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Emission Spectra of Benzene, Toluene, and Xylenes by Controlled Electron Impact

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The emission spectra of gaseous aromatic hydrocarbons under electron impact excitation (60—300 eV) were measured in the 220—450 nm region at very low pressures. A characteristic band was observed in all cases in the 240—340 nm region; this band was assigned to the transition from the lowest excited singlet state to the electronic ground state. Photoemissions from the fragment species, such as H (Balmer series) and CH (A→X, B→X), were also observed. The excited species were concluded, from the relations of the emission intensities to the electron-beam current and to the gas pressure, to be produced by one-electron processes. The relative intensity and the vibrational structure of the observed spectra were examined and compared with those of the fluorescence spectra produced by photo-excitation.

The electric discharge method has been one of the most effective ways of studying excited molecules and their emission spectra. Although the methods are very useful in the detection of unstable species, however, the complicated character of the discharge is a major obstacle for any detailed analysis of the mechanism of fragmentation and excitation of the species concerned. The ideal way to produce excited molecules by means of electrons is, in this respect, the crossed electron and molecular-beam method,[1] in which the photoemission of excited species can be obtained at very low pressures, where the effect of molecular collision is greatly reduced and the energy of electrons can be controlled. However, the disadvantage of this method is the low intensity of photoemission. Although recent developments in instrumentation have made the study of smaller molecules feasible, little has been done on complicated organic molecules.

Extensive studies have been carried out in recent years on the excited species of the aromatic hydrocarbons. The fluorescence spectra in the gas phase

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[1] T. Horie, T. Nagura, and M. Otsuka, *J. Phys. Soc. Jap.*, **11**, 1157 (1956).

at low pressures have been observed for benzene,[2–5] toluene,[5,6] and other aromatic molecules.[5] Electron impact is an effective alternate method for exciting molecules at low pressures in the gas phase. The spectroscopic investigation of the electron-molecule collisions of these molecules would not only give the emission spectra by a different excitation method, but would also reveal the mechanism of the collision and fragmentation.

The emission spectra of fragment species of methane and chlorinated methanes[7] and methanol[8] under electron impact excitation have been reported. The emission spectra of benzene by controlled electron impact have been measured in the 240—300 nm region, and the lifetime of the $^1B_{2u}$ state has been studied.[9] The emission spectra of toluene and anisole[10] and of xylenes[11] in the 250—450 nm region obtained by this method have also been communicated by the present authors. In the present report, detailed results on benzene, toluene, and xylenes will be described and the relationship between the emission spectra obtained by the controlled electron impact method and the fluorescence spectra obtained by photo-excitation will be discussed.

Experimental

The sample vapor was crossed so as to collide with an electron beam in a chamber, as is shown schematically in Fig. 1. The cell was made of glass and was about 4.5 cm in diameter and about 40 cm in length. The electron was emitted from a tungsten filament (a), was accelerated by three electrodes (c, d, e), and was introduced into the collision chamber through a slit (2 × 15 mm) in the center of one of the electrodes (c). Two electromagnets (h) were placed so as to collimate the electron beam. The voltages of the two electrodes in the collision chamber (b, c) were set equal for the quantitative measurements. After being purified in a vacuum line (j) by repeated freezing and pumping, the sample was jetted into the collision chamber through a nozzle 0.1—1.0 mm in diameter (g). The chamber was evacuated (i) continuously to a high vacuum; a Penning gauge attached to the chamber indicated a pressure of the order of 10^{-4}—10^{-5} mmHg during the electron-impact measurements. The actual pressure in the impact region was expected to be higher than the value indicated and smaller than 10^{-2} mmHg. The sample vapor was excited by the collision with the electron, and the photoemission was observed through a quartz window (f). An electron beam of 10—1000 μA at 60—300 eV was used for the excitation. The energy distribution of the incident electron was not measured; however, it is expected to be no less than the voltage used for heating the filament (6—9 V).

