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Emission Spectra of Aromatic Hydrocarbons by Controlled Electron Impact

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The emission spectra of benzene, toluene, ethylbenzene, xylenes, trimethylbenzenes, cymene, and naphthalene were investigated under controlled electron-impact excitation. These aromatic hydrocarbons showed a characteristic band in the 250—400 nm region and several bands of such excited fragment species as H and CH. The characteristic bands are similar to those of fluorescence spectra obtained by optical excitation and, thus, were assigned to fluorescence emissions of the parent molecules. The intensity of the fluorescence emission of benzene decreased at higher electron energies, and fragment emissions became dominant above 100 eV. However, its vibrational structure did not change for electron energies of 5—60 eV. This indicates that cascade processes from high-lying states are negligible for benzene. The fluorescence emission of naphthalene shifted to a shorter wavelength for low electron energies. Together with a theoretical estimation based on the Born approximation, cascade effects from higher excited states (S_2 and S_3) are found to be the major source of the fluorescence emission of naphthalene.

The emission spectrum excited by the controlled electron beam provides valuable information for a detailed analysis of the mechanism of the excitation and fragmentation of molecules at very low pressures where the effect of collisions is greatly reduced.[1)] A large molecule does not usually show photoemissions from its own excited state, but, instead, shows various fragment emissions, since non-radiative processes become more dominant for a large molecule. The aromatic molecules, however, give intense photoemissions of the parent molecules in the ultraviolet region. The emission spectra of benzene,[2–4)] toluene,[2,4,5)] xylenes,[2,5)] and naphthalene[6,7)] have been measured, and the similarity of their spectra with the fluorescence spectra has been pointed out.[2–7)] The spectra and the lifetime of benzene emission by electron impact have also been studied.[8,9)]

The fluorescence emission of aromatic molecules can be observed either by direct excitation into the fluorescing state or through the cascade process from the initially prepared states to the lower fluorescing state. These excitation processes have been studied with the Bethe theory.[10–12)] The excitation cross section to a particular excited state is proportional to the molecular oscillator strength from the ground state to that excited state; on the other hand, the probability of photoemission from a specified state is expressed by the quantum yield of fluorescence.[3,4,6)] The cascade effects from the S_n state to the S_1 state may be studied by photoexcitation; however, the electron-impact method can be applied to molecules at very low pressures, since a more intense beam is available and the cross section is large.

In the present paper, the emission spectra of nine aromatic hydrocarbons are described as an extension of previous investigations.[2,6)] The electron energy dependence of the spectra was studied for two basic molecules. The excitation processes of these aromatic hydrocarbons are also discussed.

Experimental

A schematic diagram of the apparatus is shown in Fig. 1. The collision chamber was made of stainless steel, with its inside covered with soot to suppress secondary electrons and any stray light. Thermal electrons from a tungsten filament were accelerated, collimated, and introduced into the collision region through a hole (4 mm in diameter). The sample molecule was jetted into the collision region through a needle valve and a multichannel nozzle (0.5 mm × 40). The collision chamber was continuously evacuated with two oil-diffusion pumps; the base pressure was of the order of 10^{-7} Torr, while the operating pressure was of the order of 10^{-4} Torr (uncorrected ion gauge reading). The photoemission produced in the collision region was observed through a quartz window at a angle of 90° with respect to the electron beam.

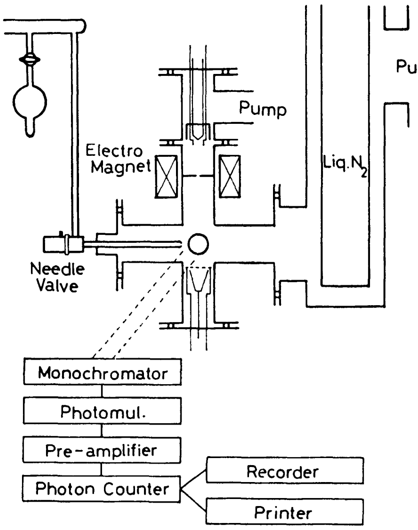

Fig. 1. Schematic diagram of the apparatus.

