Emission Spectra of Fluorobenzenes by Controlled Electron Impact

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The fluorescence emission spectra of fluorobenzene, *p*-difluorobenzene and hexafluorobenzene excited in collisions with electrons were measured for the study of the dynamics of the exciting aromatic system. These spectra showed a band assignable to the $S_1 \rightarrow S_0$ transition of the parent molecule. The bands of fluorobenzene and *p*-difluorobenzene were intense and showed a pronounced vibrational structure and the intense vibrational transitions were optically allowed. Whereas, that of hexafluorobenzene was broad and weak and did not show any clear vibrational structure.

An electron impact method has a distinctive advantage over a photoexcitation method in the excitation to highly-excited states, to optically-forbidden states and to triplet states. An interaction between an electron and a molecule is the simplest case of a chemical reaction and the elementary process in the plasma. Many organic compounds have been investigated by means of the electron impact method. Aromatic compounds have shown an intense optical emission of the S_1–S_0 transition of the parent molecule as well as bands of the fragment species such as H*, CH*, and C_2*.[1,2] Their exciting processes have been investigated and differences between the spectra excited by electrons and those by photons were revealed.[1]

Electrons can induce both optically allowed and forbidden transitions when the energy of the incident electron is close to the threshold energy of an excitation process.[3] The emission spectrum of benzene by controlled electron impact was different from the one by the photoexcitation;[4] the vibrational structure due to the $6^0 1^n$ series, which was symmetry forbidden for optical excitation, was clearly observed in the former at the electron energy of 25 eV.[5] However, comparisons of the spectra of other aromatic compounds by electron impact with those by photoexcitation remain as a subject of research.

Fluorobenzene (C_6H_5F) and *p*-difluorobenzene (*p*-$C_6H_4F_2$) have both a large optical absorption cross section and fluorescence quantum yield, and the vibrational structure of their absorption[6,7] and the fluorescence[8,9] spectra has been discussed in detail. Hexafluorobenzene (C_6F_6) showed no vibrational structure in both the absorption[10] and the fluorescence[11] spectra, although the excitation process of C_6F_6 would be expected to be identical with benzene since C_6F_6 has the same symmetry (D_{6h}). Though the emission spectrum of C_6H_5F by controlled electron impact has already been measured at 200 eV,[12] no detailed investigation on the excitation process has been reported.

In the present paper the optical emission spectra of C_6H_5F, *p*-$C_6H_4F_2$ and C_6F_6 were measured in the 250—450 nm region under the electron impact excitation as an extension of our investigation[2,12] on aromatic compounds. The electron energy dependence of the emission spectrum was also measured since the optically forbidden bands will become intense as the electron energy is decreased.[3] The vibrational structure of the S_1–S_0 transition of the parent molecule was also measured at 24 eV in order to compare it with that obtained by photoexcitation.

Experimental

The apparatus is almost identical with that described previously.[2,13] In brief, the collision chamber (20 cm) was evacuated with a 10 cm oil-diffusion pump (650 $dm^3 s^{-1}$) having a liquid nitrogen trap. The sample gas was introduced into a gas cell, and was collided with an electron beam from a tungsten filament. The base pressure was of the order of 10^{-6} Torr (1 Torr=133 Pa) and the operating pressure in the gas cell was kept at about 3×10^{-3} Torr for a single collision condition to be valid.

The optical emission was observed through a quartz window at an angle of 90° with respect to the electron beam. The overall spectrum was obtained with a SPEX MINIMATE 1670 monochromator and the high-resolution spectrum with a SPEX 1269 monochromator equipped with a 1200 grooves/mm grating blazed at 300 nm and a Hamamatsu R585 photomultiplier. Photons were counted with a Hamamatsu C1230 photon counter. When the optical emission was very weak, the electron beam was pulsed so that stray radiation from the tungsten filament could be subtracted (a digital boxcar technique). A JASCO CT-50 monochromator equipped with a 1200 grooves/mm grating blazed at 300 nm and an NF PC545 photon counter were used in such cases so as to obtain a medium-resolution spectrum with a high detection efficiency.

The instrumental response of the optical system was calibrated with a Hamamatsu L591 standard deuterium lamp. The electron energy was calibrated with the peak of N_2* (337.1 nm) at 14.02 eV and its energy resolution was about ±1—2 eV at 11eV.

C_6H_5F was obtained from the Nakarai Chemicals, Ltd. and *p*-$C_6H_4F_2$ and C_6F_6 were obtained from the Wako Pure Chemical Industries, Ltd. Each sample was frozen and pumped repeatedly to remove any dissolved gases.

