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総合論文

Emission Spectroscopic Studies on Dynamics of Molecular Excitation and Dissociation by Controlled Electron Impact

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Emission spectrum by controlled electron impact has been a successful technique for the investigation of molecular dynamics.

(1) Molecular excitation. Aromatic molecules give an optical emission similar to fluorescence. However, as is shown by the vibrational structure and the electron energy dependence of benzene emission, its excitation process is not necessarily optical. Some aliphatic molecules also exhibit an emission band at the ultraviolet region.

(2) Molecular dissociation. Analysis of the Doppler profile, the threshold energy, the excitation function and the isotope effect of the atomic emission produced in electron-molecule collisions has clarified the dynamics of the molecular dissociation. Especially the Doppler profile has given the translational energy distribution of the fragment atom, which is very useful to disclose the potential energy curve. Its angular dependence has recently found to allow determination of the symmetry of the intermediate excited state and the magnetic sublevel distribution of the fragment atom. These findings have revealed detailed state-to-state dynamics of the molecular dissociation.

1. Introduction

Collisions between a molecule and an electron are important not only in atomic physics but also as the simplest chemical reaction. Historically electric discharges of all kinds are one of the oldest spectroscopic sources of ions and radicals. Though this method is very efficient, the complicated character of the discharge is a major obstacle for a detailed analysis of the mechanism of excitation and dissociation of the species concerned. A superior way to excite molecules by electrons is the electron-impact at a low pressure where the secondary effect is negligible; this technique has been called as controlled electron impact.^{1,2)} When the sample gas and electrons are in a form of a beam in a very low pressure chamber the technique can be called as the electron-molecule collision.

The electron-molecule collision process has a few distinctive characteristics as compared with the photo-excitation.

- (1) The excitation is non-resonant. The electron can create various excited states at various excitation energies.
- (2) Excitation to an optically-forbidden state is feasible. The electron can excite a molecule easily into a doubly-excited state or a triplet state.
- (3) Experiment at 10-100 eV has no intrinsic experimental difficulty for an electron beam,

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whereas photons of this energy are hard to be created.

(4) An electron beam can easily be continuous or pulsed.

These advantages have accelerated investigations on molecular excitation and dissociation dynamics induced in the electron-molecule collision. Ionized and metastable species (High Rydberg and forbidden states) have been investigated by mass spectroscopic techniques. On the other hand, short-lived radiative species (low Rydberg and valence excited species) should be measured by the optical emission spectroscopy. The emission cross section and resonance produced in electron-molecule collisions have been measured and compared with theories by physicists. Although there are a few pioneering works,³⁾ little have been studied, however, on dynamics of excitation and dissociation of molecules.⁴⁾

With taking advantage of this technique, the following projects have been carried out in our group.

(1) Detection of new species and new excited states have been carried out to disclose spectroscopic properties of ions, radicals and triplet states.⁵⁾

(2) Emission spectra of aromatic and aliphatic molecules have been measured for the analysis of dynamics of excitation.⁶⁻⁸⁾

(3) Dissociation dynamics have been discussed by measuring emission intensity and its isotope effect at low and medium optical resolutions.⁹⁻¹¹⁾

(4) Dissociation dynamics have been discussed through an analysis of the Doppler profile and its angular dependence at a high optical resolution with the use of an interferometer.

Translational energy and magnetic sublevel distributions of fragments and symmetry of intermediate excited states have been determined.¹²⁻¹⁹⁾

(5) Absolute emission cross sections have been determined for each dissociation process. This is important for a plasma simulation and for a comparison of a theory with experiments.²⁰⁻²¹⁾

In this autoreview recent progresses on (2) and (4) among the above projects will be discussed.

2. Apparatus

The basic principle of the experiment is shown in **Fig. 1**. The sample molecule is excited in a collision with an electron in a collision chamber under a high vacuum. Optical emissions produced in the collision region are measured photoelectrically. A schematic diagram of the collision chamber and the detection system is shown in **Fig. 2**.

Electrons from a heated (oxide coated) tungsten filament were accelerated and introduced into the collision region through a hole on an electrode; the electron beam source was pumped down separately. The sample gas was jetted through a multichannel nozzle and was collided with the electron beam. The pressure was measured with an ionization gauge at the wall of the collision chamber; typical base pressure is $1 \cdot 10^{-6}$ Torr and typical operating pressure is $1 \cdot 10^{-4}$ Torr.

Optical emission produced in the collision region was observed through a quartz window typically at 90° with respect to the electron beam. A small grating monochromator (e.g. Spex 1670) was used for a low resolution (1 nm and above) measurement, a large one (Spex 1269) for a medium resolution (1–0.01 nm) measurement, and a Fabry-Perot interferometer (Mizo-

ziri Optics) for a high resolution (below 0.01 nm) work. The interferometer has a typical finesse of 120–140 and its wavelength is scanned by varying the pressure of nitrogen between the two etalon plates. Photons were measured with a photomultiplier (cooled for a high sensitivity measurement) and were counted with a photon counter. A microcomputer (NEC PC8800) was used for the accumulation of the experimental data and their numerical analysis and for the control of the whole system.

When an angular dependence should be measured, a collision chamber with a rotatable electron gun was employed; its schematic diagram is shown in **Fig. 3**, together with that of the Fabry-Perot interferometer. The observation angle can be varied from 40–140°. An experiment can be carried out for hours without human attention except occasional refilling of liquid nitrogen.

