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Emission Spectra of Benzonitrile, Aniline, and Nitrobenezene by Controlled Electron Impact

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The emission spectra of benzonitrile, aniline, *N,N*-dimethylaniline, and nitrobenzene under controlled electron-impact excitation (60—300 eV) were investigated at a very low pressure. Bands of the parent molecules were observed in the 260—410 nm region on benzonitrile and anilines, and were assigned to the S_1–S_0 transitions. However, no emission of the parent molecule was observed on nitrobenzene and this was attributed to the spin-orbit coupling effect of the nitro group and the predissociation of the excited parent molecule. Bands of the following fragment species were observed for all four compounds: H(Balmer series), CH($A^2\Delta$–$X^2\Pi$), and CN($B^2\Sigma$–$X^2\Sigma$). In addition, NH($A^3\Pi$–$X^3\Pi$) band on aniline and NO($A^2\Sigma$–$X^2\Pi$, $B^2\Pi$–$X^2\Pi$), CO($b^3\Sigma$–$a^3\Pi$), and CO^+ ($A^2\Pi$–$X^2\Sigma$, $B^2\Sigma$–$X^2\Sigma$) bands on nitrobenzene were observed. The linear relationships between the electron beam current and the emission intensities of the parent molecules and the fragment species indicated that most of the excited species were produced by primary electron-molecule collision processes (CN of anilines, CO, and CO^+ were found to be exceptional). The mechanism of the excitation and the fragmentation of the parent molecules and the comparison of the present spectra with those by discharge and by optical excitation were discussed. It was concluded that some excited species were produced through superexcited states.

As sources for exciting the electronic levels of molecules, ultraviolet radiation, such as Hg and Xe emission (5—21 eV), and X-ray radiation (1000 eV and above) have been widely used. However, few studies have been conducted in the energy region between these two methods. The excitation by electron impact is one of the most effective methods for this region. As early as 1946 the emission spectra of various benzene derivatives under electron impact in a hollow cathode discharge were investigated by Woeldike and Schüler[1] and the effects of the substituents were discussed. However, in an electric discharge, since many secondary processes occur in many cases, it is difficult to distinguish which processes are the primary ones. In this respect, the crossed electron and molecular-beam method is of great advantage as a method for exciting molecules, for the electron beam can be controlled easily and the pressure of the collision chamber can be so low that intermolecular collisional perturbation can be almost neglected during the lifetime of the excited species.

In recent years, the emission spectra of such molecules as N_2, CO, and NO and of some simple organic molecules have been extensively investigated by this method. Among the molecules which have a nitrogen atom, nitrogen,[2] ammonia,[3,4] hydrazine,[4] and methylamine[5] have been investigated, and much interesting information has been acquired regarding the excitation, the ionization, and the fragmentation processes not only of the ionized species, which can be detected by mass spectrometry, but also of neutral unstable ones. The emission spectra of benzene have been studied by this method by Vroom[6] and Smith.[7] The former has determined absolute emission cross sections for Lyman and Balmer radiation from hydrogen atoms formed in the dissociative excitation of benzene by electron impact (0.05—6 keV). The latter has measured the lifetimes of the vibrational levels of the $^1B_{2u}$ state using an electron beam phase shift method. However, few studies have been carried out on the photoemission of other aromatic molecules.

In the previous papers, the emission spectra of aromatic hydrocarbons[8] and of aromatic halides[9] by controlled electron impact (60—300 eV) have been reported. Characteristic bands of the parent molecules have been obtained from benzene, toluene, xylenes, fluorobenzene, and anisole[10] and assigned to the S_1–S_0 electronic transitions. However, chloro- and bromobenzenes failed to show such a band; instead, they showed pronounced progression bands of HCl^+ or HBr^+ and weak lines of Cl^+ or Br^+. It has been reported that benzonitrile and aniline show a strong photoemission of the parent molecules, both by discharge[1] and by optical excitation, while nitrobenzene does not. This has been ascribed to a rapid dissipation of the electronic transition energy through the nitro group and to the dissociation of the carbon-nitrogen bond.[11] In the present study, the emission spectra of these simple benzene derivatives by controlled electron impact will be reported and compared with those obtained by discharge and by optical excitation. Moreover, the mechanism of the electron-molecule collision which gives rise to the excitation, the ionization, and the fragmentation of the parent molecules will be discussed in connection with the results of the relationships between the emission intensities and the electron beam current.