The emission spectra were observed with a JASCO CT-50 monochromator equipped with a 1200 grooves/mm grating blazed at 300 nm. The photons were measured with an HTV R212UH photomultiplier and a Burr-Brown 3421K OP amplifier or with an HTV R585 photomultiplier and an NF PC-545A photon counter. The wavelength dependence of the instrumental response was not corrected.

All the spectra were measured in a region where the intensity was proportional to both the gas pressure and the electron-beam current. In the case of the $6^0_1 1^0_2$ band of benzene, the intensity was linear in the region below 600 μA and 7.0×10^{-4} Torr. The effect of secondary electrons was estimated from the ratio of the emission intensity of the first negative band of N_2^+ (391.4 nm) to that of the second positive band of N_2 (337.1 nm);[13)] the result is shown in Fig. 2.

All the compounds used were of a research grade; they were deaerated before use by repeated freeze-pump-thaw cycles.

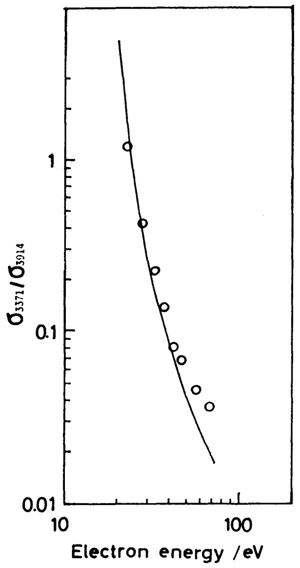

Fig. 2. Ratio of the emission intensity of N_2 (3371 Å) to that of N_2^+ (3914 Å). ○: This work.

The solid line is the estimated one.[13] The result indicates the effect of secondary electrons can be ignored below *ca.* 50 eV. The electron-beam current was 1 μA and the gas pressure was 1×10^{-4} Torr.

Results

The emission spectra of benzene, toluene, ethylbenzene, *o*- and *p*-xylenes, mesitylene, 1,2,3-trimethylbenzene, *p*-cymene, and naphthalene by controlled electron impact were measured; they are shown in Fig. 3. The energy of the incident electrons was 40 eV, and the spectral resolution was about 1 nm. All the aromatic hydrocarbons thus far studied have shown a characteristic band in the 250—400 nm region.[1] The fluorescence spectra taken in the gas phase and in the dilute solution were found to correspond well to the observed emission spectra. Thus, the characteristic bands observed in the present study were assigned to the fluorescence transition from the lowest excited singlet state (S_1) to the ground state (S_0); in the case of benzene, this is the symmetry forbidden $^1B_{2u}-^1A_{1g}$ transition.[2-4] Since Vroom and de Heer reported that the excitation cross sections of the Balmer line from various hydrocarbons differ little,[14] the relative intensity of the fluorescence emission can be estimated approximately from Fig. 3.

The spectrum of benzene has a striking dependence on the electron energy, as is shown in Fig. 4. The photoemission of the parent molecule becomes weaker at higher electron energies and almost disappears above