3. Excitation of aromatic and aliphatic molecules

A typical emission spectrum of acetylene by controlled electron impact is shown in **Fig. 4**,²²⁾ as a typical example of a spectrum of an organic molecule; this spectrum was recorded with a Spex 1269 monochromator. It shows the Balmer lines of the excited hydrogen atom and bands of the CH radical (the A-X and B-X transitions) and of the C₂ radical (the Swan system: the d-a transition). The vibrational distributions of C₂(d) were approximately Boltzman and their vibrational temperatures were 22,000 K at 100 eV and 30,000 K at 13 eV. The emission spectra of ethylene and ethane looked alike; the Balmer lines were relatively more intense for these molecules.²²⁾

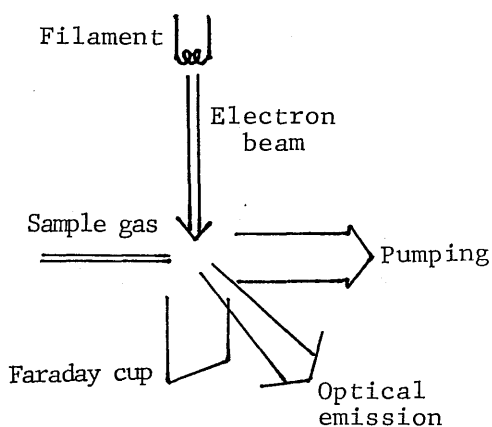


Fig. 1 The basic setup for a measurement of the emission spectrum by controlled electron impact.

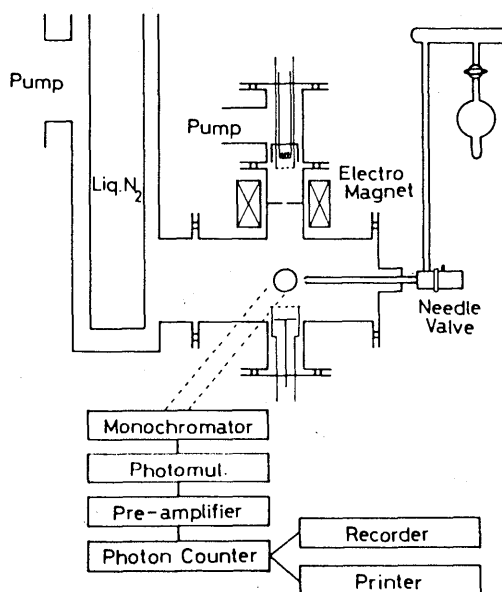


Fig. 2 Schematic diagram of the collision chamber and the optical detection system.

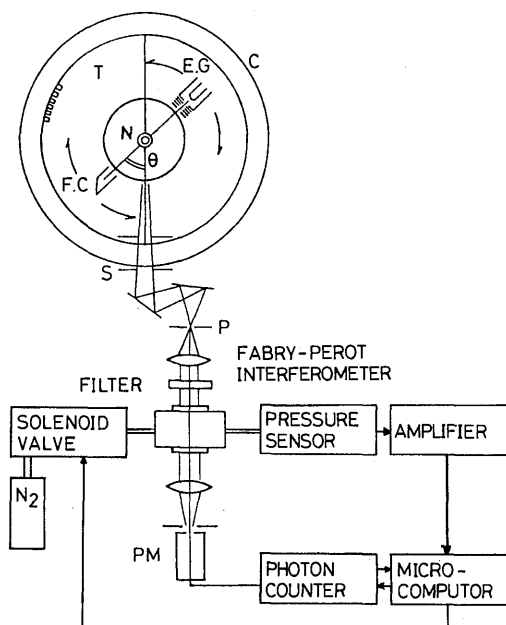


Fig. 3 Schematic diagram of the collision chamber with a rotatable electron gun and the Fabry-Perot interferometer.
C: collision chamber, EG: electron gun, F.C: Faraday cup, N: multichannel nozzle, T: turntable, S: optical aperture, P: pinhole, PM: photomultiplier.

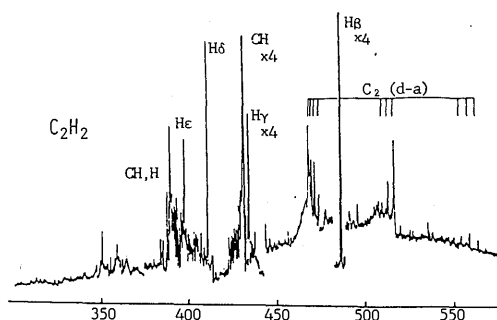


Fig. 4 A typical emission spectrum of acetylene by controlled electron impact.
Electron energy: 100 eV,
electron-beam current: 100 μ A,
gas pressure: $3 \cdot 10^{-4}$ Torr,
optical resolution: 3.2 Å.

The emission spectra of nine aromatic molecules excited by electrons are shown in **Fig. 5**; their spectra were recorded with a JASCO CT-50 monochromator. All the aromatic hydrocarbon molecules thus far studied showed a characteristic band in the 250–400 nm region.⁶⁾ The fluorescence spectra of these molecules correspond well to the observed emission spectra and, thus, these bands were assigned to the fluorescence transition from the lowest excited singlet state (S_1) to the ground state (S_0). Since the emission cross sections of the Balmer lines depend little on the size of the molecules, the relative emission cross sections of these bands can be estimated approximately from **Fig. 5**. These bands of the parent molecules looked alike with the spectra obtained in discharges, of equilibrated fluorescence and by the irradiation of white light.

The bulk of the oscillator strength of the valence shell electrons lies at very great values of the excitation energy for most molecules.²²⁾ Thus, the most important primary processes of the electron excitation are high-lying electronic excitations of the valence electrons. If the intramolecular radiationless relaxation is very fast, the primarily-excited high-lying states will fall to the lowest excited singlet (S_1) state and contribute to the observed optical emission therefrom.