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[8] T. Ogawa, M. Tsuji, M. Toyoda, and N. Ishibashi, This Bulletin, **46**, 2637 (1973).

[9] T. Ogawa, M. Tsuji, M. Toyoda, and N. Ishibashi, *ibid.*, **46**, 1063 (1973).

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[11] G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

Experimental

The electron-impact apparatus is essentially identical to that described in the previous papers.[8,12] The electrons emitted from the hot tungsten filament were accelerated by three electrodes and were led to the collision chamber through a slit. The accelerating voltage was variable from 60 to 300 V, with an energy spread of at least 6—10 eV; the electron beam current used was 10—1000 μA. The sample gas was injected through a nozzle 0.3—1.0 mm in diameter and collided with the electron beam perpendicularly. The gas pressure was estimated to be 10^{-3}—10^{-2} mmHg in the region of collisions.

The photoemission from the excited species was observed by the use of a Jarrell-Ash JE25 monochromator, which had a reciprocal dispersion of 33 Å/mm. The slitwidth of the monochromator used was 100 μm and 300 μm.

The aniline and nitrobenzene were obtained from the Kishida Chemical Co., and the benzonitrile and *N,N*-dimethylaniline, from Wako Pure Chemical Ind. All the reagents used were of a JIS guaranteed grade. They were distilled and degassed *in vacuo* a few times just before use. The mass spectrum was taken with a Hitachi RML-6E mass spectrometer. The accelerating voltage was 100 V.

Results and Discussion

Benzonitrile. A typical emission spectrum of benzonitrile under electron-impact excitation in the 250—450 nm region is shown in Fig. 1. The impact voltage was 200 V, and the electron beam current was 700 μA in this measurement. A characteristic band of the parent molecule was observed in the 260—330 nm region. This band was assigned to the electronic transition of benzonitrile from the lowest excited singlet state to the ground state, which is related to the ${}^1B_{2u}$—${}^1A_{1g}$ transition of benzene. Woeldike[1] observed a discrete emission spectrum in the 270—310 nm region in a hollow cathode discharge. Fluorescence spectra excited by Mn and Fe sparks at the vapor pressure of about 20 mmHg were photographed, and the vibronic bands were assigned, by Bass.[13] In the present spectrum, several discrete vibronic bands appear above the broad background (the continuous part of the band) and the vibrational structure closely resembles those of toluene[8] and fluorobenzene,[9] which are identical to benzonitrile in symmetry. The discrete band at the shortest wavelength (274 nm) was assigned to the (0,0) band of benzonitrile. Similar bands have been observed at 267 nm on toluene and at 264 nm on fluorobenzene. Other discrete bands on the longer-wavelength side of 274 nm may be interpreted as the vibrational structure with the fundamental frequencies given by Bass. On its shorter-wavelength side, weak unresolved features were observed; they were assigned to the transitions from the higher vibrational levels of the upper state to some vibrational levels of the ground state. These bands were also observed in the spectra of toluene and fluorobenzene. Since the pressure of the collision chamber was so low ($\leq 10^{-2}$ mmHg) that the intermolecular collisional perturbation was small in the lifetime of the excited state, the emission from the higher vibrational levels of the upper state was observed even from the molecule with less symmetry than benzene.