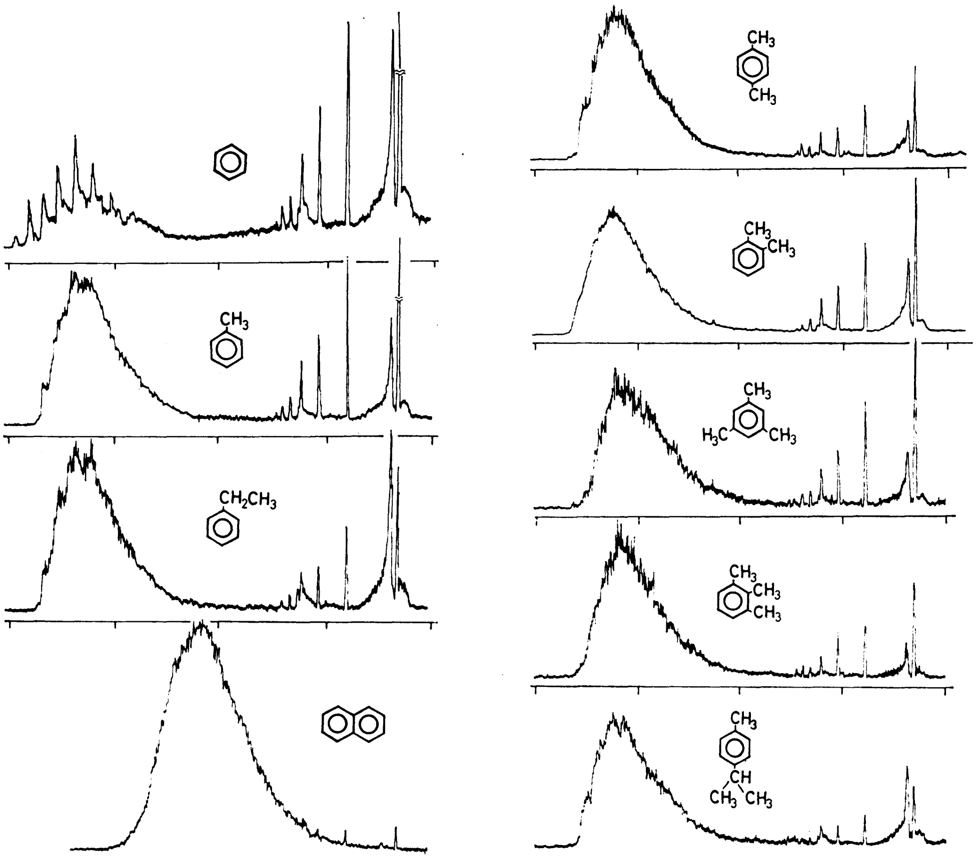

Fig. 3. Emission spectra of aromatic hydrocarbons by controlled electron impact.

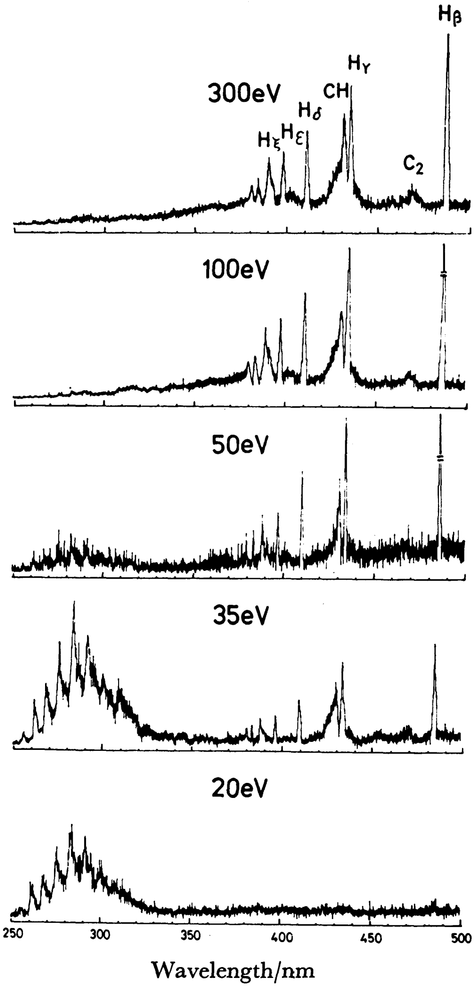

Fig. 4. Electron energy depence of the emission spectra of benzene.