The Born approximation is valid when the energy of the incident electrons exceeds substantially the threshold energy of the molecule. In this case, the cross section of the ex-

citation into the i th level (σ_i) is expressed by the optical oscillator strength (f_i) and the transition energy (E_i). The probability of optical emission from this level is proportional to the fluorescence quantum yield (ϕ_i). Thus, contribution of the i th level to the total emission (Γ_i) is as follows:

$$\Gamma_i = b \sigma_i \phi_i = b \phi_i f_i / E_i, \quad (1)$$

where b is a proportionality constant. This equation allows an estimation of importance of cascade processes over direct excitation. An order of magnitude estimation is possible with the use of average values of f_i and ϕ_i , although the transition is usually not discrete for a large molecule. The results showed that the direct excitation into the S_1 state is the

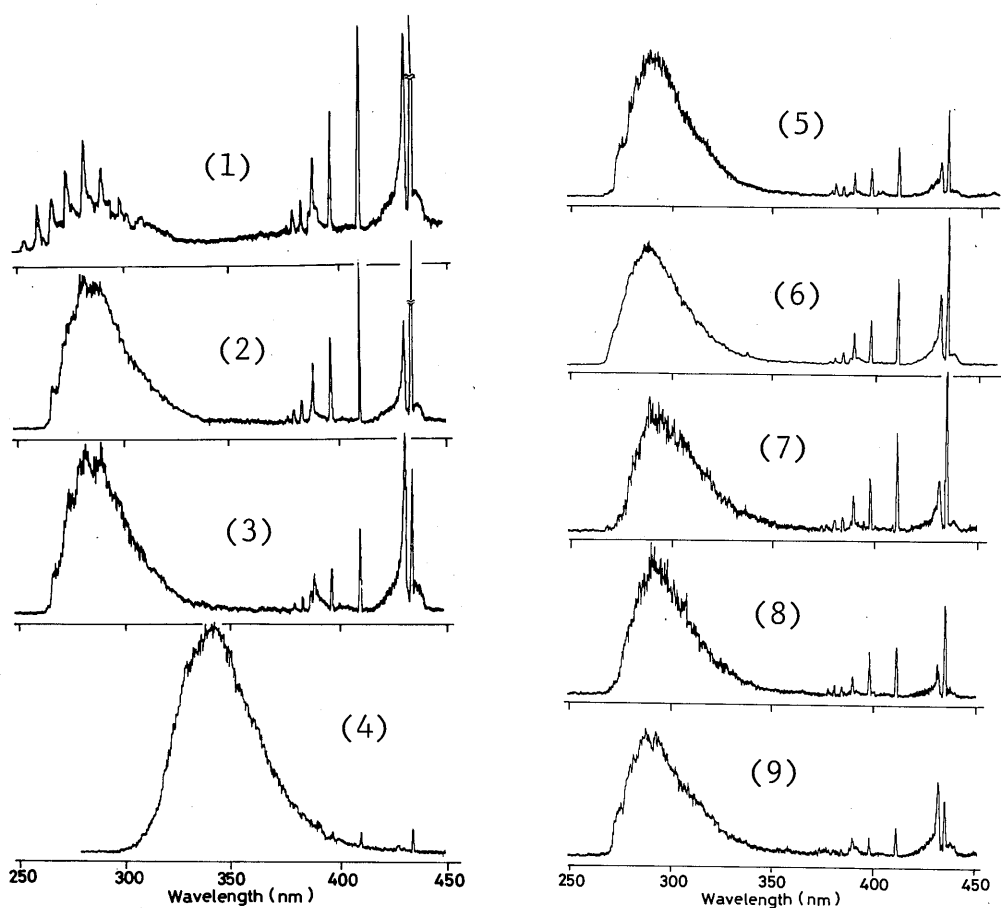


Fig. 5. Emission spectra of aromatic hydrocarbons by controlled electron impact.
Electron energy: 40 eV, optical resolution: 1 nm,
1: benzene, 2: toluene, 3: ethylbenzene, 4: naphthalene, 5: *p*-xylene, 6: *m*-xylene, 7: 1,3,5-trimethylbenzene, 8: 1,2,3-trimethylbenzene, 9: *p*-cymene.

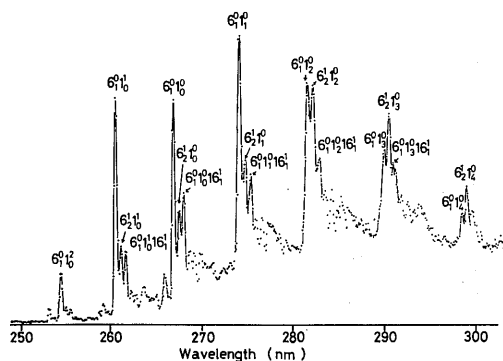


Fig. 6. Emission spectrum of benzene by controlled electron impact taken at a high optical resolution (0.2 nm).

Electron energy: 25 eV,
electron-beam current: 80 μ A,
benzene pressure: $5 \cdot 10^{-4}$ Torr.

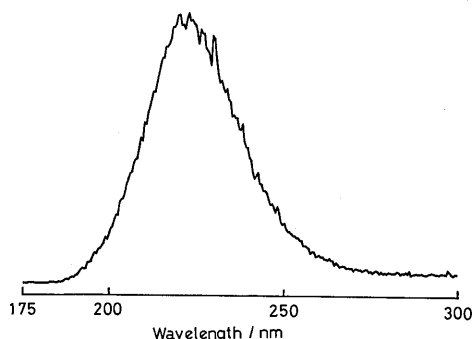


Fig. 7. Emission spectrum of methylcyclohexane by controlled electron impact at 50 eV. Optical resolution: 2.5 nm.

predominant process for benzene, while the cascade processes from the S_2 and S_3 states into the S_1 state is more important than the direct excitation into the S_1 state for naphthalene.⁶⁾

The emission intensity of benzene strongly depended on the incident electron energy; it became weaker at higher electron energies and almost disappeared above 100 eV. This finding indicates that the excitation process is not optically-allowed. The emission from naphthalene did not show such dependence and was intense even at 300 eV.

