CHEMISTRY LETTERS, pp. 493-494, 1978. Published by the Chemical Society of Japan

ISOTOPE EFFECTS IN THE EMISSION CROSS SECTION OF THE BALMER LINES (β,γ,δ) PRODUCED BY CONTROLLED ELECTRON IMPACT ON HCl AND DCl

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The relative emission cross section (σ_D/σ_H) of the excited hydrogen and deuterium atoms produced in the dissociative excitation of HCl and DCl by 300 eV electrons revealed an isotope effect, which varied with the principal quantum number of the excited atoms.

σ_D/σ_H β:0.83±0.04, γ:0.87±0.04, δ:0.93±0.05.

Platzman suggested that formation of a superexcited state with subsequent competition between pre-ionization and dissociation is the dominant primary process for electron impact and that the slower motion of the heavier atom induces the isotope effect of the dissociation.[1] This effect has been investigated on hydrogen,[2] methane,[2] methanol,[3] acetonitrile[4] etc. However, the dissociative excitation of the hydrogen atom of these molecules may be complicated because of the presence of more than two processes.[5]

The emission spectra produced by electron impact on HCl and DCl have been measured by Toyoda et al.[6] and Möhlmann et al.[7] The excited hydrogen atom thus produced was found to have a large translational energy.[8] The dissociative excitation of the hydrogen atom seems to proceed predominantly through a repulsive potential curve, predicting a simpler process and a small isotope effect in its emission cross section.[9]

A schematic diagram of the apparatus is shown in Fig. 1. The sample gas was introduced into the collision chamber through a multi-channel nozzle and was excited by a collision with the electron-beam. The base pressure in the collision chamber was of the order 10^{-7} Torr and the operating pressure was indicated to be 2.0 - 3.0 x 10^{-4} Torr (ULVAC GI-TL2 ionization vacuum gauge). The photoemission was measured with a JASCO CT-100 monochromator equipped with a HTV R585 photomultiplier. Photons were counted and accumulated.

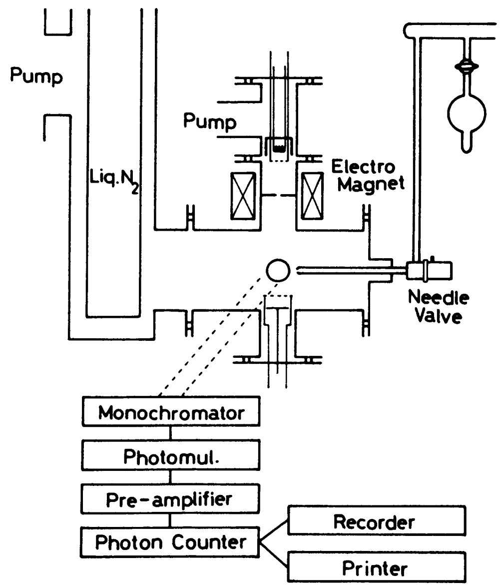

Fig. 1. Schematic diagram of the apparatus.

The quantitative measurements were carried out where the intensity of the Balmer β radiation was proportional to both the gas pressure and the electron-beam current.

A typical spectrum of the Balmer β lines from a mixture of HCl and DCl is shown in Fig. 2. The relative emission cross section of the Balmer lines was determined by comparing their areas of the spectral lines. The results were independent of the electron-beam current (0.3 - 2.0 mA), and the gas pressure (0.2 - 3.0 mTorr). The uncertainties of the results owing to the random experimental fluctuation, the line overlap, and the sample composition were estimated to be about 2 - 4 %, below 2 %, and 3 %, respectively.

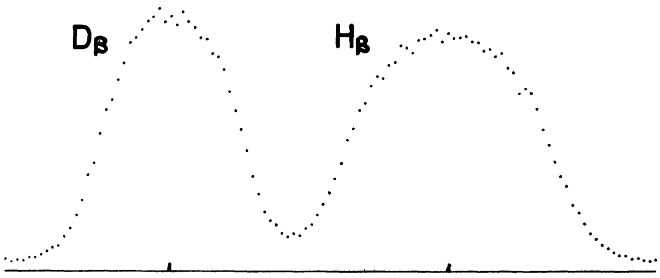

Fig. 2. Spectra of the Balmer β lines by electron impact on HCl and DCl. Electron energy, 300 eV.

The results are summarized in Table 1. The isotope effects in the emission cross section of the Balmer lines varies with the principal quantum number of the excited hydrogen atom, as in the case of acetonitrile.[4)] The excited hydrogen atom from hydrogen chloride has been estimated to be produced mainly through repulsive Rydberg states, since its translational energy is large and seems to have an almost single distribution;[9)] whereas the excited hydrogen atom from such molecules as H_2 and CH_4 seems to have more than two components.[5)] It is noteworthy that the dissociative excitation from such repulsive state has still isotope effects in the emission cross section; this finding indicates that there are competing processes even for the dissociation from a repulsive state.

Table 1. The relative emission cross section of the dissociative excitation of hydrogen and deuterium atoms from HCl and DCl.

Balmer	β	γ	δ
σ_D/σ_H	0.83±0.04	0.87±0.04	0.93±0.05

References:

1) R. L. Platzman, Vortex, 23, 372 (1962).
2) D. A. Vroom and F. J. de Heer, J. Chem. Phys., 50, 573, 580 (1969).
3) I. Fujita, M. Hatada, T, Ogawa, and K. Hirota, Bull. Chem. Soc. Jpn., 44, 1751 (1971).
4) I. Tokue, I. Nishiyama, and K. Kuchitsu, Chem. Phy. Lett., 35, 69 (1975).
5) K. Ito, N. Oda, Y. Hatano, and T. Tsuboi, Chem. Phys., 17, 35 (1976); 21, 203 (1977).
6) M. Toyoda, T. Ogawa, and N. Ishibashi, Bull. Chem. Soc. Jpn., 49, 384 (1976).
7) G. R. Möhlmann, K. K. Bhutani, and F. J. de Heer, Chem. Phys., 21, 127 (1977).
8) T. Ogawa, F. Masumoto, and N. Ishibashi, Chem. Lett., 1976, 207.
9) M. Higo, T. Ogawa, and N. Ishibashi, unpublished.

(Received February 10, 1978)