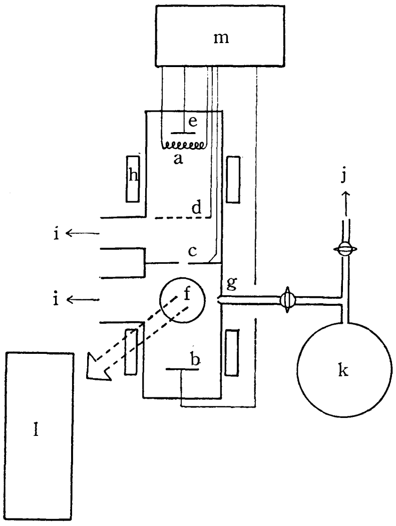

Fig. 1. Schematic diagram of the collision chamber. Controlled electron beam was introduced through a slit (c) and sample vapor was jetted through a nozzle (g). Photoemission at the collision region was observed through a quartz window (f). (a) tungsten filament, (b) electron target, (c) electrode with a slit in its center, (d) electrode, (e) electrode, (f) quartz window, (g) nozzle, 0.1—1.0 mm in diameter, (h) electromagnet, (i) to diffusion pump, (j) to vacuum line for the sample preparation, (k) gas reservoir to store sample vapor before use, (l) monochromator, (m) power supply.

The fluorescence spectra under photon-excitation were taken by the use of a standard quartz cell (10 × 10 mm) placed just in front of the entrance slit. The sample vapor in the cell was irradiated with a Hamamatsu TV L299 low-pressure mercury lamp.

The spectra were obtained with a Jarrell-Ash JE25 monochromator equipped with two 1200 groove/mm gratings blazed for 300 and 600 nm, and it had a reciprocal dispersion of about 33 Å/mm. The photons were detected photoelectrically with an EMI 9558QB photomultiplier and a Burr-Brown 3421J OP amplifier. The wavelength was calibrated by means of a low-pressure mercury lamp. The further details of the apparatus have been described elsewhere.[12]

All the compounds used were of a JIS specially pure reagent grade and were obtained from either Wako Pure Chemical Ind. or the Kishida Chemical Co.

Results and Discussion

A typical emission spectrum of benzene by electron impact is shown in Fig. 2. The impact voltage was 200 V and the electron-beam current was 1 mA in this measurement. The bands in the 250—300 nm region agreed well with those of Smith[9] and were assigned to the vibronic band of the forbidden $^1B_{2u}$—$^1A_{1g}$ transition. The transitions from vibrationally-excited states of the upper electronic level such as $6^0_1 1^2_0$ [13] (255 nm) and $6^0_1 1^1_0$ (260 nm) are quite intense.

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2) M. Nishikawa and P. K. Ludwig, *J. Chem. Phys.*, **52**, 107 (1970).

3) C. S. Parmenter and M. W. Schuyler, *ibid.*, **52**, 5366 (1970).

4) H. F. Kemper and M. Stockburger, *ibid.*, **53**, 268 (1970).

5) J. M. Blondeau and M. Stockburger, *Ber. Bunsenges. Phys. Chem.*, **75**, 450 (1971).

6) C. S. Burton and W. A. Noyes, Jr., *J. Chem. Phys.*, **49**, 1705 (1968).

7) T. Ogawa, I. Fujita, M. Hatada, and K. Hirota, This Bulletin, **44**, 659 (1971).

8) I. Fujita, M. Hatada, T. Ogawa, and K. Hirota, *ibid.*, **44**, 1751 (1971).

9) W. H. Smith, *J. Chem. Phys.*, **54**, 4169 (1971).

10) T. Ogawa, M. Tsuji, M. Toyoda, and N. Ishibashi, *Chem. Lett.*, **1972**, 233.

11) T. Ogawa, M. Tsuji, M. Toyoda, and N. Ishibashi, *ibid.*, **1972**, 1157.