Results and Discussion

Mono and Difluorobenzene. Typical emission spectra of C_6H_5F and *p*-$C_6H_4F_2$ in the 250—450 nm region with an optical resolution of 1.0 nm are shown in Fig. 1

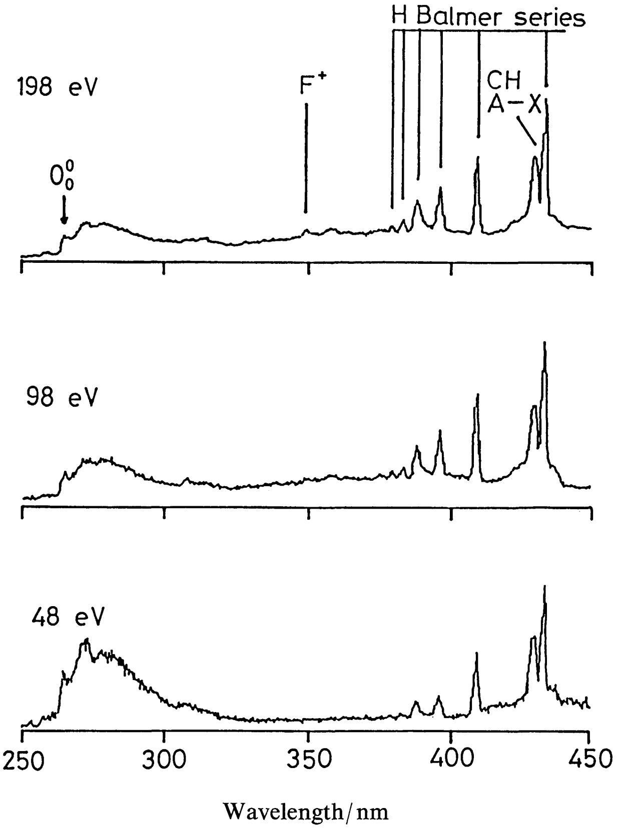

Fig. 1. Emission spectra of fluorobenzene by controlled electron impact measured by a SPEX MINIMATE 1670 monochromator. Optical resolution: 1.0 nm, electron beam current: 2—10 μA.

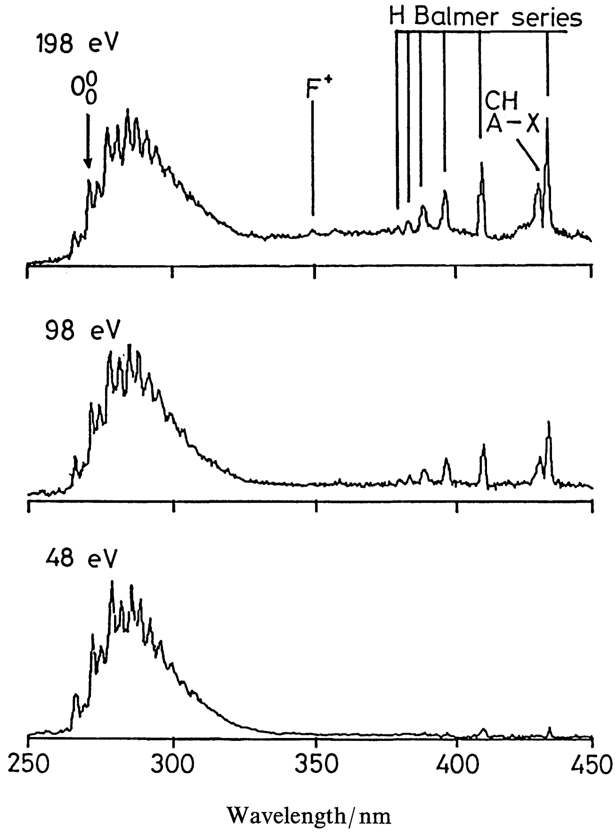

Fig. 2. Emission spectra of *p*-difluorobenzene by controlled electron impact measured by a SPEX MINIMATE 1670 monochromator. Optical resolution: 1.0 nm, electron beam current: 2—10 μA.

and Fig. 2, respectively. An intense band at 260—320 nm was assigned to the transition from the lowest-excited singlet state (S_1) to the ground state (S_0), since an optical fluorescence spectrum was located in the same region.[8,9] The excitation functions of these bands were also measured and the threshold energies were found at 4.4 eV and 4.1 eV, respectively; they agree well with the absorption edge[6,7] of the two molecules within experimental errors.

