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# Translational Energy Distribution and Relative Emission Cross Section of Excited Hydrogen Atom Produced in Electron-chloroform Collisions

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Dissociative excitation of $CHCl_3$ and $CDCl_3$ has been investigated by means of the controlled electron impact and the high resolution emission spectroscopy. The emission spectrum shows such excited species as H, CH, $CH^+$, $Cl^+$, CCl, and $HCl^+$. The excitation function of H* has two thresholds, 20.5 and 41.0 eV. The emission cross spections of H* and D* reveal an isotope effect, which is dependent on the excitation energy and the principal quantum number. Translational energy distributions of H* and D* have been determined from the Doppler line shape of the Balmer-$\beta$ line, and average translational energies from the half-width of the Balmer-$\alpha$, $\beta$, $\gamma$, and $\delta$ lines. There are no noticeable isotope effect for the translational energy; their major peaks lie at 0—1, 4, and 6—12 eV. These findings indicate that there are at least three major processes for the formation of the excited hydrogen atom. They are assigned to dissociative excitation through the Rydberg states converging to the $(2a_1)^1$ ionic states and through doubly excited Rydberg states.

An excited molecule may decompose by itself to give an excited fragment atom. An electron-molecule collision is an efficient method to trigger dissociative excitation of the molecule. A detailed elucidation of this process has become possible through the investigation of the translational energy distributions of H* and D* obtained from the analysis of the Doppler line shape of their Balmer lines.[1,2] It has been found that there are two or more processes for dissociative excitation of $H_2$,[3] $D_2$,[4] HCl,[2] and $CH_4$[5] to produce the excited hydrogen atom from such molecules. The high resolution spectroscopy of H* is equally important with the mass spectroscopy of $H^+$ for a detailed analysis of the dissociation mechanism of highly-excited molecules.

Dissociation mechanism of chloroform has been investigated under the controlled electron impact excitation of $CHCl_3$ and $CDCl_3$.[6] The photoelectron spectrum of chloroform has been measured and discussions on the excited electronic states have been given.[7—9]

The relative value of the emission cross sections of H* to those of D* produced in the collision process is also useful for the investigation of the dissociation mechanism and is related to competition among various dissociation and ionization processes of the highly-excited molecule.[10]

In the present paper, the emission spectra of $CHCl_3$ and $CDCl_3$ have been measured with a high resolution by using a Fabry-Perot interferometer. The translational energy distributions of H* and D*, the excitation function and the relative emission cross sections have been obtained in order to discuss the mechanism of dissociative excitation of chloroform.

## Experimental

The apparatus has been described previously.[2,3] The very high resolution spectrum was obtained with a Fabry-Perot interferometer (Mizojiri Optics). The $CDCl_3$ (99.8 D atom %) was obtained from Aldrich Chemical . The chloroform was used as supplied and subjected to several freeze-pump-thaw cycles before use.

## Results and Discussion

*Spectrum.* Collisions between a chloroform molecule and an electron give photoemissions of several fragments, as are shown in Fig. 1. They are the excited hydrogen atoms ($n$=3,4,5,6,7,8), CH(A–X, B–X, C–X), $CH^+$(A–X, B–A, b–a), $Cl^+$, CCl(A–X), and $HCl^+$(A–X). The spectrum of $CDCl_3$ is similar; however, the Balmer lines are relatively weaker.

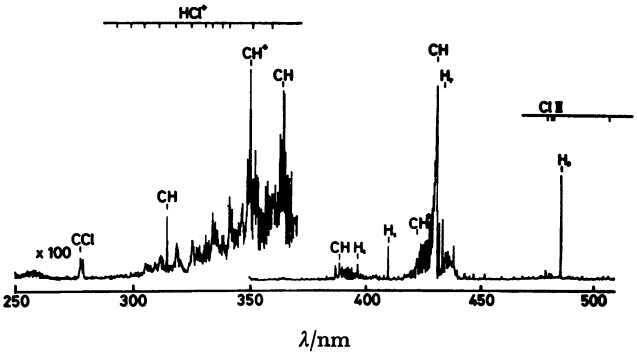

Fig. 1. Emission spectrum of chloroform by controlled electron impact. Electron energy 100 eV, electron-beam current 800 μA, spectral resolution 2 Å.