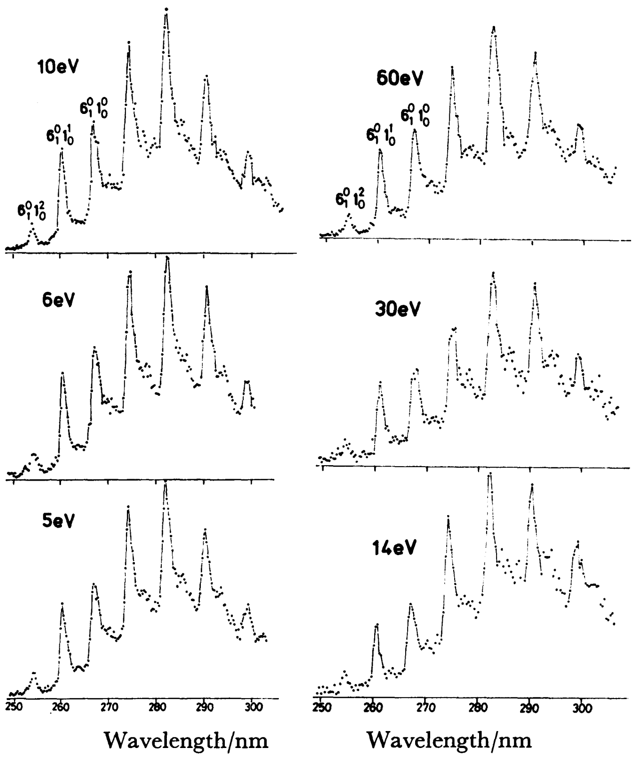

Fig. 5. Electron energy dependence of the vibrational structure of the fluorescence emission of benzene.

100 eV, as was shown by Smyth *et al.*[4] The spectrum of naphthalene, however, did not show such a dependence, and the band of its parent molecule could be observed even at 300 eV.

The shape and structure of this fluorescence emission were observed at various electron energies, as is shown in Fig. 5 for benzene and in Fig. 6 for naphthalene. The vibrational structure of the benzene emission did not change in the optical resolution of 1 nm at 5—60 eV; however, the peak of the band of naphthalene shifted to a shorter wavelength for lower electron energies.

The Balmer series of hydrogen and the $B^2\Sigma^-$—$X^2\Pi$ transition and the $A^2\Delta$—$X^2\Pi$ transition of CH were also observed in the 370—440 nm region, as is indicated in Fig. 4. In addition, the $C^2\Sigma^+$—$X^2\Pi$ transition of CH (about 315 nm) and the bands of CH^+ (423 nm and 350—370 nm) were identified in the spectrum of benzene taken at a higher sensitivity. The Schüler's T spectrum of $C_4H_2^+$ and the C_2 Swan bands were also observed in the 430—570 nm region.[15]

In all the cases measured, the intensity of the fluorescence emissions was directly proportional to the electron-beam current and to the gas pressure. This indicates that the excited states of these aromatic hydrocarbons were all produced in a one-electron primary collision process.

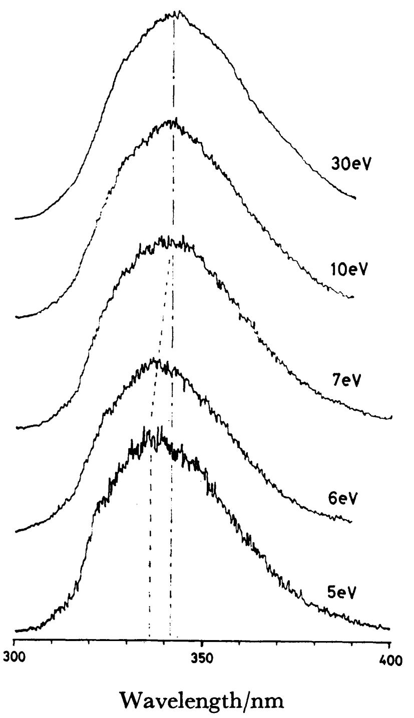

Fig. 6. Electron energy dependence of the fluorescence emission of naphthalene.