12) T. Ogawa, M. Toyoda, M. Tsuji, and N. Ishibashi, *Technology Repts. Kyushu Univ.*, **45**, 427 (1972).

13) When a certain normal mode *m* is involved in an electronic transition, the notation $m_k{}^i$ shows that there is a transition from the *i*th vibrational level m^i in the upper electronic state to the *k*th vibrational level m_k in the ground electronic state. J. H. Callomon, T. M. Dunn, and I. M. Mills, *Phil. Trans. Roy. Soc.* (London), **A259**, 499 (1966).

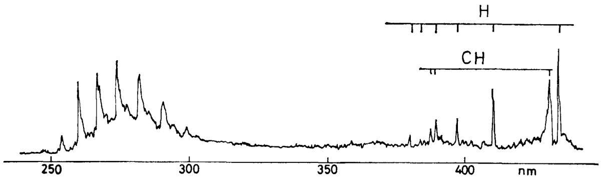

Fig. 2. Emission spectrum of benzene by electron impact. 200 V impact at 1 mA.

Balmer series of the hydrogen atom and the $B^2\Sigma^-$—$X^2\Pi$ transition and the $A^2\Delta$—$X^2\Pi$ transition of the CH radical were found in the 370—440 nm region. The Swan system of C_2 and Schüler's T spectrum of $C_4H_2^+$ were also observed in the 430—550 nm region.

The fluorescence spectra of benzene in the gas phase were taken at various excitation wavelengths; several different resonance spectra have been reported at such a low pressure as 0.2 mmHg, where collisional deactivation is not complete.[4,5] A comparison of those spectra with the present spectrum under electron-impact excitation reveals several points of interest. The equilibrated fluorescence[4] (the emission spectra of 0.2 mmHg benzene with 40 mmHg hexane, in which the Boltzmann equilibrium is established in the $^1B_{2u}$ state) shows no remarkable band above 267 nm, whereas the present spectrum has a strong band head at 261 nm ($6^0_1 1^1_0$). Since the pressure in the impact chamber was very low in the present study, molecular collisions were not so frequent that photoemission from vibrationally excited states was observed. The resonance spectra excited by irradiation with a monochromatic light[4,5] consist of only a few strong progressions and appear to be simpler than the present spectrum. This finding is probably connected with the facts that the excitation energy of the electron impact is higher and the energy distribution of the electron beam is broader than those in the case of the photon excitation with a monochromatic light. The variation in impact voltage between 60—300 V did not, however, induce any remarkable change in the appearance of the spectrum under the resolution of the spectrometer used. It seems that the molecule received enough excess energies even when excited with electrons of 60 V; a similar emission spectrum was observed upon excitation by electrons with higher energies.

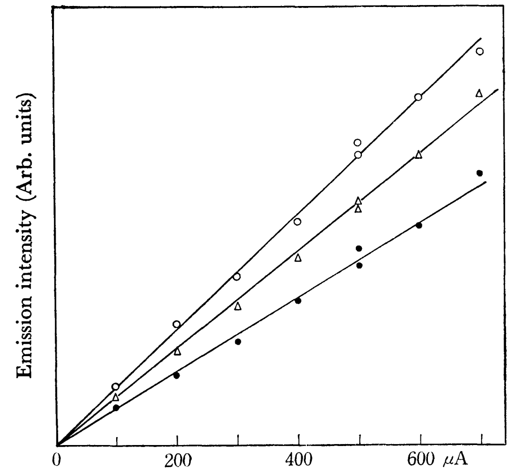

Fig. 3. Dependence of photoemission intensity on the electron beam current. Emission of excited benzene molecules at the impact voltage of 150 V.
○: $6^0_1 1^0_1$ band, △: $6^0_1 1^0_0$ band, ●: $6^0_1 1^1_0$ band.