The intensities of the Balmer lines and bands of CH(A–X), $CH^+$(B–A), and CCl(A–X) are proportional to the electron-beam current and the gas pressure. Thus, these species should be produced in a one-electron-one-molecule primary collision. On the other hand, the square root of the emission intensity of $HCl^+$(A–X) is proportional to the electron-beam current (Fig. 2), although this intensity is directly proportional to the gas pressure. These results indicate that $HCl^+$ is produced in a two-step molecular elimination mechanism as in the case of $CH_2Cl_2$.[6]

*Thresholds.* The excitation functions of CH(A–X)

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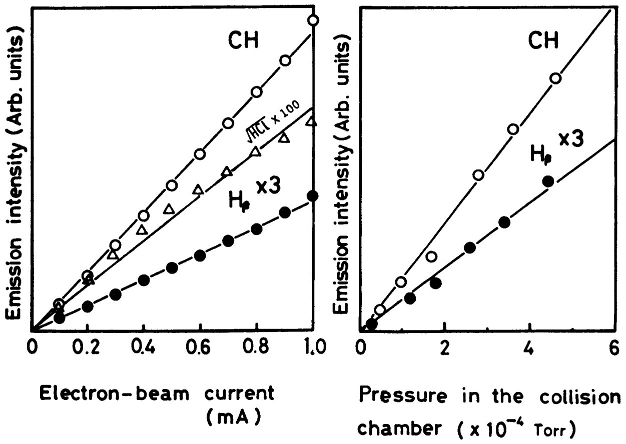

Fig. 2. Dependence of emission intensities on the electron-beam current and the gas pressure. Electron energy 100 eV.

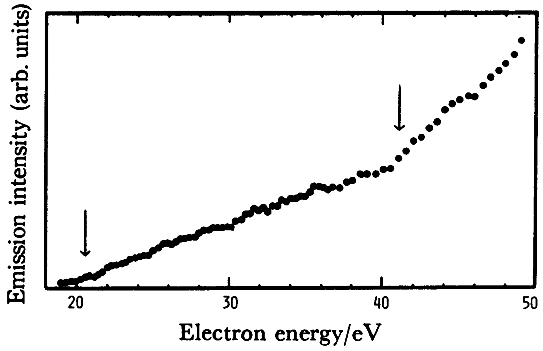

Fig. 3. Excitation function of the dissociative excitation of chloroform to yield the excited hydrogen atom ($n$=4).
Thresholds are indicated by arrows. The electron-beam current is 1 μA.

and H($n$=4) have been measured and the latter is shown in Fig. 3. The threshold energies for the formation of CH(A) lie at 16.8±1.0 and 34.0±2.5 eV, and those of H($n$=4) lie at 20.5±1.7 and 41.0±2.5 eV. These values are shown in Table 1, together with the previous results$^{6)}$ and several possible dissociation processes.

The first threshold of CH(A) at 16.8 eV can be assigned to some of the processes (a), (b), or (c) in Table 1. The first threshold of H*($n$=4) at 20.5 eV can be assigned to process (f), since the excited hydrogen atom carries some translational energy. The excess energy above the dissociation limit is partitioned into the translational, vibrational and rotational energies of the fragments. For the process (f), the law of conservation of momentum requires that H*($n$=4) carries 99% of the total translational energy, and the residual energy should be the vibrational and rotational energies of CCl$_3$.

*Isotope Effect.* The emission cross sections of the excited hydrogen atom produced in electron-hydrogen and electron-hydrogen chloride collisions have isotope effects.$^{10-12)}$ One of the main sources of this isotope effect is competition between dissociation and autoionization of superexcited states produced in the collision process.$^{13)}$

The emission spectra of H* and D* have been measured for mixtures of CHCl$_3$ and CDCl$_3$ in the equal amount; typical spectra of the Balmer-α line are shown in Fig. 4.

