Doppler Profiles of the Balmer- α and - β Lines of the Excited Hydrogen Atoms (n=3,4) Produced in Ar⁺-C₂H₆ Collisions

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The Doppler profiles of the Balmer lines are very broad; their width decreases at lower ion energies. The translational energy distributions of H* calculated from the Doppler profile have two major components at about 10 eV and at about 100 eV for 2.5 keV of Ar*.

A spectral line may be broadened due to the Doppler effect. Its width and profile contain information on dynamics of formation of the emitting species. 1,2 When the profile is approximately isotropic, the translational energy distribution (TED) could be calculated by differentiating the Doppler line profile. 3,4 Its angular dependence was closely related with symmetry in the dissociation process. 5,6

The TED of atomic and molecular fragments produced in electron collisions and photodissociation have been measured. However, there have been no investigations on excited fragments produced in ion-molecule collisions. In this letter we are reporting the first measurement of this kind: the Doppler profile of the Balmer- α and - β lines and the TED of the excited hydrogen atoms (n=3,4) produced in Ar*-C₂H₆ collisions.

A schematic diagram of the experimental apparatus is shown in Figure 1. Briefly, the Ar † beam was generated and collimated with a Colutron ion source, ion optics and a Wien filter. The target gas pressure was about 2×10^{-2} Pa. The Balmer emission of the fragment hydrogen atom created in collision region was measured at 90° with respect to the ion beam using a grating monochromator (SPEX 1269, $\Delta\lambda$ =0.24 Å) and a liquid-nitrogen-cooled CCD camera (Princeton Instrument, LN/CCD-576EUV). The data were stored and analyzed with a CCD controller (Princeton Instrument, ST-130) and a microcomputer. All of measurements were carried out in a primary collision condition as confirmed by the previous procedure. 8

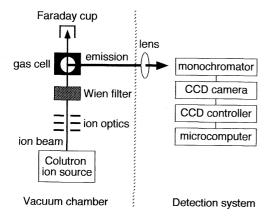


Figure 1. Schematic diagram of the experimental apparatus.

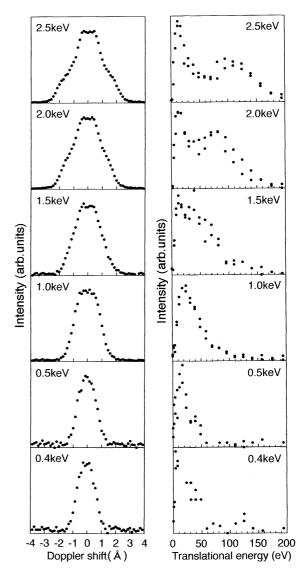


Figure 2. (a) Doppler profiles of the Balmer- α line and (b) TED of $H^*(n=3)$ produced in Ar^+ - C_2H_6 collisions.

The Doppler profiles of the Balmer- α line at ion energies of 0.4-2.5 keV are shown in Figure 2(a). The Doppler profiles apparently depended on ion energies; the profiles were broader at higher ion energy and became narrower at lower energies. They are much broader than those produced in e-C₂H₆ collisions;⁷ the half-width of the present profile is about 2 Å, whereas the half-width of that produced in electron collisions was about 0.5 Å. The Doppler profiles of the Balmer- β line at ion energies of 0.5-2.5 keV are shown in Figure 3(a). The

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profiles are similar to those of the Balmer- α line, and showed similar energy dependence; the half-width of the present profile is much larger than that produced in collisions with electrons. Thus the excited hydrogen atom produced in ion-molecule collisions has much larger translational energy than that produced in electron-molecule collisions.

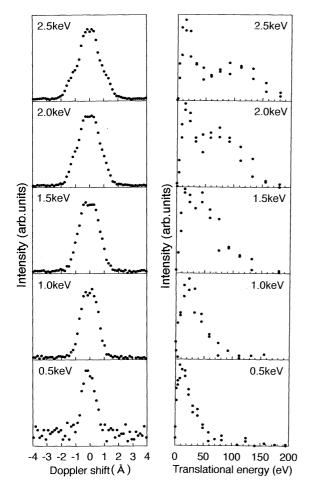


Figure 3. (a) Doppler profiles of the Balmer- β line and (b) TED of $H^*(n=4)$ produced in Ar^+ - C_2H_6 collisions.

The Doppler profile has a pair of inflection point and thus should be composed of two major components. The inflection point is clearer at higher ion energies and is the clearest at 2.5 keV. The broad component has a width of about 4 Å; its width decreases with the ion energy, indicating that the broad

component is produced in a momentum transfer process. The width of the narrow component is about 0.5 Å, which is approximately identical with the total width of the Doppler profile obtained in e-C₂H₆ collisions; thus the narrow component is produced as in e-C₂H₆ collisions.

The TED of an emitting species can be calculated by differentiating the Doppler profile, if the spatial distribution of the fragment is isotropic. The profiles are approximately symmetric, and we could calculate TED as before. Then we can obtain TEDs as shown in Figure 2(b) and Figure 3(b). There are two points at a translational energy in these figures. They were obtained by differentiating the left and right sides of the Doppler profile, and their difference indicates experimental uncertainty. The TEDs from both Balmer lines clearly indicate that there are two major components: one at about 100 eV and the other at about 10 eV for the ion energy of 2.5 keV. The former corresponds to the broad component of the Doppler profile and the latter to the narrow component.

The TEDs of the fast component decreased when the ion energy decreased. Thus the fast component should be produced through a momentum transfer process. Those of the slow component is approximately identical to that produced in e- C_2H_6 collisions. Thus, the slow component should be produced through dissociation of excited C_2H_6 molecules.

The detailed discussions on the dissociation dynamics should appear in a succeeding paper.

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References and Notes

- 1 Y.Hatano, *Comments At. Mol. Phys.*, **13**, 259 (1983); Y.Hatano in "Dynamics of Excited Molecules," ed by K.Kuchitsu, Elsevier, Amsterdam (1994), Vol.82, Chap.6, 163.
- 2 T.Ogawa, Eng. Sci. Rept. Kyushu Univ., 7, 231 (1986).
- 3 J.L.Kinsey, J.Chem.Phys., 66, 2560 (1977).
- 4 T.Ogawa and M.Higo, Chem.Phys.Lett., 65, 610 (1979); Chem.Phys., 44, 279 (1979).
- 5 R.N.Zare and D.R.Herschbach, *Proc.IEEE*, **51**,173 (1963).
- 6 K.Nakashima and T.Ogawa, J.Chem.Phys., 83, 4920 (1985).
- 7 T.Ogawa, T.Tsuboi, and K.Nakashima, *Chem.Phys.*, **156**, 465 (1991).
- 8 M.Tokeshi, K.Nakashima, and T.Ogawa, *Chem. Phys.*, 206, 237 (1996).