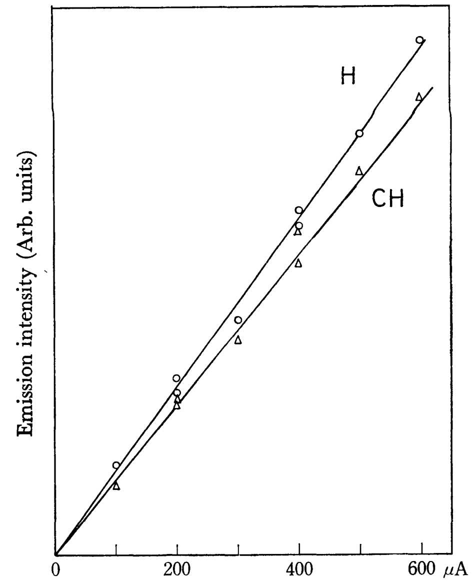

Fig. 4. Dependence of photoemission intensity on the electron beam current. Emission of fragment species at the impact voltage of 150 V.
○: atomic hydrogen, △: CH radical.

The dependence of the emission intensity on the electron-beam current was measured; the results are shown in Figs. 3 and 4. The intensities of the photoemission of the excited parent species of benzene and of the fragment species (H and CH) were proportional to the electron-beam current. Thus, the excitation of a π electron of benzene is concluded to be a one-electron process, as is that of fluorobenzene.[14] The fragmentations of benzene to H and to CH are also concluded

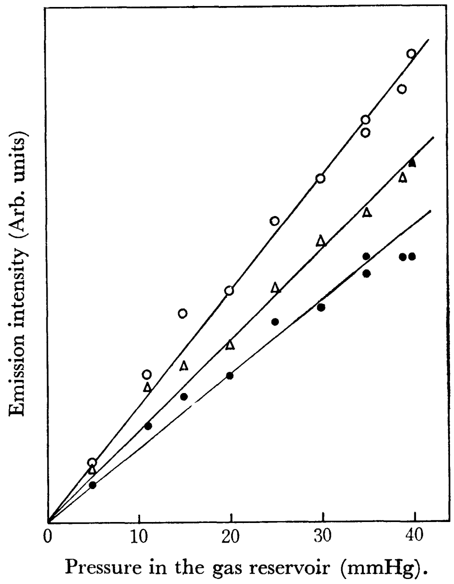

Fig. 5. Dependence of photoemission intensity on the gas pressure in the gas reservoir. Emission of excited benzene molecules. Impact voltage 200 V; electron beam current 70 μA.
○: $6^0_1 1^0_1$ band, △: $6^0_1 1^0_0$ band, ●: $6^0_1 1^1_0$ band.

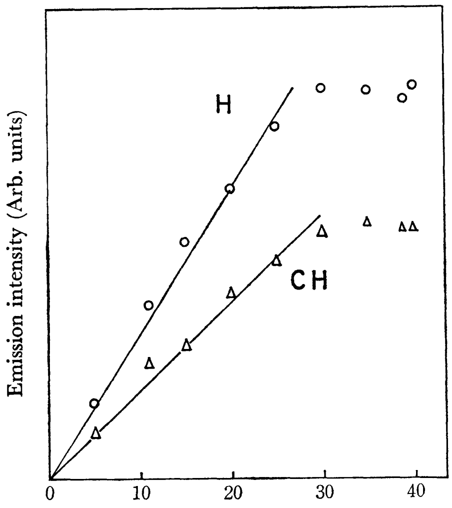

Fig. 6. Dependence of photoemission intensity on the gas pressure in the gas reservoir. Emission of fragment species. Impact voltage 200 V; electron beam current 70 μA. ○: atomic hydrogen, △: CH radical.

to be one-electron processes; an identical conclusion has previously been obtained in the case of methane.[7]

The relationship between the emission intensity and the gas pressure in the gas reservoir was also measured in the case of benzene; the results are shown in Figs. 5 and 6. The intensities of the photoemission of the excited parent species and of the fragment species (H and CH) were found to be proportional to the gas pressure in the gas reservoir. The gas pressure in the gas reservoir can be expected to be proportional to the pressure in the impact region since the gas is jetted through a small nozzle; this presumption was confirmed in the case of nitrogen by measuring the pressure in the impact chamber. This finding indicates that intermolecular quenching processes by collisions are not important.