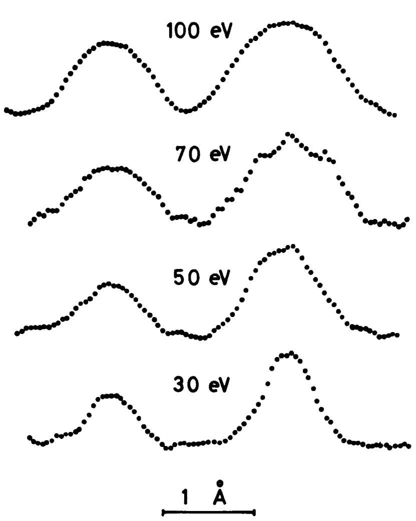

Fig. 4. High resolution spectra of the Balmer-α lines of H* and D* measured for mixtures of CHCl$_3$ and CDCl$_3$ in the equal amount. The left peak (smaller) is D* at 6561.0 Å and the right one (taller) is H* at 6562.8 Å. The resolution was 0.08—0.15 Å (Spex 1269 monochromator).

TABLE 1. THRESHOLD ENERGIES FOR DISSOCIATIVE EXCITATION OF CHLOROFORM

| | Process | Calculated dissociation limit | Observed threshold energy | |
|---|---|---|---|---|
| | | | This work | Toyoda *et al.*$^{6)}$ |
| (a) | $CHCl_3 \xrightarrow{e} CH(A)+Cl_2(X)+Cl(3P^5\ ^2P)$ | 12.0 | 16.8±1.0 | 17.6±1.0 |
| (b) | $CH(A)+Cl_2(A)+Cl(3P^5\ ^2P)$ | 14.2 | | |
| (c) | $CH(A)+3Cl(3P^5\ ^2P)$ | 14.4 | | |
| (d) | $CH(A)+Cl_2(C)+Cl(3P^5\ ^2P)$ | 19.1 | | |
| (e) | $CH(A)+Cl_2(X)+Cl(4S^1\ ^4P)$ | 20.9 | | |
| (f) | $CHCl_3 \xrightarrow{e} H(n=4)+CCl_3(X)$ | 16.7 | 20.5±1.7 | |
| (g) | $H(n=4)+CCl_2(X)+Cl(3P^5\ ^2P)$ | 19.0 | | |
| (h) | $H(n=4)+CCl(X)+Cl_2(X)$ | 20.0 | | |
| (i) | $H(n=4)+CCl(X)+Cl_2(A)$ | 22.2 | | |
| (j) | $H(n=4)+CCl(X)+2Cl(3P^5\ ^2P)$ | 22.5 | | |

Table 2. Relative emission cross sections ($\sigma_D/\sigma_H$) of the Balmer lines of the excited hydrogen atoms in electron-chloroform collisions

| Electron energy/eV | | Balmer-$\alpha$ $n=3$ | Balmer-$\beta$ $n=4$ | Balmer-$\gamma$ $n=5$ | Balmer-$\delta$ $n=6$ |
|---|---|---|---|---|---|
| 100 | | 0.61±0.07 | 0.61±0.07 | 0.65±0.09 | 0.72±0.09 |
| 70 | | 0.63±0.07 | 0.54±0.07 | 0.59±0.09 | 0.68±0.08 |
| 50 | | 0.56±0.07 | 0.61±0.07 | 0.58±0.10 | 0.66±0.08 |
| 40 | | — | 0.51±0.08 | 0.53±0.11 | 0.62±0.09 |
| 30 | | 0.50±0.08 | 0.52±0.08 | — | 0.60±0.09 |
| Optical resolution used/Å | above 50 eV | 0.13 | 0.08 | 0.08 | 0.08 |
| | 30, 40 eV | 0.15 | 0.11 | 0.11 | 0.11 |

The relative emission cross sections ($\sigma_D/\sigma_H$) have been determined from the relative area of the Balmer lines; the area was measured with a planimeter. The optical resolution of the measurements is so good that we can ignore the distortion of the line shape. The relative emission cross sections are dependent on the excitation energy and the principal quantum number of the excited hydrogen atom, as are shown in Table 2.

