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Isotope Effect on the Emission Cross Section and Translational Energy of Excited Hydrogen Atoms Produced in Electron-Hydrogen Chloride Collisions

Morihide HIGO,[†] Satsuo KAMATA,[†] and Teiichiro OGAWA*
Department of Molecular Science and Technology, Kyushu University, Kasuga, Fukuoka 816
[†]*Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890*

(Received September 6, 1982)

The Balmer-α, β, γ lines of the excited hydrogen atoms (n=3, 4, 5) produced in e-HCl and DCl collisions have been measured in the energy range of 30—300 eV. The average translational energies of H* and D* are 4—5 eV at higher electron energies and 2—2.5 eV at lower electron energies; no appreciable isotope effect is found for the translational energy. The relative emission cross section of D* and H* shows an isotope effect and this effect is larger in the lower electron energy range; σ_D/σ_H's are 0.74 for n=3, 0.71 for n=4 and 0.78 for n=5 at 30 eV. These results show that there are two groups of the excited hydrogen atoms and their relative cross sections vary with the electron energy. The existence of the isotope effect indicates a competing decay process in the repulsive excited states of HCl.

Electron-impact excitation of a hydride molecule leads to the formation of an excited hydrogen atom (H*). The translational energy[1-6] of H* and its distribution[7-16] have clarified the highly excited states and their dissociation mechanism. The Rydberg states converging to the ionic states which produce H^+ play an important role for the formation of H*; comparison of the translational energy distributions of H* with those of H(HR) and H^+ justifies an extension of the core-ion model to the low-Rydberg emissive atoms.[10-14,16] Curve crossing between potential curves is involved in the formation of the excited hydrogen atom.[9-11,13,16]

The translational energy distribution of H*(n=4) from HCl has two major components; their peaks lie at about 5 eV (the fast component) and 2.5 eV (the slow component).[9] The former is important at higher electron energies, whereas the latter is important at lower electron energies. The production mechanism of the fast component has been assigned to dissociation through Rydberg states converging to the $^2\Pi$ state of HCl^+, and that of the slow component to excitation to Rydberg states converging to the $^4\Pi$, $^4\Sigma^-$ and/or $^2\Sigma^-$ states of HCl^+ followed by curve crossing and succeeding dissociation through those converging to the $^2\Sigma^+$ state.[9]

The investigation of the isotope effect in the emission cross section of H*(D*)[1,15,17-22] is equally important for the elucidation of the molecular dissociation dynamics and for their theoretical interpretation.[23,24] In our previous paper,[20] it has been shown that the isotope effect of H*(D*)(n=4,5,6) from HCl(DCl) exists even in the repulsive Rydberg states at an electron energy of 300 eV, and principal quantum number dependence has been discussed.

In the present paper, we have observed the Balmer-α,β,γ lines from HCl and DCl at various electron energies, and measured the average translational energy of H*(D*)(n=3,4,5) and the isotope effect of their emission cross sections in order to discuss the mechanism of dissociative excitation of hydrogen chloride.

Experimental

The apparatus consists of a stainless-steel collision chamber, a 1.26 m monochromator and a photon counting system. The details of the collision chamber have been published previously.[25] The mixture of HCl (99.7%, Tsurumi Souda) and DCl (99%, Merk) gases were jetted into the collision region and collided with electrons. The base pressure was of the order of 10^{-7} Torr (1 Torr≈133.322 Pa) and the operating pressure was of the order of 10^{-4} Torr.

The spectra were measured with a Spex 1269 monochromator equipped with a 1200 grooves/mm grating blazed at 500 nm. Photons were detected with an HTV R585 photomultiplier for the Balmer-β and γ lines or with a cooled HTV R649 photomultiplier for the Balmer-α line, and were counted with an NF PC545A photon counter.

Measurements were carried out where the intensity of the Balmer radiation was proportional to both the gas pressure and the electron-beam current. The energy of the electron was calibrated with the threshold of N_2^+ (3914 Å) at 18.75 eV and its energy resolution was ±1 eV.

Results and Discussion

Average Translational Energy. Collisions between HCl(DCl) and electrons give the excited H*(D*) atoms. The spectra of the Balmer-α,β,γ lines observed at an angle of 90° with respect to the electron beam and at various electron energies are shown in Figs. 1—3, respectively. The line shape depends on the electron energy; it becomes narrower with decreasing the electron energy.

The true width of the Balmer line, $\delta\lambda_t$, was calculated from the observed half-width, $\delta\lambda_{obsd}$, by the following relation:[5]

$$\delta\lambda_{obsd}^2 = \delta\lambda_t^2 + S^2 + a^2, \tag{1}$$

where S is the resolution of the monochromator and a the fine structure splitting.[26] The results are shown in Table 1. The uncertainty is mainly caused by random experimental fluctuation. The true width obtained here agrees well with that observed at higher resolution (0.033 Å) in our previous measurement[9] as shown in parentheses in Table 1.