Discussion

Spectrum of the Fluorescence Emission. The emission spectrum excited by controlled electron impact resembles the discharge spectrum and the equilibrated fluorescence;[16,17] all of these have a prominent vibrational

TABLE 1. ESTIMATION OF CONTRIBUTIONS OF THE S_1, S_2, AND S_3 EXCITATION PROCESSES TO THE OBSERVED FLUORESCENCE EMISSION

	Benzene				Naphthalene			
	E_i/eV	f_i	ϕ_i	Γ_i[a)]	E_i/eV	f_i	ϕ_i	Γ_i[a)]
$S_1 \rightarrow S_0$	4.9	0.0013	0.16	1.0	4.1	0.003	0.75	13
$S_2 \dashrightarrow S_1 \rightarrow S_0$	6.2	0.090	$<8\times10^{-4}$	<0.27	4.7	0.109	0.32	176
$S_3 \dashrightarrow S_1 \rightarrow S_0$	7.0	0.90	$<10^{-5}$	<0.03	6.0	1.3	0.01	52
$S_2 \rightarrow S_0$	6.2	0.090	8×10^{-6}	0.003	4.7	0.109		
$S_3 \rightarrow S_0$	7.0	0.90			6.0	1.3	2×10^{-5}	0.01

a) Value relative to the $S_1 \rightarrow S_0$ process of benzene. $\rightarrow$Radiative process. $\dashrightarrow$Non-radiative process.

structure and a broad background continuum. The present spectrum of benzene, however, clearly indicates the $6^0_1 1^2_0$ and $6^0_1 1^1_0$ transitions at 255 and 260 nm, which are not appreciable in the equilibrated fluorescence. The resonance fluorescence spectrum of benzene reveals a group of sharp lines,[17,18)] whereas the present spectrum is broader and has a more vibrational structure. These facts indicate that the electron energy is large enough to excite many vibronic levels of the S_1 state simultaneously because of the non-resonant character of the electron excitation; however, the pressure is so low that the excited molecules undergo no collisional deactivation, and the vibrational population is not distributed in a 300 K Boltzman distribution. The electron impact spectrum is, thus, similar to the one excited by the irradiation of white light, whose maximum photon energy is that of the electrons.

The equilibrated fluorescence of toluene,[19)] and the resonance fluorescence of toluene and xylenes[17)] have previously been reported. The comparison of the present spectra with them leads to a conclusion similar to that in the case of benzene; the emission spectrum by controlled electron impact has some vibrational structure, including one above the 0-0 transition, and a broad background continuum. In the case of naphthalene, the vibrational structure becomes very diffuse, and the broad background continuum consists of the major part of the spectrum.

The fluorescence emissions of the other hydrocarbons may be compared with those of the fluorescence spectra taken in solution.[20)] For all of the aromatic hydrocarbons studied, the emission spectra by controlled electron impact are more similar to the equilibrated fluorescence spectra in the gas phase or to the fluorescence spectra in solutions than to the resonance fluorescence in a low pressure gas.

Estimation of Excitation Processes. For most molecules, the bulk of the oscillator strength of the valence shell electrons lies at very great values of the excitation energy.[11)] Thus, the most important primary processes of the electron-molecule collisions are high-lying electronic excitations of the valence electrons. If the intramolecular radiationless relaxation is very fast, the primarily-excited high-lying states can fall to the lowest excited singlet (S_1) state and contribute to the observed photoemission.

When the energy of the incident electrons for the excitation substantially exceeds the threshold energy of the molecule, the Born approximation is applicable;[10,12)] the cross section of the excitation into the ith level (σ_i) is expressed by the optical oscillator strength (f_i) and the transition energy (E_i). The probability of photoemission from this level is proportional to the fluorescence quantum yield (ϕ_i). Thus, the contribution of the photoemission process involving the ith level on the total photoemission (Γ_i) is given as follows:[6)]

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

where b is a proportionality constant. Thus, Eq. 1 allows an estimation of the excitation and cascade processes with the available spectroscopic parameters. In actuality, the transition to a particular excited state is not very discrete, and both ϕ_i and f_i are dependent on the excitation energy; however, average values can be used for an order of magnitude estimation.

