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# TRANSLATIONAL ENERGY OF THE EXCITED HYDROGEN ATOM PRODUCED BY CONTROLLED ELECTRON IMPACT (300 eV) ON HYDROGEN CHLORIDE AND WATER

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The emission of the Balmer β line by 300 eV electrons were measured by use of a Fabry-Perot etalon. The translational energies of H and D atoms (n = 4) were determined by its Doppler width.

| | | | |
|---|---|---|---|
| HCl | 7.3 ± 0.2 eV, | DCl | 7.5 ± 0.2 eV, |
| $H_2O$ | 2.3 ± 0.2 eV, | $D_2O$ | 3.1 ± 0.2 eV. |


The most familiar primary process in the radiation-induced chemical reaction is the excitation, ionization, and decomposition of a molecule after a collision with an electron. However, the direct observation of an excited neutral species thus produced has seldom been carried out. 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.[1,2)]

The analysis of the product of the radiation-induced reaction has revealed the importance of a "hot" hydrogen atom,[3)] which is reactive because of its large translational energy. However, little is known on the translational energy of the excited neutral hydrogen atom.[4)] The Doppler width of the emission spectra by controlled electron impact exhibits the translational energy of the species concerned and the results of the excited hydrogen atom from hydrogen chloride and water under a higher resolution are communicated in the present letter.

The sample gas (either hydrogen chloride or water) was jetted through a nozzle and collided with the controlled electron beam of 300 eV. The electron beam current was 1 - 2 mA. The pressure in the collision region is estimated to be of the order of $10^{-2}$ - $10^{-3}$ mmHg. The details of the apparatus were described elsewhere.[1)]

The photoemission produced in the collision was observed by use of a Fabry-Perot etalon (the Mizoziri Optics Inc.). Its effective diameter is 30 cm and its surface was coated for 486 nm ($\lambda_0$, $H_\beta$ and $D_\beta$). The resolution of the etalon, which was dependent on the thickness (d) of the spacer used, was determined by use of an Fe arc, the spectral (Doppler) width of which was calculated to be about 0.03 Å. The resolution was 0.20 Å for 0.4 mm spacer and 0.15 Å for 0.6 mm spacer.

The spectrum of the Balmer β line was photographed by use of the Kodak Tri-X Pan film, and was analyzed by a Shimadzu #3 microdensitometer. The linearity of film response was examined by measuring the spectrum at various densities. The line shape of the Balmer line is assumed to be Gaussian, since the line width is determined by the Doppler effect for the emission of an atom in a very low pressure. A typical spectrum of water is shown in Fig. 1. The half width was determined with reference to the free spectral range ($\lambda_0^2/2d$). The observed half width ($\delta\lambda$) was calibrated for the instrument resolution by the following formula,[5)]

$$\delta\lambda = 0.5\,\delta\lambda_a + \delta\lambda_c \qquad (\delta\lambda_a < \delta\lambda_c)$$

where $\delta\lambda_a$, and $\delta\lambda_c$ are the instrumental and the calibrated half widths.

The hydrogen Balmer line has fine structures. Since the splitting (0.08 Å)[6)] is much smaller than the Doppler width, the effect of fine structures may be corrected by the following formula,

$$\delta\lambda_c^2 = 0.08^2 + \delta\lambda_t^2$$

where $\delta\lambda_t$ is the true half width, which is the Doppler width of the hydrogen atom.

The translational energy of the hydrogen atom is assumed to be isotropic; this assumption is valid if the superexcited parent molecule can take any spacial direction indiscriminately. The translational energy (E) is calculated by,

$$E = (3c^2m/16\cdot\ln 2)(\delta\lambda_t/\lambda_0)^2$$

where m is the mass of the hydrogen atom ( H or D ).

The results are summarized in Table 1. The translational energy thus measured may, however, be an average value of energies of the hydrogen atom of various speed. Thus, as is shown in the table, the excited hydrogen atom produced in the collision of an electron and a molecule is proved to have a large amount of the translational energy. This excited "hot" hydrogen atom is probably very reactive and may play a significant role in the radiation-induced chemical reaction.

The hydrogen atom produced from HCl and DCl reveals no isotope effect in the translational energy, while that from water reveals it. This is probably because there is no internal freedom(vibrational and rotational) left after splitting of HCl and DCl into separate fragments. The result also suggests that the predominant process of the excited hydrogen atom formation from water is the splitting of water molecule into a hydrogen atom and a hydroxyl radical.

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Table 1. The observed half width and the translational energy of H and D (n=4)

| | $H_2O$ | $D_2O$ | HCl | DCl |
|---|---|---|---|---|
| $\delta\lambda$(0.4 mm spacer) | 0.57 ± 0.03 | 0.47 ± 0.02 | 0.93 ± 0.02 | 0.70 ± 0.02 |
| $\delta\lambda$(0.6 mm spacer) | 0.55 ± 0.02 | 0.49 ± 0.02 | | |
| $\delta\lambda_c$ | 0.47 ± 0.03 | 0.39 ± 0.03 | 0.83 ± 0.02 | 0.60 ± 0.02 |
| $E_{trans}$ (eV) | 2.3 ± 0.2 | 3.1 ± 0.2 | 7.3 ± 0.2 | 7.5 ± 0.2 |

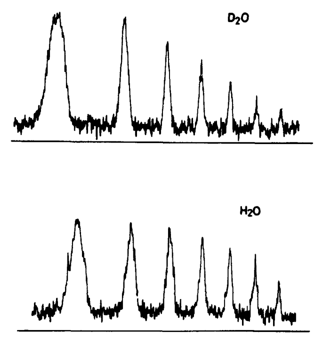


Fig. 1. Spectra of the Balmer lines.
top: D* from $D_2O$
bottom: H* from $H_2O$

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