The proportionality between the emission intensity and the amount of electrons and molecules mentioned above is also found in the photoemission of various molecules.[7,14] This result seems to indicate that the excitation and the fragmentation take place through one-electron processes, such as;

$$X \xrightarrow{\text{electron}} X^* \qquad (1)$$

$$X \xrightarrow{\text{electron}} X^{**} \begin{cases} \xrightarrow{\text{fast}} X^* \\ \xrightarrow{\text{fast}} H^*, CH^* \cdots \end{cases} \qquad (2)$$

where X stands for benzene, where * indicates the lower electronically excited state from which the photoemission was observed, and where ** indicates highly excited states, which are probably some kinds of superexcited states.[15] Although the relative importance of the two processes, (1) and (2), could not be determined in the present study, the observation of the Balmer series of hydrogen implies the importance of the second process, since the excitation energy of a typical line of this series (12—13 eV) is more than the typical ionization potential of aromatic hydrocarbons (*ca.* 9 eV). The role and the importance of the superexcited states have also been discussed in the case of the electron impact of CH_4[16] and in the field of radiation chemistry[15] and mass spectrometry.[17]

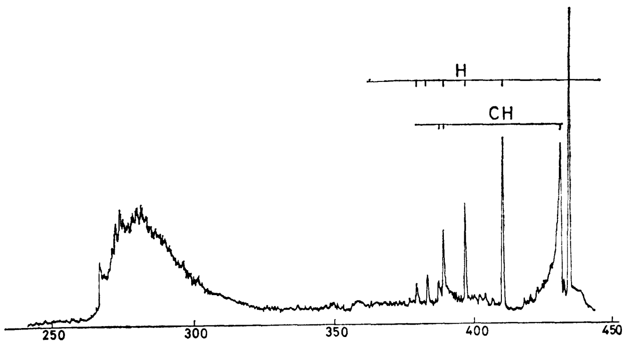

Fig. 7. Emission spectrum of toluene by electron impact. 300 V impact at 1 mA.

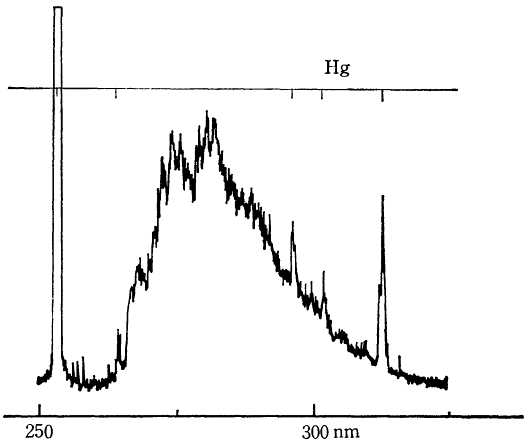

Fig. 8. Emission spectrum of toluene under photon excitation by a low-pressure mercury lamp (2537 Å). vapor pressure, about 10 mmHg.

A typical emission spectrum of toluene under electron-impact excitation is shown in Fig. 7, and that under photon excitation in Fig. 8. A characteristic band was observed in the 270—320 nm region, and the band in Fig. 7 is very similar to that in Fig. 8. The photoemission of H and CH was also observed in the case of electron impact. Since the symmetry of the molecule is C_{2v} for toluene, the 0—0 transition (267 nm) is allowed, unlike the case in benzene. The characteristic band of toluene is located in a longer wavelength region than that of benzene. This band is broader than that of benzene; however, several fine structures between 267—300 nm could be observed above the non-resolved background.