The electron energy dependence of the relative cross sections indicates that there are two or more processes for the formation of the excited hydrogen atom and that their relative contribution is dependent on the electron energy, since the value of a single dissociation process is expected to be independent of the excitation energy.[10]

Dissociation through a repulsive potential curve has a smaller isotope effect than that through a bound potential curve, since the former is expected to be faster than the latter and, as a result, affects a smaller competition with preionization. The difference of the Franck-Condon region may be important for the dissociation through a bound curve.[14] The decrease of the observed isotope effect (approach of the value of $\sigma_D/\sigma_H$ to 1.0) indicates that dissociation through a repulsive curve becomes more important at higher electron energies.

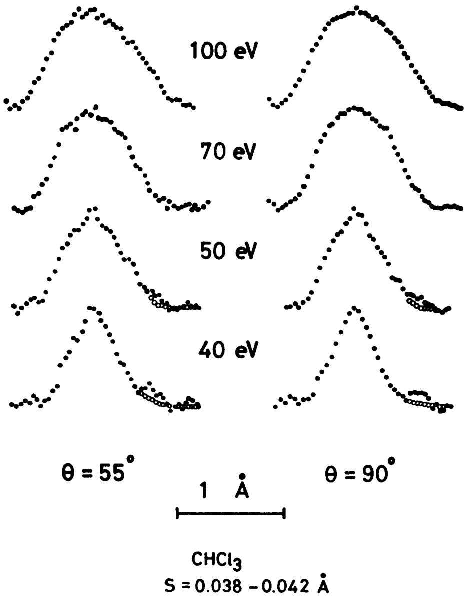

Fig. 5. Very high resolution spectra of the Balmer-$\beta$ lines of H* obtained by a Fabry-Perot interferometer at a optical resolution of 0.038—0.042 Å.

Solid dots: experimental data, open circles: corrected for background radiation. Electron-beam current 800 μA.

*Translational Energy Distribution.* Translational energy distribution of the fragment atom has much to do with the shape of the potential curve for the formation of this fragment atom. Dissociation through a repulsive curve results in fragments with high velocity, and that through a bound curve with low velocity.

The high resolution spectra of H* from $CHCl_3$ taken with a Fabry-Perot interferometer are shown in Fig. 5. The lines are distorted by some background lines, possibly, of Cl or $Cl^+$. This distortion was manually corrected as shown in the Figure.

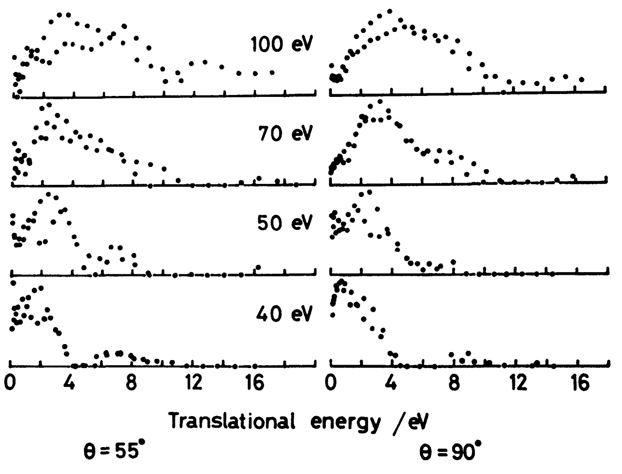

Fig. 6. The translational energy distribution of H* produced in electron-$CHCl_3$ collisions. Distributions were taken at 55° and 90° and they agree within experimental uncertainty.

The line shapes taken at 90° and 55° with respect to the electron-beam are in agreement with each other; thus, the effect of anisotropy is smaller than the experimental uncertainty. The differentiation of the line shape gives the translational energy distribution.[1,2] The results are shown in Fig. 6 for H* from $CHCl_3$ and in Fig. 7 for D* from $CDCl_3$.

