass, the electron-beam current, the gas pressure and the magnetic field used in the preceding measurements were so large that the effects of the secondary electrons on the spectral linewidths might be present. Thus, new measurements were carried out with a smaller electron-beam current, a lower gas pressure and a lower magnetic field and with a stainless-steel collision chamber. The effects of these experimental parameters and of the secondary electrons on quantitative measurements were examined.

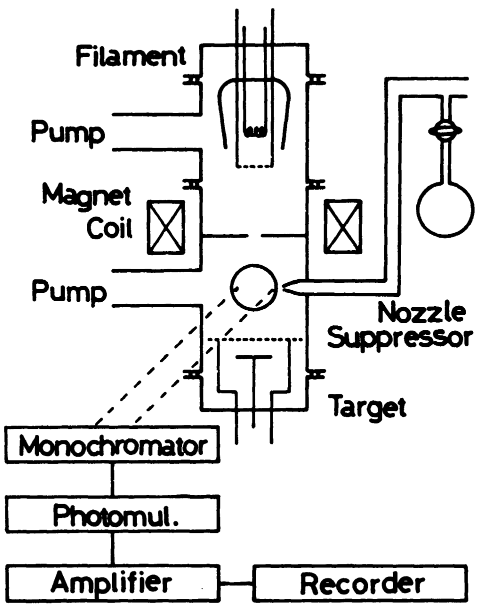

Fig. 1. Schematic diagram of the apparatus.

A schematic diagram of the apparatus is shown in Fig. 1. The chamber was made of stainless-steel, and its inside was covered with soot. The electrons from a tungsten filament were accelerated, collimated, and introduced into the collision chamber through a hole (4 mm in diameter). They were crossed with the molecular jet from a nozzle of 0.2 - 0.3 mm in diameter. The pressure in the collision chamber was measured with an ULVAC G1-TL2 ionization vacuum gauge; the base pressure was of the order of 10^{-6} Torr and the operating pressure was 0.3 - 3.0 x 10^{-3} Torr. The electromagnet consisted of a 3000 turn electric coil, the diameter of which was about 12 cm. The photoemission was observed perpendicularly to both beams through a quartz window and was measured with a JASCO CT-100 1 m monochromator equipped with a 1200 groove/mm grating blazed for 5000 Å and with an EMI 9558QB photomultiplier.

The linewidth of the excited hydrogen atom from H_2 was measured; the result agreed satisfactorily with that reported by Freund et al.[7] Quantitative measurements were carried out under such a condition that the intensity of the Balmer β radiation was proportional to both the gas pressure and the electron-beam current. Accordingly, the excited hydrogen atom was considered to be produced in a primary collision. The spectral linewidth of the Balmer β radiation was independent of the electron-beam current (40-550 μA) and the gas pressure (0.3-3.0 x 10^{-3} Torr). However, the linewidth decreased at higher electron-beam current by about 25 % at 5 mA. The linewidth was independent of the electron energy between 100-350 eV and of the current of the electromagnet between 0.2-1.2 A.

The spectra of the Balmer lines are shown in Fig. 2. The true spectral linewidth, $\delta\lambda_t$, was obtained from the observed half-maximum linewidth, $\delta\lambda_{obs}$, by the following equation:[8]

$$\delta\lambda_{obs}^2 = \delta\lambda_t^2 + S^2 \qquad (1)$$

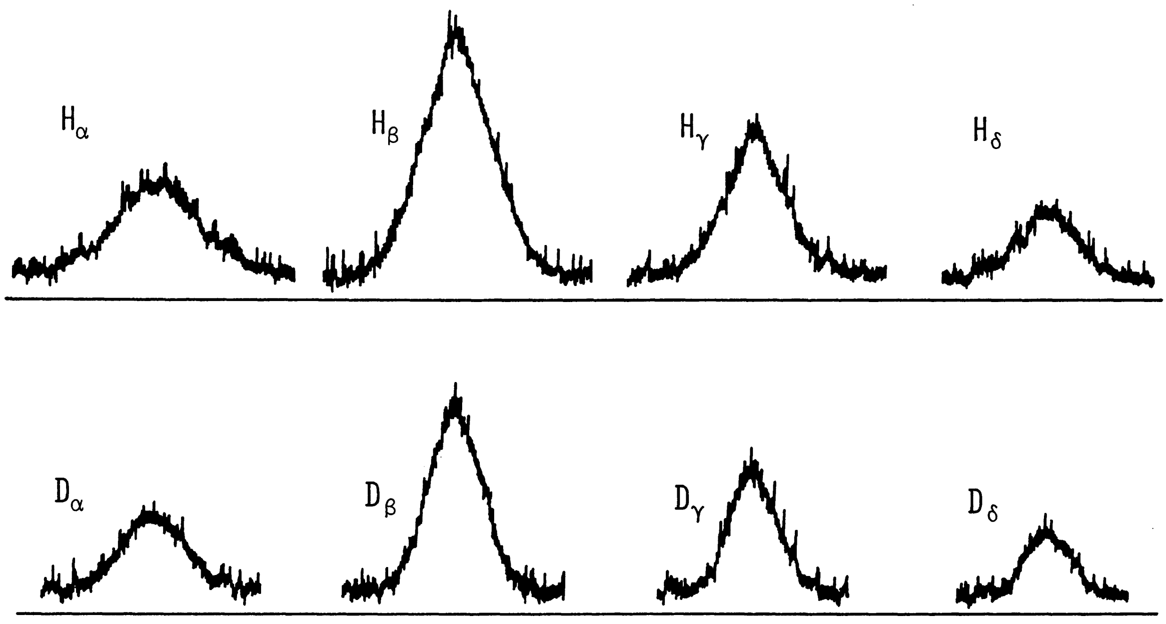

Fig. 2. Spectra of four Balmer lines by electron impact on H_2O and D_2O. Electron energy, 300 eV; electron-beam current, 550 μA; spectral slit width, 0.25 Å.