The fluorescence spectra of toluene in the gas phase were observed at 0.1 mmHg[5] and at 20 mmHg.[6] The location and the shape of the present spectrum

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[14] T. Ogawa, M. Tsuji, M. Toyoda, and N. Ishibashi, This Bulletin, **46**, 1063 (1973).

[15] R. L. Platzman, *Radiation Res.*, **17**, 419 (1962).

[16] D. A. Vroom and F. J. de Heer, *J. Chem. Phys.*, **50**, 573 (1969).

[17] K. Hirota, *Nippon Kagaku Zasshi*, **89**, 327 (1968); **91**, 585 (1970).

under electron-impact excitation are similar to those of the latter, as is shown in Fig. 8. The most striking features of the former experiment are the loss of structure and the increase in the fraction of the background as the excitation energy is increased to higher vibronic levels. Blondeau and Stockburger[5] concluded that vibrational rearrangement dominated at higher vibrational levels and that discrete bands no longer were observable. Their spectrum excited at 932 cm^{-1} above the 0—0 level almost lost its vibrational progression. On the other hand, the present spectrum keeps some of its vibrational features even when the molecule is excited at 200 V. This finding is noteworthy, since the pressure in the impact chamber of the present study is extremely low. However, a detailed comparison of their spectra with the emission spectra obtained by electron impact would require a further improvement in the resolution of the present spectra. The fluorescence spectrum of toluene in solution[18] was found to correspond well to the emission spectrum obtained by electron impact.

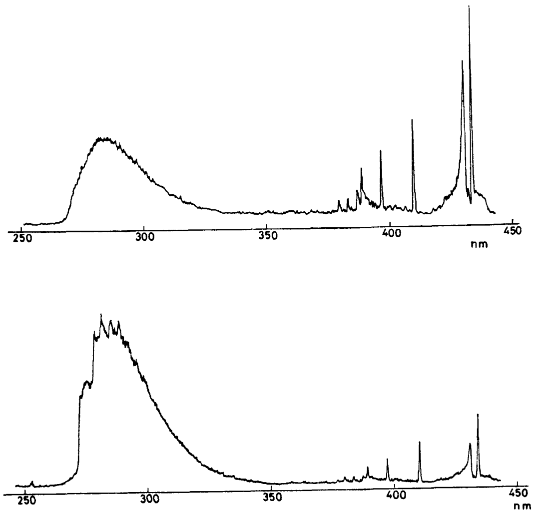

Fig. 9. Emission spectra of xylenes by electron impact.
Top; *o*-xylene, 300 V impact at 1 mA.
Bottom; *p*-xylene, 200 V impact at 1 mA.

Typical emission spectra of xylenes under electron-impact excitation in the 250—450 nm region are shown in Fig. 9. The spectrum of *m*-xylene is similar to that of *o*-xylene. A characteristic band is observed in the 270—340 nm region in all cases, though its location and the vibrational structures differ from each other. Thus, such aromatic molecules as benzene, toluene, xylenes, cumene,[19] and cymene[19] show a characteristic band in this region, and it may well be concluded that this band is a feature common to all aromatic hydrocarbons. The fluorescence spectra of aromatic hydrocarbons in dilute solutions[18] were found to correspond well to the emission spectra by electron impact for various molecules. Thus, all the characteristic bands observed in the present study were assigned to the transition from the lowest excited singlet state to the electronic ground state, as in the case of the fluorescence spectra. Although the energy of the electrons in the present study is much larger than that of the photons in the fluorescence study, the spectra under electron-impact excitation are in many cases similar to those under photon-impact excitation. This is superficially correlative to the fact that the electron-impact (energy-loss) spectra are closely related to the photoabsorption spectra of the same molecules.[20]