The vibrational structure of benzene measured at a higher optical resolution at 25 eV is shown in **Fig. 6**; this spectrum was recorded with a Spex 1269 monochromator. The spectrum showed well-resolved vibrational structure. The intense bands could be assigned as are indicated in the Figure. The vibrational structure did not change appreciably at electron energies of 4-100 eV.

The spectrum shows a preferential excitation into the 0 vibrational level of the S_1 state. Since intramolecular relaxation processes and secondary collision processes are negligible, the 0 level should be produced by the direct transition from the ground state. The 0-0 transition is strictly forbidden for an electric-dipole transition of benzene, and the 0 level is not found in a gas-phase fluorescence of benzene. A non-dipole transition was observed in the electron energy-loss spectra, and was assigned as an octupole transition²³⁾ or an electron exchange transition.²⁴⁾ The transition from a triplet state to the ground state should not give an intense optical emission. Thus, the present results should be assigned to a multipole transition.⁷⁾

The saturated hydrocarbon has the intense absorption band in the far ultraviolet region and show a very weak broad fluorescence by excitation of VUV photons.²⁵⁾ The optical emissions of cyclohexane, methylcyclohexane and *trans*-decalin excited by electrons showed a similar band in the 180-270 nm region as by optical excitation for neat liquid. A typical spectrum of methylcyclohexane recorded by a Spex 1670 monochromator is shown in **Fig. 7**. The intensity of this band was proportional to both the electron beam current and the gas pressure; this finding indicates that the band was produced in a pri-

mary process. The threshold energy of this band (6.9 eV) agreed with the onset of the absorption spectrum within experimental uncertainties. Thus, the observed band was assigned to the transition from the S_1 state to the S_0 state.

The electron-impact excitation is a nonresonant process and electrons can excite many vibronic levels simultaneously. Cyclohexane and methylcyclohexane have a number of vibrational modes, and optical emission from highly excited vibronic levels would lack any structural features.

4. Dissociation of simple molecules

Electrons of 10–100 eV can excite molecules in a highly excited state. Since most of the highly excited states are doubly excited states, excitation to these state are optically forbidden and difficult to be obtained by photons. Most important relaxation processes are ionization and dissociation. If an excited fragment is produced, the emission spectroscopy can disclose the dynamics of its formation.

There are several observable parameters in the dissociation of a molecule, as is shown in Fig. 8.

- (1) Threshold energy. ---This is the lowest energy required for dissociation ($\sim E_{\text{excit}}$).
- (2) Excitation function. ----This is electron energy dependence of the emission cross section. Fano plot of the excitation function can indicate whether the process is optically allowed or forbidden.²⁶⁾
- (3) Vibrational and rotational structure of the spectrum. The excess energy (E_{excess}) may be partitioned by vibrational and rotational energies of the fragment.²⁷⁾
- (4) Isotope effect of the emission cross section.^{10,22)}
- (5) Doppler profile. ---The excess energy (E_{excess}) may be converted into the translational energy of an excited fragment, and this induces a Doppler shift of the emission spectrum.¹³⁾
- (6) Angular dependence of the Doppler profile. --- This is determined by the symmetry of the intermediate state and the magnetic sublevel distribution of an atomic fragment.¹⁹⁾

Among these parameters, the Doppler profile has recently found to carry a mass of valuable information. In the beginning, its half-width was measured and analyzed.^{12,28–30)} Then the whole profile was carefully examined.¹³⁾ The Doppler profile of the atomic fragment is, in principle, anisotropic, since the dissociation process is in general anisotropic. However, it may be approximately isotropic in many cases, and its analysis on an assumption that it is isotropic is often a useful approximation.

If the dissociation is isotropic, the translational energy distribution ($\Pi(E)$) of the fragment can be obtained by differentiating its Doppler profile ($F(\lambda)$):¹³⁾

$$\Pi(E) \propto dF(\lambda)/d\lambda. \quad (2)$$

A δ -function distribution of the translational energy gives a rectangular Doppler profile, as is shown in Fig. 9.

The translational energy distributions of the ionized fragment were measured by mass spectroscopic techniques and have been useful in the analysis of molecular dissociation

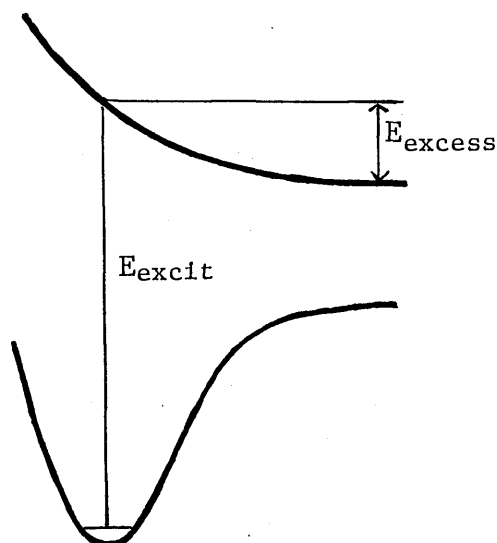


Fig. 8. Schematic diagram of molecular dissociation.

When a molecule is excited into an excited state (excitation energy: E_{excit}), the energy difference between the excited state (Franck-Condon) and the dissociation limit is the excess energy (E_{excess}), which will be divided into the translational, vibrational and rotational energies of fragments.

dynamics. Those of excited species should give similar information, if the core-ion model³⁰⁾ of molecular dissociation is valid. Relationship of the potential curve, the excitation function, the threshold energy and the translational energy distribution is shown in **Fig. 10** as a hydrogen molecule for an example. Hydrogen has a bonding and a repulsive curve highly above the ground state; they are Rydberg states converging to the lowest and the second lowest ionized states. A threshold energy corresponds to an onset of a new dissociation channel. Dissociation through a repulsive curve gives a large translational energy and that through a bonding curve a small translational energy. Thus analysis of the threshold and the translational energy can disclose energy and shape of the potential curve which is important in the dissociation process. Actually the excited hydrogen atom is the easiest to be investigated, because it has a higher velocity for an identical translational energy and thus a wider Doppler profile, which makes an optical measurement easier.