where S is the spectral slit width (equal to the resolution). The linewidth of the Balmer β radiation was independent of the spectral slit width between 0.18 - 0.25 Å. The differences between $\delta\lambda_t$ and $\delta\lambda_{obs}$ were smaller than or equal to the experimental uncertainty. The hydrogen Balmer lines have fine structures.[7,9] The splitting is much smaller than the observed widths and may be corrected similarly.[6]

The motion of the excited hydrogen atom may be anisotropic. However, the angular distribution of the fragment (H^+) produced in the dissociative ionization of H_2 by electron impact was calculated following the Born approximation;[10] anisotropy was found to be at a maximum at threshold and it was about 10 % for the 300 eV electron impact. When the predissociation is involved in the dissociative process as is expected in the present case, anisotropy will decrease since the primarily excited molecule may rotate. This estimation has also been confirmed by the observation of no polarization of the Balmer radiation.[11] Furthermore, the electromagnet used in the present measurements to collimate the electron beam would induce spiral motions of the electron and obscure possible anisotropy. Thus, anisotropy is estimated to be less than the experimental uncertainty.

The average velocity[7,12] of the excited hydrogen atom was obtained from the spectral linewidth. The translational energy (E) was calculated by

$$E = (mc^2/8)\cdot(\delta\lambda_t/\lambda_0)^2 \qquad (2)$$

where m is the mass of the hydrogen atom (H or D). The velocity of the excited hydrogen atom is expected to have some distribution and the translational energy thus calculated may be approximate.

The results are summarized in Table 1. The spectral linewidths reported here are larger than those in our preceding report;[6] this is probably because the larger electron-beam current and the higher gas pressure used in the preceding report introduced some reduction in the linewidths.

Table 1. The Doppler width and the translational energy of the excited hydrogen atom.

Balmer	α	β	γ	δ
$\delta\lambda_{tH}$/Å	0.84±0.06	0.67±0.04	0.60±0.04	0.55±0.04
$\delta\lambda_{tD}$/Å	0.69±0.04	0.53±0.03	0.48±0.03	0.47±0.03
E_H/eV	1.9±0.3	2.3±0.2	2.3±0.3	2.1±0.3
E_D/eV	2.6±0.3	2.7±0.3	2.9±0.4	3.1±0.4

The uncertainty given in the Table is the standard deviation of the experimental data. The systematic error of $\delta\lambda_t$ was estimated to be smaller than the experimental uncertainty.

It has been clarified that the excited hydrogen atom produced in the dissociative excitation of water has a large translational energy.[6] The translational energies of four excited states of hydrogen atom agreed within the limits of uncertainty of the measurements. The translational energy of the excited hydrogen atom revealed an isotope effect; that of D* is larger than that of H* by about 20 - 50 %. This is probably because the translational and rotational energies carried by the other fragment, OH or OD, depend on their masses. When water was dissociatively ionized into H^+ + OH or D^+ + OD and ions with a large translational energy were analyzed, the vibrational and rotational energies carried by OH and OD were estimated to be 23 % and 13 % of the total translational energies of the fragments.[2]

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References:

1) G. H. Dunn and L. J. Kieffer, Phys. Rev., 132, 2109 (1963); A. Crowe and J. W. McConkey, Phys. Rev. Lett., 31, 192 (1973).
2) J. Appell and J. Durup, Int. J. Mass Spectrom. Ion Phys., 10, 247 (1972/3).
3) Y. Hatano, Nippon Kagaku Zasshi, 91, 1009 (1970).
4) T. Ogawa, M. Tsuji, M. Toyoda, and N. Ishibashi, Bull. Chem. Soc. Jpn., 46, 2637 (1973).
5) K. Hirota, M. Hatada, and T. Ogawa, Int. J. Radiat. Phys. Chem., 8, 205 (1976).
6) T. Ogawa, F. Masumoto, and N. Ishibashi, Chem. Lett., 1976, 207. The translational energy was calculated in this letter by assuming that the distribution of the velocity was similar to the Maxwell distribution. This gave appreciably higher values than the method used in the present letter would do.
7) R. S. Freund, J. A. Schiavone, and D. F. Brader, J. Chem. Phys., 64, 1122 (1976).
8) S. Brodersen, J. Opt. Soc. Am., 44, 22 (1954).
9) E. C. Condon, and G. H. Shortley, The Theory of Atomic Spectra, Cambridge Univ. Press, (1935).
10) R. N. Zare, J. Chem. Phys., 47, 204 (1967).
11) G. R. Möhlmann, S. Tsurubuchi, and F. J. de Heer, Chem. Phys., 18, 145 (1976).
12) K. Ito, N. Oda, Y. Hatano, and T. Tsuboi, Chem. Phys., 17, 35 (1976).

Note added after the paper was submitted:

After the writing of this manuscript was completed, Kochi et al. (N. Kochi, K. Ito, N. Oda, Y. Hatano, and T. Tsuboi, Abstr. No. 1N24, 36th National Meeting of the Chem. Soc. of Japan, Osaka, April 1977) read a paper on the Doppler profile of H_α radiation. The resolution of the monochromator they used was higher than that of ours and they concluded the observed profile consisted of two components. However, if their spectrum were analysed as a single component, the results of ours and theirs would be in good agreement.

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