In the wavelength region longer than 350 nm, there are several lines and bands of excited fragment species as in the case of other aromatic molecules.[2] They have been assigned to H (the Balmer lines), F^+ ($3p^5\,P$–$3d^5\,D$), and CH (the A–X transition), as shown in the figures. No CF* (A–X) emission at 220—280 nm was observed; whereas, it was intense in the spectra of CF_4 excited by He(2^3S), He^+, and He_2^+.[14] At higher incident electron energy, a continuous emission becomes clear in the region longer than 320 nm. This may be due to the excited fragment species made of 3—4 atoms such as C_2H^* and C_2F^*; C_6F_6 shows this continuous emission as will be mentioned later.

As the electron energy increases, the dipole Born approximation becomes valid, the optically allowed transition becomes dominant, and finally the process would be equivalent to the photoexcitation process.[3] For example, the $S_0(^1A_{1g})$–$S_1(^1B_{2u})$ excitation of benzene is the symmetry-forbidden transition; this band almost disappears at 100 eV.[2,15] On the other hand, the corresponding transitions of toluene and *p*-xylene are no longer optically forbidden because of their descending symmetry (C_{2v} or D_{2h}), and they are intense even at higher energy.[16] The spectra of C_6H_5F and *p*-$C_6H_4F_2$ would be similar to those of toluene and *p*-xylene. Indeed, the S_1–S_0 emission of these molecules is intense at higher energy as shown in Figs. 1 and 2. A rough estimate of the S_1–S_0 emission intensity can be done in comparison with the intensity of the Balmer line.[17] At the electron beam energy of 50 eV, the relative S_1–S_0 emission intensity of C_6H_5F and *p*-$C_6H_4F_2$ is about 2 times and 40 times as large as that of benzene, respectively.

Hexafluorobenzene. Typical emission spectra of C_6F_6 in the 250—470 nm region are shown in Fig. 3. At an excitation energy of 9 eV, the emission spectrum of C_6F_6 shows a broad band in the 290—470 nm region; this spectrum is noisy in the region longer than 450 nm owing to an intense stray radiation from the tungsten filament. This broad band was assigned to the S_1–S_0 transition since its fluorescence spectrum was located in the same region.[11] The threshold energy could not be measured owing to its small intensity. The fluores-

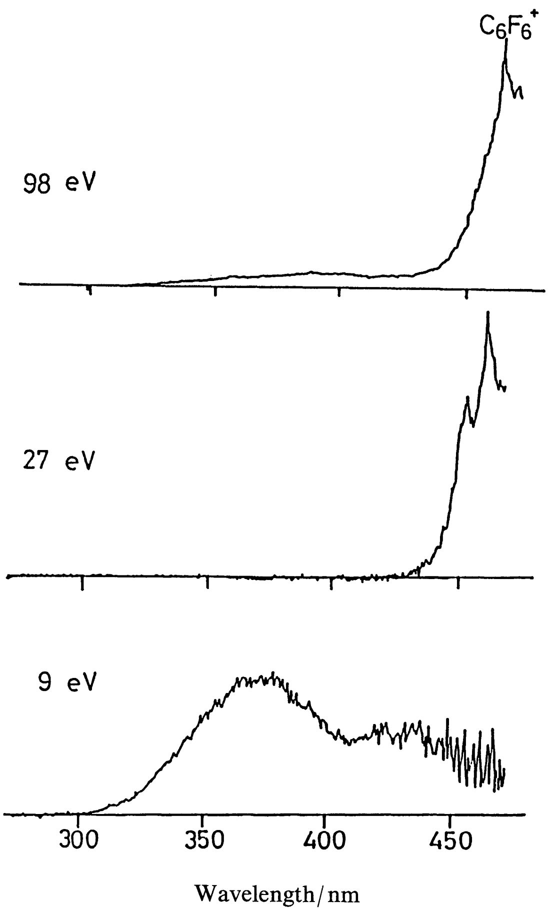

Fig. 3. Emission spectrum of hexafluorobenzene by controlled electron impact. 9 eV: The electron beam was pulsed to subtract the stray radiation. Optical resolution: 3.0 nm, monochromator used: JASCO CT-50, electron beam current: 8—10 μA. 27 eV and 98 eV: The electron beam was direct. Optical resolution: 1.0 nm, monochromator used: SPEX MINIMATE 1670, electron beam current: 2—5 μA.