The Doppler profiles of the Balmer α line of $\text{H}^*(n=3)$ produced in collisions of hydrogen, methane and water with electrons are shown in **Fig. 11**. The Balmer line is just a line if measured with an ordinary grating monochromator, but it has structure if measured with a high resolution Fabry-Perot interferometer. The translational energy distribution is unique to the parent molecule. The difference in the Doppler profile and in the translational energy distribution indicate difference in the dissociation dynamics. Thus, the Doppler profile is very useful for an analysis of the dissociation dynamics.

The Doppler profile of $\text{H}^*(n=3)$ produced in electron- H_2 collisions were measured at various electron energies and at 90° with respect to the electron beam, as are shown in **Fig. 12**. The fact that profiles taken at 55° were similar to those taken at 90° justified the

assumption that the anisotropy should be smaller than the experimental uncertainties. This assumption seemed to be valid both for H^* ($n=3, 4, 5$) and for D^* ($n=3, 4, 5$).¹⁴⁾

The translational energy distributions of H^* ($n=3, 4, 5$) and D^* ($n=3, 4, 5$) were calculated by differentiating the Doppler profile; those of H^* ($n=3$) and D^* ($n=3$) are shown in **Fig. 13**.¹⁴⁾ There are two major groups in the translational energy distributions; the slow group has a peak of translational energy distribution at 0 eV and the threshold at about 17 eV, and the fast group has a peak of translational energy distribution at 7-8 eV (at 100 eV of incident electron energy) and has the threshold at about 24 eV. Careful examination of the excitation function, the translational energy distribution and the isotope effect of HD have showed that the fast group consists of three components.^{11, 14)} The assign-

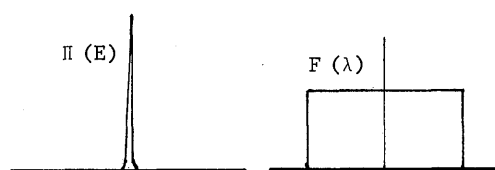


Fig. 9. Relation between the translational energy distribution and the Doppler profile.
A δ -function distribution gives a rectangular profile, if the dissociation is isotropic.

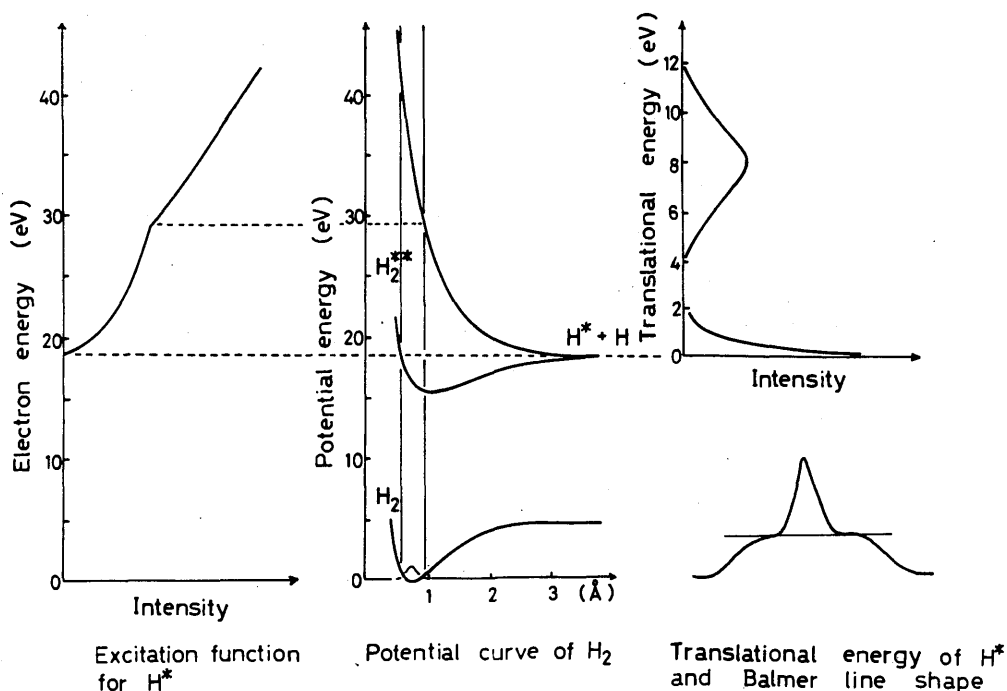


Fig. 10. Schematic representation of relationship of potential curves, excitation functions, threshold energies and translational energy distributions.
Those of hydrogen are shown for an example.