At lower gas pressures, the spectral line shape of the emissive atom is determined by the Doppler effect[26] and, thus, has information on the velocity. The translational energy distribution can be calculated from the

TABLE 1. THE CORRECTED HALF-WIDTHS ($\delta\lambda_t$/Å) OF THE BALMER LINES OF THE EXCITED HYDROGEN AND DEUTERIUM ATOMS IN ELECTRON-HYDROGEN CHLORIDE COLLISIONS

Electron energy/eV	Balmer-α		Balmer-β		Balmer-γ	
	H	D	H	D	H	D
300	1.21	0.89	0.96 (0.96)[a)]	0.72	0.88	0.62
200	1.23	0.92	0.98	0.72	0.89	0.61
100	1.23	0.89	0.96 (0.99)	0.70	0.88	0.61
50	1.18	0.89	0.94 (0.92)	0.68	0.83	0.57
40	1.09	0.79	0.84 (0.76)	0.60	0.71	0.49
35	0.97	0.75	0.73	0.50	0.61	0.44
30	0.85	0.67	0.68 (0.72)	0.48	0.55	0.42

a) Calculated from the Balmer-β line taken at a high resolution (0.033 Å).[9)]

The uncertainties are about 5 and 7% for higher electron energies ($\geq$50 eV) and lower electron energies, respectively.

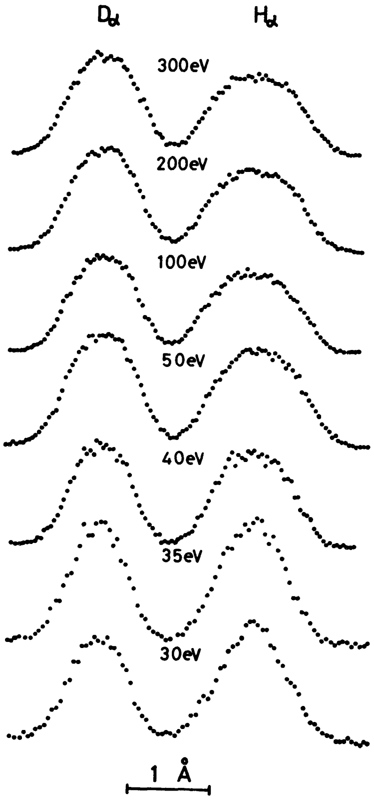

Fig. 1. The spectra of the Balmer-α lines produced in e-HCl and DCl collisions observed at 90° with respect to the electron beam. Spectral resolution: 0.32 Å. Electron-beam current: 220—770 μA. Operating pressure: (1.0—4.0) × 10^{-4} Torr.

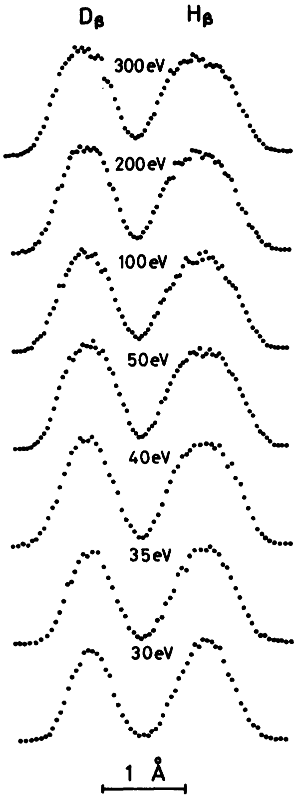

Fig. 2. The Spectra of the Balmer-β lines produced in e-HCl and DCl collisions. Spectral resolution: 0.31 Å. Electron-beam current: 420—740 μA. Operating pressure: (1.5—4.0) × 10^{-4} Torr.

line shape taken at a high optical resolution.[7,9)] Since resolution used here was not good enough to obtain the distribution, we have calculated the average translational energy instead of its distribution.

The average translational energy, E, of H* and D* was calculated by the following equation by assuming the distribution of the velocity to be a delta function:[3—6,15)]

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

where m is the mass of H*(D*), c the velocity of light and λ_0 the characteristic wavelength of its radiation. The results are shown in Table 2. The electron energy dependence is similar for all of them. The average translational energy of the H*(n=4) is in agreement with the peak of the distribution. Neither the isotope effect nor the dependence on the principal quantum number is clear in the average translational energy of H*(D*) within the experimental uncertainty.