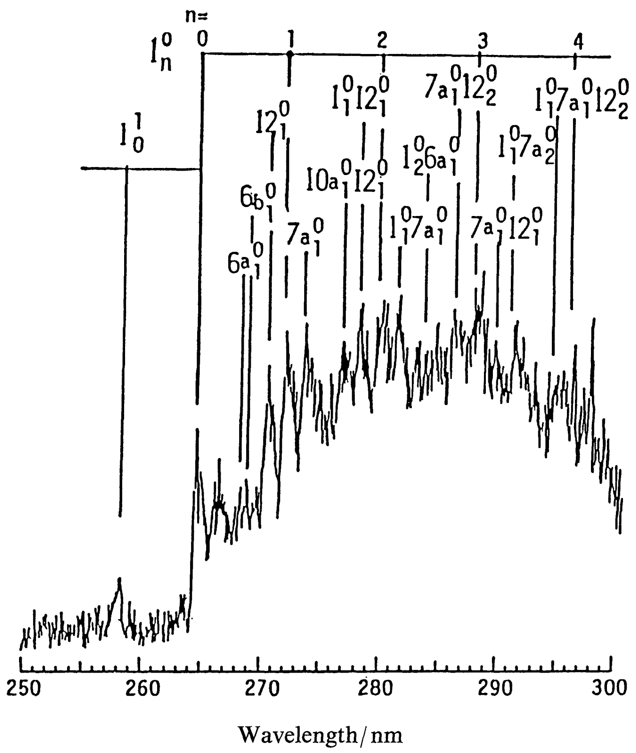

Fig. 4. High-resolution emission spectrum of fluorobenzene by controlled electron impact measured by a SPEX 1269 monochromator. Optical resolution: 0.20 nm, electron energy: 24 eV, electron beam current: 3 μA.

cence quantum yield of C_6F_6 is 1.4×10^{-3} (excited by a medium-pressure mercury arc at 235 nm).11) Such a small value is consistent with the observed weakness of the emission of the parent molecule. The observation of this band of C_6F_6 was made possible by lowering the electron beam energy to 9 eV so as to remove all bands of the fragment species and of the parent ion which has a threshold energy of 12.56 eV.18) There are, however, some contributions of the parent ion in the spectrum due to a low energy resolution of the electron beam at 9 eV.

At excitation energies of 27 and 98 eV, in contrast with C_6H_5F and *p*-$C_6H_4F_2$, C_6F_6 shows no detectable optical emission of the S_1–S_0 transition but shows intense bands of the parent molecule ion ($C_6F_6^+$).18) A continuous band, which has a peak at about 400 nm, is also shown in the region longer than 320 nm at the electron energy of 98 eV. This band can be assigned to the emission of the excited fragment species made of 3—4 atoms as in the case of the other two molecules, since a fluorescence spectrum by photoexcitation was located nearly in the same region (ca. 290—470 nm) with a peak at 365 nm11) and the threshold energy of this band is considerably higher. No CF* emission was also observed as in the case of the other two molecules.

Vibrational Structure. The high-resolution emission spectra of the S_1–S_0 transition of these molecules were also measured and are compared with those obtained by photoexcitation. A typical spectrum of C_6H_5F and that of *p*-$C_6H_4F_2$ with an optical resolution of 0.20 nm are shown in Figs. 4 and 5. The vibrational structure was well resolved and assigned by referring to the fluorescence spectra by the photoexcitation8,9) as partly described in the figures with the Wilson notation.19) However, no vibrational structure was resolved for C_6F_6 in the spectrum taken at a resolution of 0.60 nm.

C_6H_5F shows the following bands:20) 6a (517 $\mathrm{cm^{-1}}$ at S_0), 6b (612), 16a (411), 12 (808), 1 (1012), 18a (1030), 9a (1153), 7a (1220), and C–F stretching (824), and combinations of these bands such as 1^0_n, $12^0_1 1^0_n$, $6a^0_1 1^0_n$, $6b^0_1 1^0_n$, $6b^0_1 12^0_1 1^0_n$, $7a^0_1 1^0_n$, $6b^1_1 1^0_n$, $6b^1_2 12^0_1 1^0_n$, $6b^1_1 7a^1_0 1^0_n$, and $6b^1_2 1^0_n$. *p*-$C_6H_4F_2$ shows the following bands:21) 6a (451), 6b (507), 16a (370), 1 (859), and 7a (1245), and combinations of these bands such as 1^0_n, $7a^0_1 1^0_n$, $7a^0_1 16a^1_1 1^0_n$, $16a^1_1 7a^0_n$, $16a^1_1 1^0_n$, and $1^0_1 7a^0_n$. Since *p*-$C_6H_4F_2$ has higher symmetry than C_6H_5F, its vibrational structure is simpler than that of C_6H_5F. The bands due to the skeletal vibration are