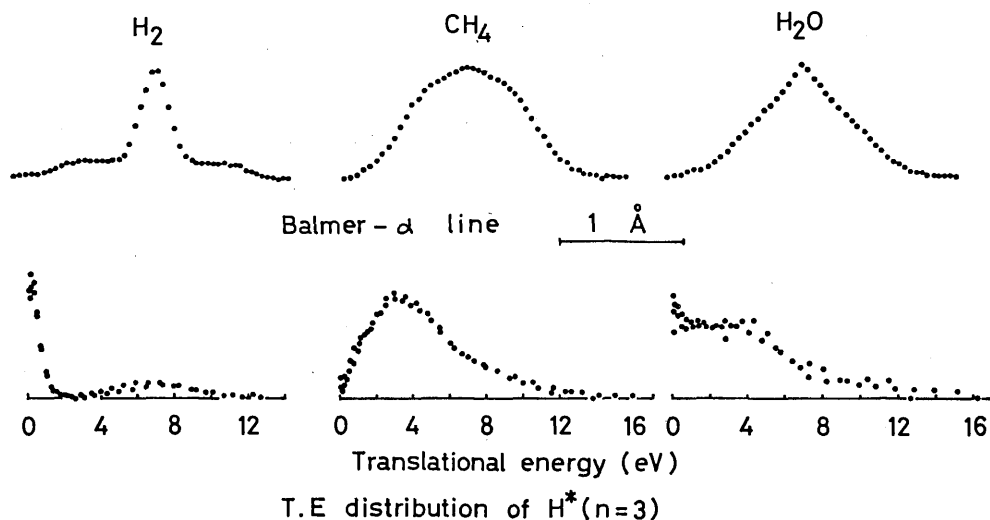


Fig. 11. The Doppler profiles of the Balmer α line and the translational energy distributions of $H^*(n=3)$ produced in electron- H_2 , CH_4 , H_2O collisions. Electron energy: 100 eV, optical resolution: 0.03 Å.

ments of these components are indicated on the potential energy diagram of hydrogen as is shown in **Fig. 14**; each component is shown with a number in a circle.

Component 1, which is slow (0–2 eV), can be assigned to direct dissociation and predissociation through Rydberg states ($1s \sigma_g$) ($4l$), which are converging to the lowest ionized state, $H_2^+(1s \sigma_g)$; $4l$ represents a molecular orbital correlating with $H^*(n=4)$ in the dissociation limit.¹⁴⁾ Since these Rydberg states are bonding, dissociation takes place only when the molecule is excited to the left of the curve above the dissociation limit and the translational energy of H^* should be small.

The three components of the fast group have large translational energies because they are produced through repulsive potential energy curves. Component 2 should be produced by predissociation through the lowest Rydberg state, $(2p \sigma_u)^2$, which is converging to the excited ionized state, $H_2^+(2p \sigma_u)$.¹⁴⁾ Since the formation of this component involves a curve crossing, its cross section depends on the mass of the nuclei and the principal quantum number of the excited atom. Component 3 was assigned to direct dissociation through the Rydberg states, $(2p \sigma_u)$ ($4l$), which are converging to the excited ionized state, $H_2^+(2p \sigma_u)$.¹⁴⁾ These states are highly repulsive, and this component has large translational energies. Component 4 was found from the analysis of the isotope effect of HD and was assigned to direct dissociation of the excited ionized state.^{11,14)}

The analysis of the Doppler profile makes it possible to determine the emission cross section for each dissociation channel; this is important for a comparison of the experimental value with the theoretical one and for basic data for a simulation. The absolute emission cross sections of the slow and fast groups of the excited hydrogen atom produced in e - H_2 collisions are shown in **Fig. 15**.

Similar investigations have been carried out for hydrogen chloride,¹³⁾ methane,¹⁵⁾ water, ammonia and benzene.¹⁶⁾ These results indicate that the analysis of the Doppler profile is very effective for an investigation of molecular dynamics and that the core-ion model is generally a good approximation.

5. Angular dependence of dissociation

The electron-impact dissociation of a molecule has in principle an angular dependence. The Balmer line has a positive polarization at lower electron energies,³¹⁾ as shown in **Fig. 16**. The angular distribution in its emission intensity showed that the fast group has a

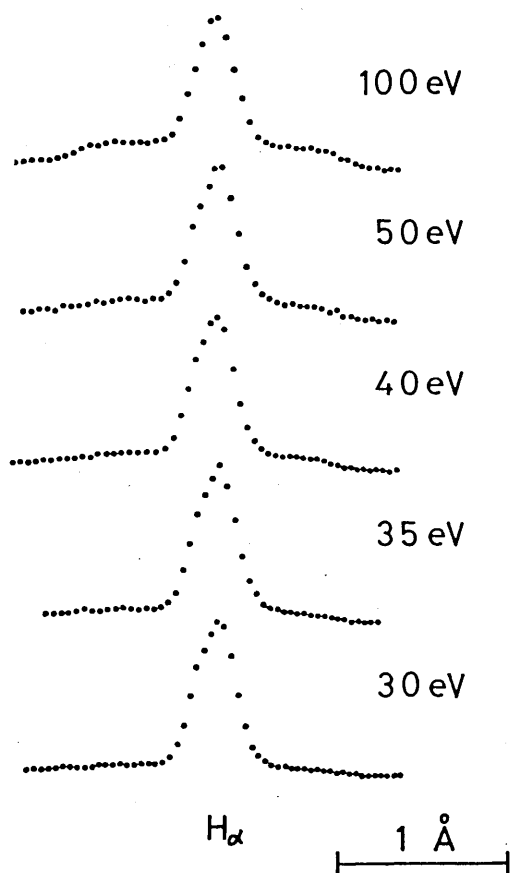


Fig. 12. High resolution spectra of the Balmer α lines produced in $e\text{-H}_2$ collisions. Spectral resolution: $0.031\text{--}0.039\text{ \AA}$, electron energy resolution: 1 eV , electron-beam current: $300\text{--}800\text{ }\mu\text{A}$, gas pressure: $4 \cdot 10^{-4}\text{ Torr}$, observation angle: 90° . Slight distortion is due to the fine-structure splitting.

