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Translational Energy Distribution of the Excited Hydrogen Atom (n=4) Produced in Electron-Benzene Collisions

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Synopsis. Line shapes of the Balmer-β line of H* produced in dissociative excitation of C_6H_6 were precisely measured. The translational energy distributions of H* (n=4) have two peaks at about 1 and 4 eV, and their relative intensity depends on incident electron energy.

Benzene is a basic organic molecule with a high symmetry. All six hydrogen atoms are equivalent. The dissociation mechanism of benzene for the formation of the excited hydrogen atoms should be a key process for dissociation dynamics of the organic molecule.

Benzene gives photoemissions of both its own excited states and fragment species such as H* and CH* upon collision with electrons.[1—4] Balmer series are intense, and the analysis of the Doppler line shape can give the translational energy distribution of the excited hydrogen atom.[5] The translational energy distribution is useful not only for an elucidation of dissociation mechanism of highly excited molecule but also for a correction of optical signal losses due to the high velocity of the fragments in the determination of the absolute emission cross section.

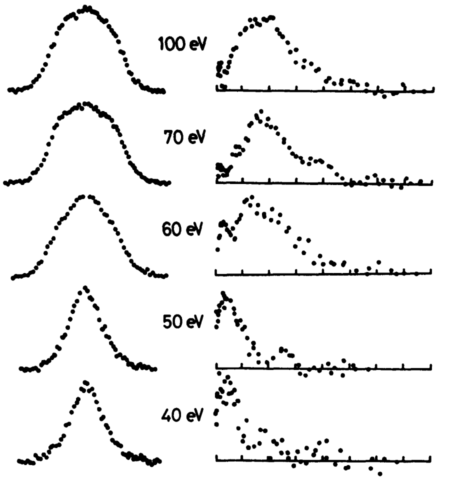

Fig. 1. High resolution spectra and translational energy distribution of H*(n=4) produced in e-C_6H_6 collisions. Electron energy: 40—100 eV, optical resolution: 0.0031—0.0042 nm.

This note presents the translational energy distributions of H* (n=4) and D* (n=4) produced by controlled electron impact on C_6H_6 and C_6D_6 and their incident electron energy dependence.

Experimental

The apparatus has been described in detail previously.[6] The Balmer lines were measured at optical resolution of 0.0031—0.0042 nm with a Fabry-Perot interferometer; this resolution is sufficient for the analysis of the Doppler profile. Excitation function was measured with an interference filter (band width 2 nm). Benzene (research grade) was deaerated before use.

Results and Discussion

The line shapes of the Balmer-β emissions produced in e-C_6H_6 collisions were measured precisely at 90° with respect to the electron beam and the results taken at various incident electron energies are shown in the left of Fig. 1. The translational energy distributions calculated from them are shown in the right of Fig. 1.

The line shapes of H* (n=4) from C_6H_6 taken a 90° and at 55° (magic angle) and D* (n=4) from C_6D_6 taken at 90° were also recorded for comparison at an electron energy of 100 eV, as shown in Fig. 2; their translational energy distributions have been obtained. The line shapes and the translational energy distributions at 90° and at 55° agreed with each other within the experimental uncertainty; thus, effect of anisotropy seems to be small.

The translational energy distribution has a peak at 1 eV when excited at electron energies of 40—50 eV. With increasing the incident electron energy, a new peak appears at about 4 eV; the distribution shifts toward higher energy. There seems to be an additional shoulder at 6—8 eV at an electron energy of 100 eV. The translational energy distribution of H* (n=4) measured at 100 eV looks similar to those from CH_4[7)]

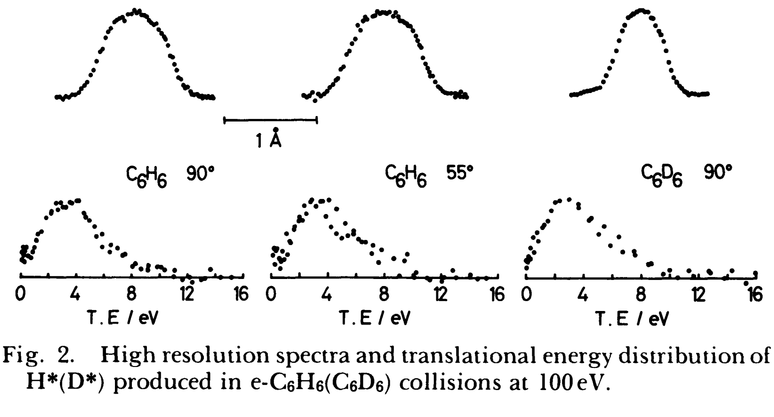

Fig. 2. High resolution spectra and translational energy distribution of H*(D*) produced in e-C_6H_6(C_6D_6) collisions at 100 eV.

and $CHCl_3$.[8] These results indicate that a few electronic excited states and a few dissociation processes take part in the production of the excited hydrogen atoms. The dissociation process, which has the peak of the translational energy distribution at 4 eV, is the major process at higher excitation energy and should proceed through repulsive potential surfaces. This process should also be symmetry forbidden, since the slope of the Fano plot for the Balmer-β emission is zero.[4]

The excited hydrogen atom with 4 eV of the translational energy has a velocity of 28000 $m \cdot s^{-1}$ and about 3 mm in 119 ns (average lifetime of H^* ($n=4$)). A correction for the loss of the excited species is necessary for the determination of the absolute emission cross section and this correction should be estimated from the translational energy distribution. Furthermore, the fly-out rate of H^* from the collision volume and the correction for the absolute emission cross section depend on the incident electron energy.

The dissociation processes are expected to be identical for isotope molecules such as H_2 and D_2,[9] and H_2O and D_2O,[10] however, the relative importance of coexisting processes are often different. In the case of benzene there is no clear quantitative difference in the translational energy distributions of H^* and D^* (Fig. 2).

The measured excitation function for the Balmer-β emission (0—100 eV) is similar to that reported by Beenakker and de Heer.[4] The threshold energy are 19.6±0.6 eV for C_6H_6, which agrees well with previous papers,[4,11] and 19.5±1.3 eV for C_6D_6; no obvious onset was observed except the first threshold.

The observed translational energy distributions and threshold energy indicate that a major route for the formation of the excited hydrogen atoms as lower incident electron energies is as follows:

$$C_6H_6(19.6\,\mathrm{eV}) \rightarrow C_6H_5(\tilde{X}\,^2A_1) + H^*(n=4) + E_{\mathrm{excess}}(2.0\,\mathrm{eV})$$

$$E_{\mathrm{excess}}(2.0\,\mathrm{eV}) = E_{\mathrm{trans}}(\approx 1\,\mathrm{eV}) + E_{\mathrm{int}}(\approx 1\,\mathrm{eV}),$$

where (19.6 eV) represents the excitation energy, E_{excess} the energy equal to the difference between the excitation energy and the calculated dissociation limit, E_{trans} the translational energy of H^* and E_{int} the internal energy.

At higher incident electron energies, an enormous number of direct and multistep fragmentation paths can be estimated from thermochemical data. Doubly excited Rydberg states converging to excited ion states or doubly ionized states, which are optically forbidden and generally repulsive, should play important roles.

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