Other bands in the 355—430 nm region were assigned to the bands of fragment species. The lines at 434, 410, and 397 nm, decreasing in intensities as the wavelength becomes shorter, belong to the Balmer series of the hydrogen atom, which are denoted by H_γ, H_δ, and H_ε respectively. The band at 431 nm belongs to the (0,0) band of CH($A^2\Delta$–$X^2\Pi$). These band systems have always been observed in various benzene derivatives.[8–10] The most intense band systems in the 358—359 nm, 385—388 nm, and 415—422 nm regions were assigned to the main sequences with $\Delta v=1$, 0, -1 of CN($B^2\Sigma$–$X^2\Sigma$), and several weak bands in the 363—403 nm region, to the tail bands of this violet system.

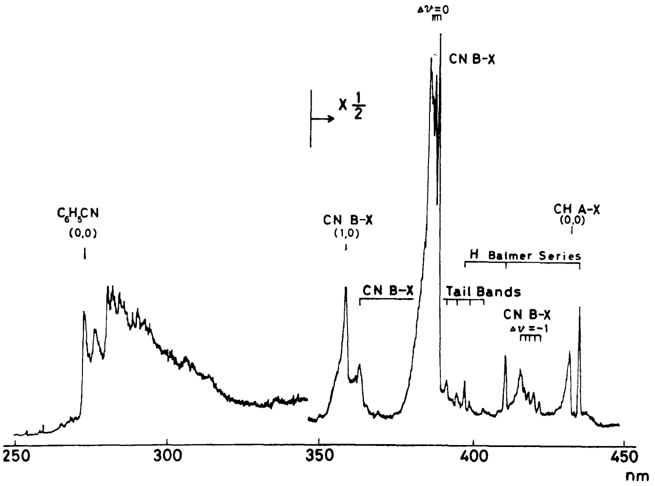

Fig. 1. Emission spectrum of benzonitrile by controlled electron impact. Impact voltage 200 V, electron beam current 700 μA.

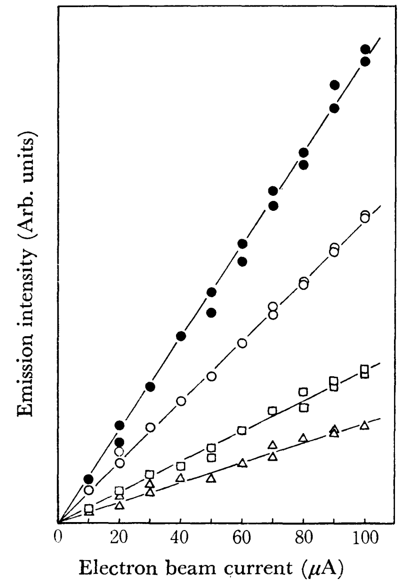

Fig. 2. Dependence of photoemission intensities of benzonitrile on the electron beam current. Impact voltage 200 V. ○: C_6H_5CN (282 nm), ●: CN (388 nm), □: H_γ, △: CH (431 nm).

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

13) A. M. Bass, *J. Chem. Phys.*, **18**, 1043 (1950).

The relationships between the emission intensities and the electron beam current are shown in Fig. 2. The emission intensities of the parent molecule and of the fragment species of H, CH, and CN are proportional to the electron beam current. This finding indicates that the excitation and the fragmentation of benzonitrile take place through primary electron-molecule collisions, just as in the cases of other benzene derivatives.[8,9] The excitation of a π electron of benzonitrile is concluded to be a one-electron process. The mechanism of the excitations and fragmentations can, then, be described as below:

$$\mathrm{PhCN} \xrightarrow{e} \mathrm{PhCN}^* \xrightarrow{h\nu} \text{ground state} \qquad (1)$$

$$\mathrm{PhCN} \xrightarrow{e} \mathrm{PhCN}^{**} \left\{ \begin{array}{l} \xrightarrow{\text{fast}} \mathrm{PhCN}^* \\ \xrightarrow{\text{fast}} \mathrm{H}^*, \mathrm{CH}^*, \mathrm{CN}^* \end{array} \right\} \xrightarrow{h\nu} \text{ground state} \qquad (2)$$

where superscript * signifies excited states from which the molecules radiate and where ** indicates a superexcited state, as was pointed out by Platzman,[14] which lasts for a length of time shorter than or equal to one period of vibration of the molecule. Since the excitation energy of the hydrogen Balmer series is larger than the first ionization potential of benzonitrile, it can be concluded that hydrogen atoms are produced through superexcited states. It seems that PhCN* is produced through two processes, (1) and (2), although their relative importance cannot be determined in the present study.