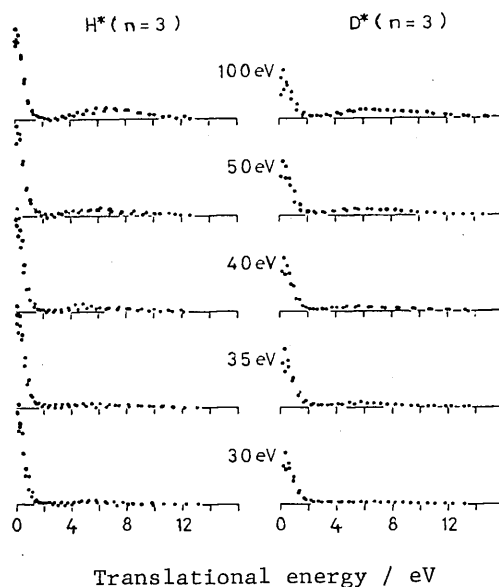


Fig. 13. Translational energy distributions of $\text{H}^* (n=3)$ and $\text{D}^* (n=3)$ produced in $e\text{-H}_2$, D_2 collisions.

$\sin^2\theta$ angular dependence,¹⁷⁾ as is shown in **Fig. 17**; it becomes smaller at higher electron energies. The angular distribution of emission intensity and polarization are physically identical. Both of them depends on the symmetry of the dissociation process.³²⁾

When the fragment has an anisotropic angular distribution, the Doppler profile should vary with the observation angle, as theoretically predicted;^{29,33)} but no measurement was carried out.

There are two important parameters for angular dependence of dissociation: angular distribution of dissociation and magnetic sublevel distribution of the excited atom. The former depends on the direction of the transition moment with respect to the electron beam, and the latter is the anisotropy of emission with respect to the dissociation axis, which is induced by a preferential population in magnetic sublevels (polarization in magnetic sublevel).

The angular dependence of the Doppler profile accordingly depends on these two parameters.¹⁹⁾ The Doppler profile can be expressed for an excited atom of a velocity v observed at an angle θ with respect to the electron beam as:¹⁹⁾

$$F(\Delta\lambda, \theta, v) = (3c/16\pi\lambda_0v) (J_{\parallel} + J_{\perp}) (1 - J_p (\Delta\lambda_c / \lambda_0v)^2) \times (1 + bP_2(\cos\theta)P_2(\Delta\lambda_c / \lambda_0v)), \quad (3)$$

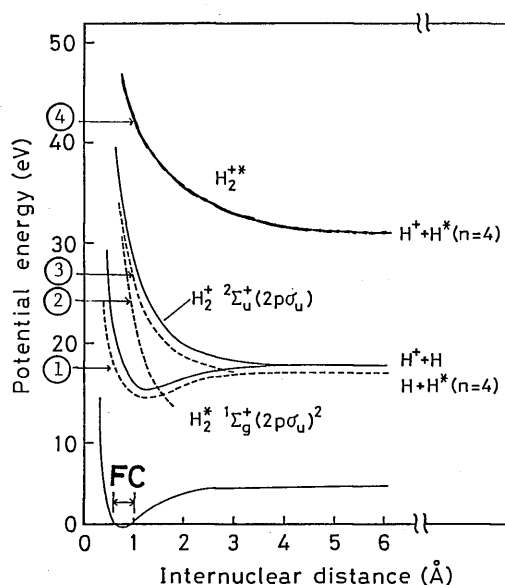


Fig. 14. Schematic potential energy diagram of hydrogen. The solid lines are potential curves for the ground state and ions, and the broken lines are those for Rydberg states converging to the ionized states.

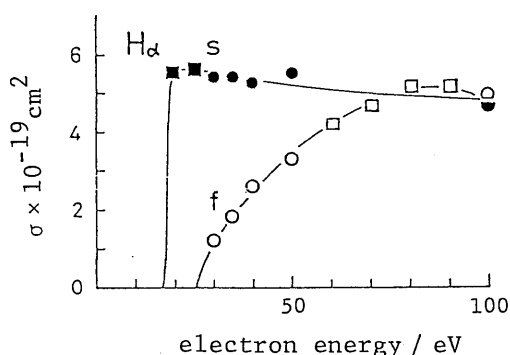


Fig. 15. Emission cross sections of the slow and the fast groups of H^* ($n=3$) calculated from the relative intensity of the two groups.

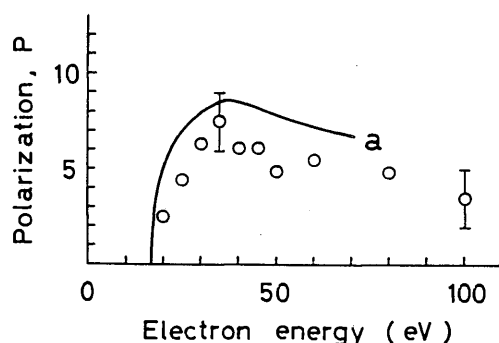


Fig. 16. Polarization of the hydrogen Balmer β line.
Circle: present data, solid line: Ref. 31.

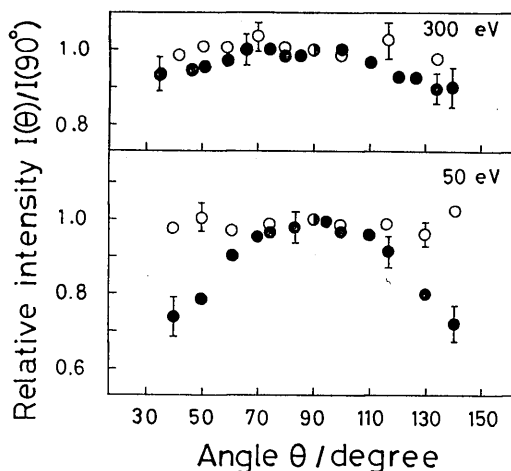


Fig. 17. Angular distributions of the slow (open circle) and the fast (solid circle) groups of H^* ($n=4$).
 θ : angle between the electron-beam and the observation direction.

where $\Delta\lambda$ is the Doppler shift, b is the parameter for the angular distribution of dissociation, J_p is the parameter for the anisotropy of emission ($J_p = (J_{\parallel} - J_{\perp}) / (J_{\parallel} + J_{\perp})$) and P_2 is the Legendre polynomial of second order. Actually the velocity of the atomic fragment is not uniform and the profile should be integrated over the velocity distribution of the excited atom.

