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Translational Energy Distribution of the Excited Hydrogen Atom ($n=3$) Obtained by Controlled Electron Impact on CH_4

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Synopsis. Dissociative excitation of CH_4 has been investigated through the analysis of the high resolution spectra of the Balmer-α line. Translational energy distribution of $H^*(n=3)$ obtained in e-CH_4 collisions has three distinct components and another indefinite component; their peaks lie at 3, 0—1 and 4, and 8—12 eV, respectively.

Translational energy distribution of a fragment produced in a collision process gives valuable information for the detailed analysis of the mechanism of dissociative excitation of the molecule. Translational energy distributions of ionic and metastable fragments have been obtained by mass-spectroscopic or time-of-flight techniques, whereas those of excited short-lived fragments have recently become possible by an analysis of the Doppler profiles of their emission spectra.[1]

We have recently reported the translational energy distribution of $H^*(n=4)$ from methane obtained in e-CH_4 collisions and their assignments together with discussion on the mechanism of dissociative excitation of methane.[2] The results on $H^*(n=3)$ will be described in this note.

Experimental

The apparatus consists of an electron-molecule collision chamber, a Fabry-Perot interferometer and a data acquisition system. The details were reported previously.[3]

Results and Discussion

Since the line shape of the Balmer line obtained in an electron-molecule collision process is determined by the Doppler effect, analysis of the line shape should clarify the kinetic behavior of the excited hydrogen atom produced. The high resolution spectra of the Balmer-α lines have been taken with the use of an interferometer. Typical results of $H^*(n=3)$ from CH_4 are shown in Fig. 1.

For a successful analysis of the line shape, it has to be determined without distortion due to such as insufficient resolution of the optical system or the effect of anisotropy.[3] The optical resolution used here was 0.029—0.032 Å, and distortion from this source should be negligible. The line shapes were measured from 55° and 90° with respect to the electron-beam. Since the line shapes show no obvious difference for the two angles (Fig. 1), the effect of anisotropy should be smaller than the experimental uncertainty. Thus, we assume that the effect of anisotropy is negligibly small for the analysis of the translational energy distribution.

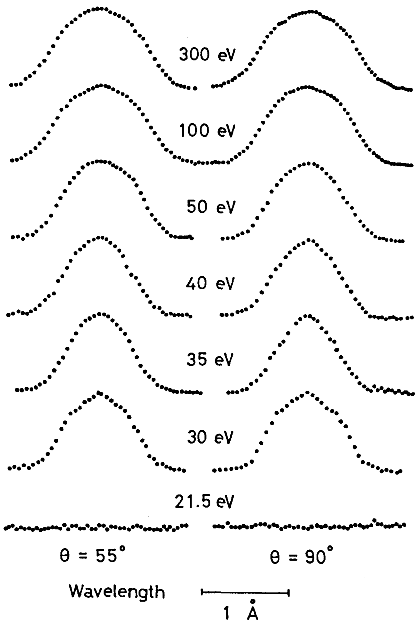

Fig. 1. High resolution spectra of Balmer-α line produced by controlled electron impact on CH_4. Electron energy: 21.5—300 eV, electron energy resolution: 1—2 eV, spectral resolution: 0.029—0.032 Å.

Ito *et al.* measured the Doppler profiles of the Balmer-α emission from methane with an etalon grating monochromator.[4] The observed linewidths of their measurement and of ours agree well within experimental uncertainties. They obtained the average translational energy from the halfwidth; however, the translational energy distribution calculated in this note contains more abundant and detailed information for the excitation process.

The differentiation of the line shape gives the translational energy distribution of the excited hydrogen atom;[3] the results are shown in Fig. 2. At an electron energy of 30 eV, the distribution has a peak at about 3 eV. As the electron energy increases, there appears a component with a peak at 0—1 eV. At higher electron energies, there is an intense peak at about 4 eV, and there seems to be another component in the 8—12 eV region. Thus, the translational energy distribution of $H^*(n=3)$ from methane has three distinct components and one indefinite component.

The translational energy distribution of $H^*(n=3)$ looks similar with those of $H^*(n=4)$,[2] H(HR),[5,6] and H^+.[7,8] Thus, the dissociative excitation of the short-lived and long-lived excited atoms and dissociative ionization proceed in similar processes. This finding is consistent with the core-ion model,[6] and justifies an

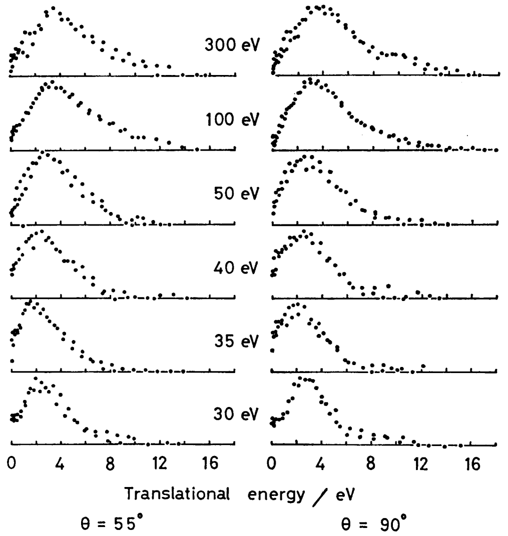

Fig. 2. Translational energy distribution of H*(n=3) produced by controlled electron impact on CH_4. Electron energy: 21.5—300 eV.

extension of this model to the formation of a low Rydberg atom.[2,4] Accordingly, we can conclude that the dissociative excitation of H*(n=3) proceeds through potential energy surfaces almost parallel to and reasonably close to that of the excited molecular ion core.

The component with the peak at 3 eV corresponds to component 1 of H*(n=4),[2] and the threshold of this component will be at about 21 eV. Thus, we can conclude that the formation of this component proceeds through excitation to Rydberg states converging to the $\tilde{A}^2A_1$ state of CH_4. The other components may be produced in a dissociative excitation through doubly excited Rydberg states converging to some excited ionic states or to some doubly ionized states.

The electron impact method has an distinct advantage for the investigation of molecular dissociation process, since optically-forbidden doubly excited states play important roles.

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