The similarity in both the translational energies of H*(D*) (n=3,4,5) and their electron energy dependence obtained in this measurement indicates that the excited states and their dissociation mechanisms for the formation of H*(n=3,5) and D*(n=3,4,5) are similar

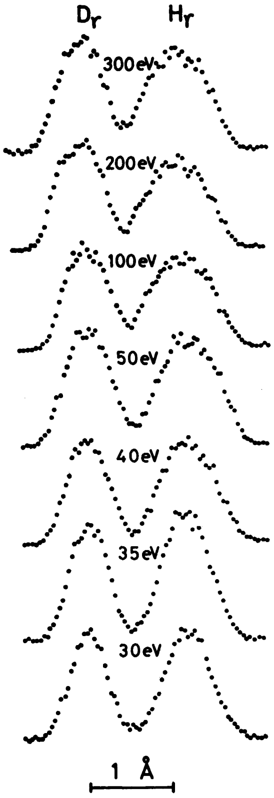

Fig. 3. The spectra of the Balmer-γ lines produced in e-HCl and DCl collisions. Spectral resolution: 0.31 Å. Electron-beam current: 360—820 μA. Operating pressure: (1.5—4.0) × 10^{-4} Torr.

Table 2. Average translational energies (E/eV) of the excited hydrogen and deuterium atoms produced in electron-hydrogen chloride collisions

Electron energy/eV	Balmer-α		Balmer-β		Balmer-γ	
	H	D	H	D	H	D
300	4.0	4.4	4.6	5.1	4.8	4.8
200	4.2	4.6	4.8	5.1	5.0	4.7
100	4.1	4.4	4.6	4.8	4.8	4.6
50	3.8	4.3	4.4	4.6	4.3	4.0
40	3.3	3.4	3.5	3.6	3.1	3.0
35	2.5	3.1	2.6	2.5	2.3	2.4
30	2.0	2.5	2.3	2.3	1.9	2.2

The uncertainties are about 10 and 15% for higher electron energies (≥50 eV) and lower electron energies, respectively.

Table 3. Relative emission cross sections (σ_D/σ_H) of the Balmer lines of the excited hydrogen atoms in electron-hydrogen chloride collisions

Electron energy/eV	Balmer-α	Balmer-β	Balmer-γ	Balmer-δ
300	0.90	0.84 (0.83)[a]	0.86 (0.87)[a]	(0.93)[a]
200	0.91	0.87	0.89	
100	0.90	0.83	0.84	
50	0.90	0.84	0.82	
40	0.87	0.81	0.80	
35	0.81	0.69	0.76	
30	0.74	0.71	0.78	

a) Ref. 20. The uncertainty is estimated to be about 7%.

to those of H*(n=4).[9] This finding is consistent with the core-ion model.[27] Thus, it is concluded for all of n=3,4,5 of H* and D* that the repulsive Rydberg states converging to the $^2\Pi$ state of HCl^+(DCl^+) produce the fast component and the slightly repulsive Rydberg states which cross the $^2\Sigma^+$ state produce the slow component.

It can generally be concluded that the translational energy for a single component has no isotope effect since the potential curve is common. The traslational energy of H*(D*)(n=3) at higher electron energies, however, is somewhat smaller than those of others. This may suggest that the slow component has a relatively larger contribution for the formation of H*(D*)(n=3) even at higher electron energies; singlet Rydberg states converging to the $^2\Sigma^-$ states may be involved in such a process.

Isotope Effect on the Emission Cross Section. The relative emission cross section (σ_D/σ_H) has been obtained by comparing the areas of its spectrum. The results are shown in Table 3, with values measured in our previous paper[20] in parentheses. The main sources of uncertainty are random experimental fluctuation (5%), the sample preparation (4%) and the line overlap between H* and D* (2%). The cascade effect has been neglected; this effect has been estimated to be small for the Balmer-α line and negligible for the other Balmer lines by electron impact on H_2.[17,28]

The relative emission cross section shows an isotope effect ($\sigma_D/\sigma_H<1$), which depends on the electron energy as the translational energy does. Since the isotope effect for a single dissociation process is expected to be independent of the electron energy,[21,22] this dependence shows that two or more processes are involved for the formation of H*(D*) and that their relative cross sections vary with the electron energy. This is consistent with the result obtained in the translational energy.

Rydberg states converging to the $^2\Pi$ state are highly repulsive and produce the fast component. Dissociation and autoionization are main competing decay processes in these repulsive excited states. Since the heavier nuclei of DCl separate more slowly along the repulsive potential curve, more DCl molecules autoionize before they dissociate to neutral atoms (D*+Cl). Such a velocity dependent isotope effect has also been observed in the formation of H*(D*) from H_2(D_2),[11,13] and $CHCl_3$($CDCl_3$)[15] by electron impact.

Repulsive Rydberg states which cross the $^2\Sigma^+$ state produce the slow component. Its isotope effect is larger than that of the fast component; however, its n dependence is not clear. The probability for curve crossing depends on the velocity of nuclei[29] and the slower motion of DCl results in a larger probability for curve crossing. In addition to competition with autoionization, the probability difference can induce an isotope effect, which may be dependent on n. An n dependence of the isotope effect for the formation of H*(D*) has been observed in the case of CH_3CN (CD_3CN),[1] H_2(D_2),[21,22] and $CHCl_3$($CDCl_3$).[15]

The authors thank Junichi Kurawaki and Yasuhiro Ueda for their cooperation and Professor Nobuhiko Ishibashi of Kyushu University for his encouragement. The present study was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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