The spectrum of *p*-xylene has more vibrational structures and is less diffuse than that of *o*-xylene. This difference in the appearance of the spectra of the two molecules was also observed in the fluorescence in the gas phase[5] and in solution.[18] The relative intensities of the bands of the parent species over the hydrogen Balmer series are also remarkably different in the two spectra, as is shown in Fig. 9. (The cross sections for the formation of excited hydrogen atoms are reported to be almost the same for the different hydrocarbons.[16]) The fluorescence yield of *p*-xylene has been reported to be larger than those of *o*- and *m*-xylenes.[21] It can be concluded that molecules with higher symmetry have sharper and stronger bands than those with less symmetry in the emission spectra obtained by electron impact, just as in the fluorescence. In molecules with high symmetry, there are less vibrational modes which may interact with the electronic level than in those with low symmetry. The more complicated structure and the higher intensity of the emission band of *p*-xylene are probably to be ascribed to the difference in this vibronic interaction. The de-

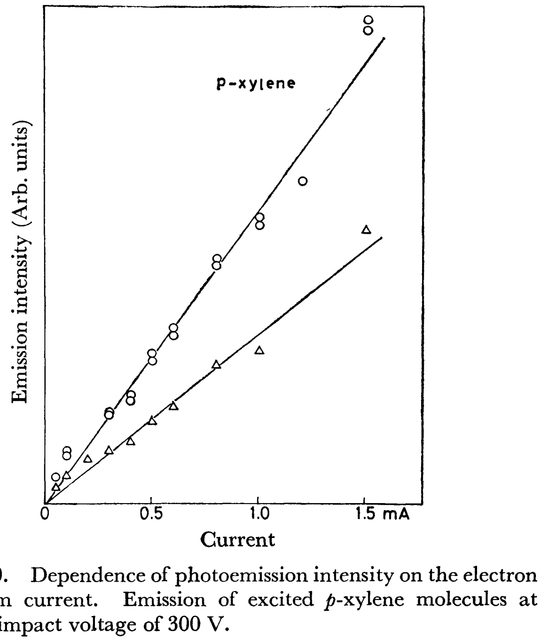

Fig. 10. Dependence of photoemission intensity on the electron beam current. Emission of excited *p*-xylene molecules at the impact voltage of 300 V.
○: features at 286, 302, and 312 nm (Since these three features have almost equal intensities, these are shown on the identical line).
△: feature at 277 nm.

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18) I.S. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, N. Y. (1971).

19) T. Ogawa, M. Tsuji, M. Toyoda, and N. Ishibashi, unpublished.

20) E. N. Lassettre, A. Skerbele, M. A. Dillon, and K. J. Ross, *J. Chem. Phys.*, **48**, 5066 (1968).

21) W. A. Noyes Jr. and D. A. Harter, *J. Phys. Chem.*, **75**, 2741 (1971).

pendence of the intensity of the photoemission of *p*-xylene on the electron-beam current was measured. The four features of the band of the parent species at 277, 286, 302, and 312 nm showed a linear relationship, as is shown in Fig. 10. This linear relationship indicates that the excitation of a π electron of *p*-xylene is a one-electron process. The identical relationship was also observed for the photoemission of the hydrogen atom and the CH radical just as in the case of benzene.

In the emission spectra under electron-impact excitation, the photoemission from the small fragments of large molecules was usually observed more easily than that from the large parents themselves. It seems likely that larger species have more freedom of motion and of fragmentation and that non-radiative processes become more predominant. The aromatic molecules are exceptional molecules in that the excited large parent species give intense photoemission. The intensities of the photoemission of all the species mentioned above were found to be proportional to the electron-beam current and to the gas pressure. These results indicate that intermolecular quenching processes by collisions are unimportant and that superexcited states may be involved in the excitation.[14)]

The few examples which have been discussed in this paper show that the electron-impact method is a useful one for studying electronic excited states. Further research with a higher resolution would reveal even more details on the mechanism of the excitation.

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