The translational energy distribution excited by 100 eV electrons has a peak at about 4 eV. Upon decreasing the electron energy, the distribution shifts toward the lower energy and it has another peak at 0—1 eV when

Table 3. The corrected half-width ($\delta\lambda_t$) (Å) of the Balmer lines of the excited hydrogen and deuterium atoms in electron-chloroform collisions

| Electron energy/eV | Balmer-$\alpha$ $n=3$ | Balmer-$\beta$ $n=4$ | Balmer-$\gamma$ $n=5$ | Balmer-$\delta$ $n=6$ |
|---|---|---|---|---|
| $CHCl_3$ | | | | |
| 300 | 1.17±0.08 | 0.88±0.05 | 0.76±0.05 | 0.71±0.08 |
| 100 | 1.19±0.06 | 0.89±0.05 | 0.77±0.06 | 0.77±0.07 |
| 70 | 0.96±0.07 | 0.78±0.05 | 0.67±0.06 | 0.68±0.07 |
| 50 | 0.84±0.07 | 0.62±0.05 | 0.58±0.06 | 0.59±0.07 |
| 40 | — | 0.44±0.07 | 0.43±0.07 | 0.42±0.07 |
| 30 | 0.59±0.08 | 0.47±0.09 | 0.39±0.08 | 0.38±0.08 |
| $CDCl_3$ | | | | |
| 300 | 0.87±0.07 | 0.64±0.04 | 0.56±0.06 | 0.56±0.06 |
| 100 | 0.85±0.06 | 0.64±0.04 | 0.53±0.06 | 0.60±0.06 |
| 70 | 0.82±0.06 | 0.54±0.04 | 0.44±0.07 | 0.48±0.07 |
| 50 | 0.64±0.07 | 0.42±0.04 | 0.32±0.07 | 0.46±0.08 |
| 40 | — | 0.30±0.07 | 0.28±0.08 | 0.29±0.09 |
| 30 | 0.50±0.09 | 0.34±0.09 | — | 0.35±0.10 |

The optical resolution (s) is 0.04—0.20 Å.

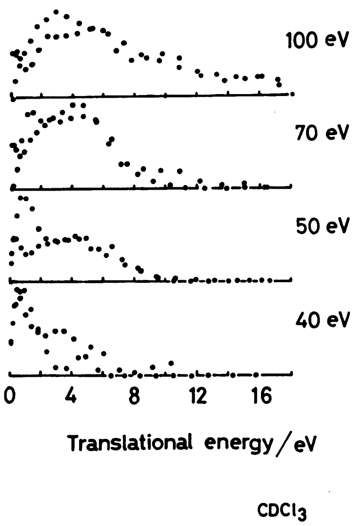

Fig. 7. The translational energy distribution of D* produced in electron-$CDCl_3$ collisions. The data were taken at 90°.

excited at 40 eV electrons. The distributions of H* and D* are, on the whole, similar; accordingly, the dissociation processes are qualitatively equal for two molecules. Furthermore, it is noteworthy that the distributions are similar to those of methane;[5] this finding suggests that dissociation processes of hydrogen from chloroform and from methane are similar. Molecules of similar structure and similar chemical bond may dissociate similarly.

*Average Translational Energy.* The translational energy distribution gives detailed and precise information of the kinetic character of the fragment produced in the collision processes. However, requirement of very high resolution makes it very difficult to apply the method for a weak line. Balmer-$\alpha$, $\gamma$, and $\delta$ lines from chloroform are such cases. Thus, instead of the translational energy distribution, an average translational energy has been obtained through the measurement of the half-width of the Balmer lines by use of a grating monochromator.

There are two methods to take the average of the translational energy; one assumes a Maxwell distribution[15,16] and the other a $\delta$-function distribution.[17,18] The value of the average depends substantially on the method used.[19]

$$E\ (\text{Av. }\delta\text{-function}) = 0.462\ E\ (\text{Av. Maxwell})$$

We have calculated the average translational energy with both methods and found that the average obtained by assuming a $\delta$-function distribution agrees more with the peak of the translational energy distribution shown in Figs. 6 and 7 than the average obtained by another method does.