The Doppler profile can be simulated with the above equation for a given translational energy distribution. The simulated profile for an fast excited hydrogen atom is shown in the top of **Fig. 18** for representative values of b and J_p . The result indicates that when b is positive, $F(45^\circ)$ is slightly broader than $F(90^\circ)$ and that when b is negative, it is narrower.

There are usually more than one dissociation processes for H^* formation in electron-molecule collisions. Each of them may have a different symmetry and a different angular distribution. Thus, the angular dependence of the profile is complicated, and, accordingly, it would be difficult to estimate b and J_p just by comparing the observed profile with the simulated one.

The difference of the Doppler profiles taken at two different angles is more useful for such investigations, because the effect of an isotropic process can be ignored and the effect of anisotropy becomes clearer. The difference of the two Doppler profiles measured at 90° and 45° with respect to the electron beam is

$$\Delta F(\Delta\lambda, v) \propto (1 - J_p(\Delta\lambda c / \lambda_0 v)^2) \cdot b P_2(\Delta\lambda c / \lambda_0 v). \quad (4)$$

The difference, ΔF , was denoted as angular difference Doppler profile; b affects its sign and height, and J_p its shape.¹⁹⁾

The angular difference Doppler profile ΔF should actually be calculated by the integration over ν . The simulated difference profiles are also shown in **Fig. 18** for the fast group of H^* produced in $e-H_2$ collisions.¹⁹⁾

The observed results for H^* produced in $e-H_2$ collisions are shown in **Fig. 19**. The angular difference Doppler profiles measured at 35, 50 and 65 eV clearly shows b is positive for the major component of the fast group (component 3).³⁴⁾ A simulation of the difference profile indicated that J_p is 0.7 ± 0.1 .³⁴⁾

This finding indicates that the symmetry of the intermediate excited state of H_2 for the formation of component 3 is Σ_u and the excited hydrogen atom is in the $d\sigma$ state.³⁴⁾ This finding makes it possible to select one dissociation channel out of many possible candidates. Thus, the analysis of the Doppler profile has been proved to be very useful and effective for the analysis of the dissociation dynamics.

6. Concluding remarks

Investigations of the dynamics of molecular excitation, ionization and dissociation are

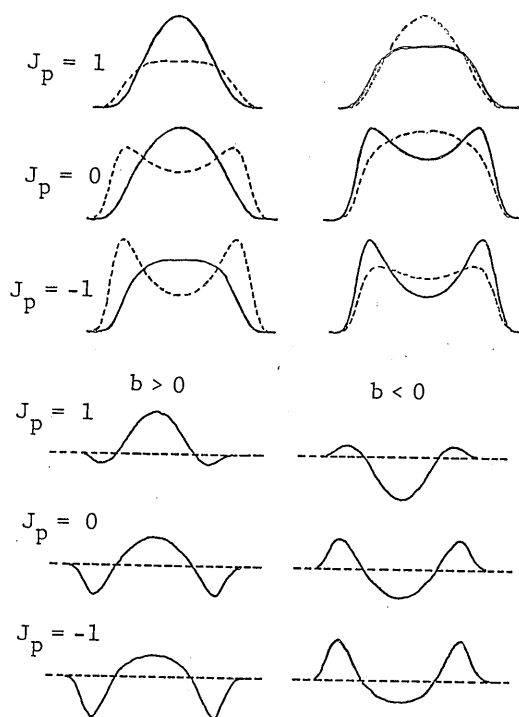


Fig. 18. Simulated Doppler profiles and their angular difference profiles for a fast excited hydrogen atom.

—: profiles at an angle of 90° ,
 ----: profiles at an angle of 45° .

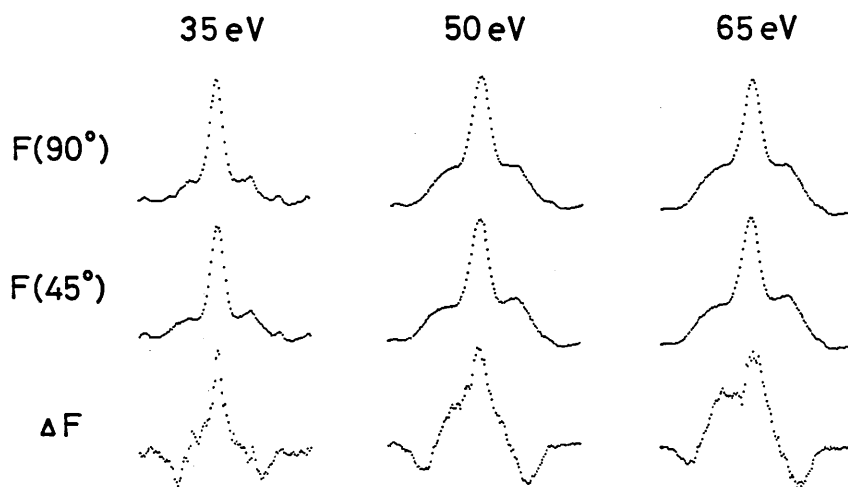


Fig. 19. The observed Doppler profiles (F) and their angular difference profiles (ΔF) for H^* ($n=4$) produced in $e-H_2$ collisions.

important for the understandings not only of chemical reactions but also of radiation effects, plasma physics and atmospheric processes. Emission spectroscopy is one of the most powerful technique.

Interaction of the molecule with the electron is interesting because of its large cross section, possibility of optically forbidden excitation and experimental feasibility at higher energies. In spite of the recent advent of the synchrotron radiation there are still many possibilities and challenges in the field of electron-molecule collisions.

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