The very high-lying states seem not to be important for the observed fluorescence emission, since the spectra do not change above 7 eV (Figs. 5 and 6). Accordingly, the estimation of the cascade processes has been confined to the lower three excited states (S_1, S_2, and S_3). The dipole oscillator strength can be obtained from the electron energy loss spectrum.[21,22)] The electron energy loss spectrum is closely related with the photoabsorption; the optical values[23)] were used for benzene because of the lack of an explicit value of f in the electron energy loss spectrum. The quantum yields were taken from the vapor fluorescence of benzene[24–26)] and naphthalene.[27–30)] The results are shown in Table 1. The preliminary result[6)] was revised by using more recent spectroscopic parameters.

Excitation Processes of Benzene and Naphthalene. The calculation (Table 1) shows that the direct excitation into the S_1 state is the most important process for benzene, while the contribution of the cascade process from the S_2 and S_3 states into the S_1 state is more predominant for naphthalene.

The observed spectrum of benzene has a characteristic vibrational structure, which does not change upon 5—60 eV excitation. This finding leads to the conclusion that the fluorescing S_1 state, whose excitation energy is about 5 eV, does not originate from a cascading process from the higher excited states. The smaller contribution of the higher excited states is due to the faster photochemical process of benzene and/or the direct internal conversion to the ground state, when benzene is excited into the S_2 or S_3 states.[24,25)]

The vibrational structure of the fluorescence emission of naphthalene is less pronounced. The intramolecular internal conversion from the higher excited states causes a high vibrational excitation of the emissive S_1

state and makes the appearance of the spectrum more diffuse. The onset of the emission of naphthalene was found at 4.45 eV, which is the spectroscopic energy of the S_2 state.[7] Since a radiationless relaxation of the higher excited states results in the formation of the vibrationally highly-excited S_1 state, the Franck-Condon transition energy from such a highly-excited S_1 state is smaller than that of the directly excited S_1 states. The peak shift (Fig. 6) can be ascribed to the decrease in the contribution of cascading for the low energy excitation. The optical measurement also indicated that the fluorescence shifts to the red and becomes increasingly diffuse as the excitation energy increases.[31] Thus, the calculated and the observed findings are consistent.

The fact that the intensity of the fluorescence emission of benzene decreases rapidly as the increase of the electron energy and becomes negligibly small at a higher electron energy (Fig. 4) indicates that the major process of the excitation is neither a typical optically-allowed nor a typical symmetry-forbidden transition, since a Fano plot of an optically-allowed or a symmetry-forbidden transition has a positive or a zero slope. This finding indicates that another excitation process plays a more important role than those calculated. Smyth *et al.*[5] suggested the contribution of the resonance. Klump and Lassettre[32] indicated the importance of an electric octupole transition. Whereas, Doering,[33] and Wilden and Comer[34] showed the formation of the $^3E_{1u}$ state in this energy region; Matsuzawa[35] calculated that the excitation cross section to the $^3E_{1u}$ state is as large as that to the $^1B_{2u}$ state at a low incident energy and at a large angle. Such processes may be important in the excitation of the fluorescing S_1 ($^1B_{2u}$) state of benzene.

The spectroscopic data for other hydrocarbons in the vapor phase are so scanty that it is difficult to carry out similar estimations for them. However, the spectroscopic parameters obtained for the dilute solution often agree approximately with those in the gas phase, and the oscillator strength and the quantum yield in the dilute solution can be carried over to the rough estimation of the excitation processes. Those of some substituted aromatic molecules have been discussed in this approximation.[36,37]

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