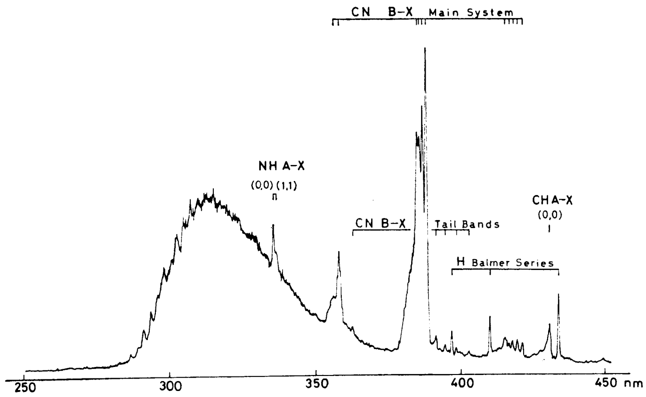

Fig. 3. Emission spectrum of aniline by controlled electron impact. Impact voltage 300 V, electron beam current 1 mA.

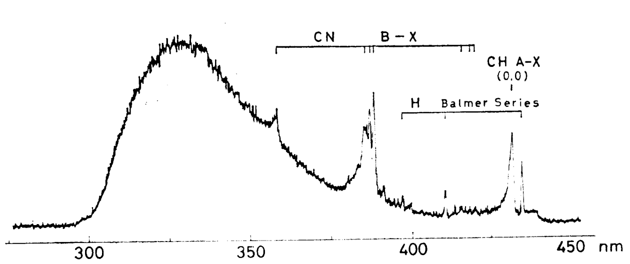

Fig. 4. Emission spectrum of *N,N*-dimethylaniline by controlled electron impact. Impact voltage 200 V, electron beam current 700 μA.

Aniline and N,N-*Dimethylaniline*. Typical emission spectra of aniline and *N,N*-dimethylaniline under electron-impact excitation in the 250—450 nm region are shown in Figs. 3 and 4 respectively. The electron beam of 300 eV at 1 mA was used for the measurement of the former, while that of 200 eV at 700 μA was used for the latter. Bands of the parent molecules were observed in the 280—375 nm region on aniline and in the 295—410 nm region on *N,N*-dimethylaniline. These bands are shifted to longer wavelengths by about 10 nm and about 25 nm from the (0, 0) band of toluene (267 nm) respectively, and they agree well with the fluorescence bands in solution.[15] The former band was assigned to the A^1B_2–X^1A_1 electronic transition for aniline.[16] The vibrational structure of aniline is more complicated than that of benzonitrile, and the fraction of the background is larger. The emission spectrum of *N,N*-dimethylaniline is very broad, and the fine structure is no longer observed, probably because the symmetry of the aniline molecule is destroyed, as has been shown in the case of the absorption spectrum.[17] Woeldike[1] observed a continuous emission spectrum of aniline in the region from 285 to 330 nm. Blondeau, Quack, and Stockburger[18,19] investigated the resonance fluorescence spectra of various benzene derivatives, such as benzene, toluene, xylenes, and aniline, at low pressures ($\leq$0.1 mmHg) by irradiation with light of narrow bandwidth; they concluded that aromatic molecules exhibit resonance fluorescence. It was shown that the difference in the initially-irradiated levels resulted in different progression bands, and the most striking feature was the loss of structure and an increase in the fraction of the background when the molecules were excited to higher vibronic levels. It is known that, in the spectrum of aniline, pronounced progression bands due to the strongly anharmonic inversion vibration of NH_2 group exist in addition to those due to the symmetric vibration,[16,18,19] and that these progression bands complicate the vibrational structure. In addition, since the exciting energy of the present study is higher than the optical excitation, molecules are expected to be excited to the closely-spaced higher vibrational levels of the upper state, from which the fast intramolecular vibrational rearrangement occurs. Since aniline has more vibrational states which can strongly interact with the initially-excited state than do benzene, toluene, and fluorobenzene, the initial vibrational modes will be converted to other modes more easily. Thus, the complex vibrational structure and the large fraction of the background in the present spectrum are partly due to the appearance of the complicated progression bands, and partly due to the further overlapping of these progression bands because