The observed half-widths are shown in Table 3 and the average translational energies obtained by assuming a $\delta$-function distribution in Table 4. The results indicate that there seems no isotope effect in the average translational energy just as in the case of the distribution. This is superficially evident since the potential energy diagram should be identical for isotopic molecule; a

Table 4. Average translational energies (eV) of the excited hydrogen and deuterium atoms produced in electron-chloroform collisions

| Electron energy/eV | Balmer-$\alpha$ $n=3$ | Balmer-$\beta$ $n=4$ | Balmer-$\gamma$ $n=5$ | Balmer-$\delta$ $n=6$ |
|---|---|---|---|---|
| $CHCl_3$ | | | | |
| 300 | 3.7±0.5 | 3.8±0.5 | 3.6±0.5 | 3.5±0.7 |
| 100 | 3.8±0.4 | 3.9±0.5 | 3.7±0.6 | 4.1±0.7 |
| 70 | 2.5±0.4 | 3.0±0.4 | 2.8±0.5 | 3.2±0.7 |
| 50 | 1.9±0.3 | 1.9±0.3 | 2.1±0.5 | 2.4±0.6 |
| 40 | — | 1.0±0.3 | 1.2±0.4 | 1.2±0.4 |
| 30 | 0.9±0.3 | 1.1±0.4 | 1.0±0.4 | 1.0±0.4 |
| $CDCl_3$ | | | | |
| 300 | 4.1±0.7 | 4.0±0.5 | 3.9±0.8 | 4.4±0.9 |
| 100 | 3.9±0.6 | 4.0±0.5 | 3.5±0.8 | 4.9±1.0 |
| 70 | 3.6±0.5 | 2.9±0.4 | 2.4±0.8 | 3.2±0.9 |
| 50 | 2.2±0.5 | 1.7±0.3 | 1.3±0.6 | 2.9±0.9 |
| 40 | — | 0.9±0.4 | 1.0±0.5 | 1.2±0.7 |
| 30 | 1.4±0.5 | 1.1±0.6 | — | 1.7±0.9 |

difference, however, has been found for hydrogen molecules.[4]

*Dissociation Process.* The translational energy distributions and the average translational energies of the excited hydrogen atoms produced in electron-chloroform collisions show that there are more than one major dissociation processes just as in the case of methane. Methane has the fourth component, which is very fast.[5] The translational energy distribution of chloroform (Figs. 6 and 7) may have a corresponding component at 6—12 eV region. Thus, there are at least three major components of the excited hydrogen atom from chloroform with peaks of the distribution at 0—1, 4, and 6—12 eV, respectively.

The $2a_1$ molecular orbital of chloroform, which is C–H bonding, is located at 19.8—20.8 eV vertically above the ground state.[7,8] The corresponding molecular orbital of methane lies at 22.4 eV and is concluded to play an important role for the formation of the component with the peak of the translational energy distribution at about 3 eV and with the threshold at 21.6 eV.[5] Since the first threshold of H* from chloroform is 20.5 eV, we can conclude that one of the components of H* from chloroform is produced through excitation to Rydberg states converging to the $(2a_1)^1$ ionic state, just as in the case of methane. This component has the average translational energy of about 1 eV (Table 4); this component may be different from the one which has the peak at 0—1 eV at the excitation of 40 eV.

Higher doubly excited states have been found to be important for molecular dissociation and formation of the excited hydrogen atom.[3–5] There seems to be few reports on such excited states of chloroform and neither their location nor their electronic configuration are clear. However, similarity of the translational energy distribution with that of methane suggests that similar doubly excited states with those of methane play important roles in the formation of other components of H*(D*) from $CHCl_3$ ($CDCl_3$). One of the components with the peak of translational energy distribution at 4 eV may correspond to the excited hydrogen atom with the threshold at 41.0 eV.

*Concluding Remarks.* The translational energy distribution of the fragment atom gives useful information of the highly excited states and their dissociation. The detailed understanding, however, becomes possible by combining various information on highly excited states, which is in serious lack for chloroform.

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