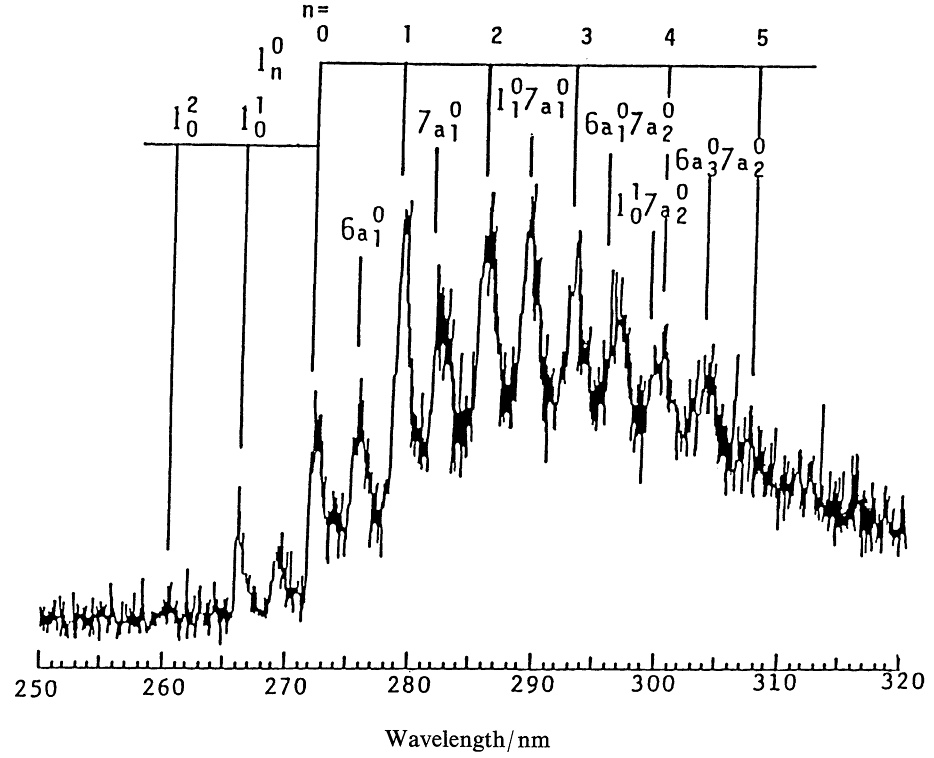

Fig. 5. High-resolution emission spectrum of *p*-difluorobenzene by controlled electron impact measured by a SPEX 1269 monochromator. Optical resolution: 0.20 nm, electron energy: 24 eV, electron beam current: 3 μA.

intense in both molecules. Furthermore, the bands from the vibrationally excited states of the S_1 state (1_0^n series and combinations with them) are also shown although these hot bands did not appear in the spectra excited by monochromatic light even at a low operating pressure.[8,9] This finding is characteristic of the excitation process by electron impact.

Although benzene showed the optically forbidden (6^01^n series) vibrational bands,[5] major bands observed for C_6H_5F and *p*-$C_6H_4F_2$ are due to optically allowed transitions; they were also found in the fluorescence spectra[8,9] and/or the SVL spectra[19] by photoexcitation. The optically-forbidden transitions of C_6H_5F and *p*-$C_6H_4F_2$ are the out-of-plane vibrations, and their Franck–Condon factors are small, thus, the transitions from the S_0 state to these modes in the S_1 state would be very weak. Indeed, benzene also showed no band assignable to an out-of-plane mode.[5]

On the other hand, C_6F_6 does not show any vibrational bands though it has the same symmetry with benzene. None of the optical absorption,[10] the fluorescence[11] and the electron energy loss[22] spectra of C_6F_6 shows vibrational structure. It has been suggested that upon fluorination $\pi\rightarrow\pi^*$ transitions will not show any substantial shift and $\pi\rightarrow\sigma^*$ transitions will be red shifted.[10] As a result of this shift, the $^1A_{1g}\rightarrow{}^1B_{2u}$ transition and the $\pi\rightarrow\sigma^*$ transition (the C band[22]) would overlap[10,22] and the band becomes broad and structureless.

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