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14) R. L. Platzman, *Radiation Res.*, **17**, 419 (1962).

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

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17) A. Mangini, A. Trombetti, and C. Zauli, *J. Chem. Soc. B*, **1967**, 153.

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of the wider energy distribution of the incident electrons used and because of the higher excitation energy used in the present study.

A doublet band at 336—337 nm was assigned to the (0,0) and (1,1) bands of NH($A^3\Pi$–$X^3\Pi$). All the other bands on anilines were assigned to the H, CH, and CN bands, which appeared also on benzonitrile.

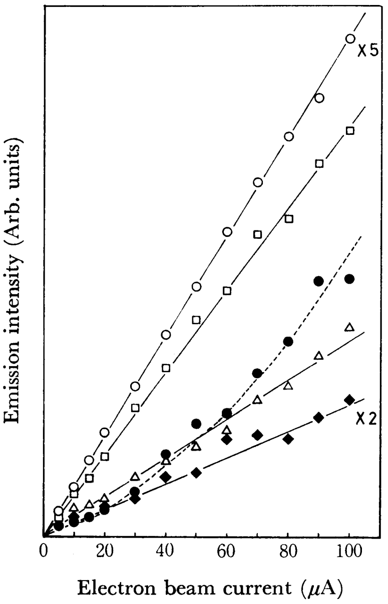

Fig. 5. Dependence of photoemission intensities of aniline on the electron beam current. Impact voltage 200 V. ○: $C_6H_5NH_2$ (314 nm), ●: CN (388 nm), □: Hγ, △: CH (431 nm), ◆: NH (336 nm).

The emission intensities of the parent molecules and the fragment species, such as H, CH, and NH of aniline and *N,N*-dimethylaniline, are found to be proportional to the electron beam current, as is shown in the case of aniline in Fig. 5. Similar results have been obtained from various benzene derivatives[8,9] and other organic molecules, such as methane,[20] methanol,[21] and amines.[5] Consequently, the excitations of the parent molecules and the fragmentations of H, CH, and NH by electron impact under the present crossed-beam method are concluded to take place generally through one-electron processes.

The emission intensities of the CN bands of aniline and *N,N*-dimethylaniline are found to be proportional to about 1.4 and about 1.2 powers of the electron beam current respectively, as is shown in Fig. 5. These results indicate that the photoemission processes of CN produced from anilines are different from those of other fragment species, such as H, CH, and NH, and that of CN produced from benzonitrile. It seems that a certain secondary process is involved in the production of the excited CN species. It is noteworthy that a similar result was obtained for the CN produced from pyridine,[22] whose emission intensity was found to be proportional to 1.5 powers of the electron beam current. Since the radiation lifetime of the CN $B^2\Sigma(v'=0)$ state was measured[23] as 39—85 ns, collisions between the excited species and the neutral molecule can be neglected at such a low pressure as 10^{-3}—10^{-2} mmHg. Furthermore, in the present experimental situation, the possibility of the second collision of one neutral species with another electron is also expected to be small. A collision process between an electron and a positive-ion may be involved in the production of CN. It should be noticed that the production of CN from benzonitrile, whose emission intensity is proportional to the electron beam current, proceeds with one C–CN bond scission, whereas the production of CN from anilines and pyridine, whose emission intensities are not linear, needs the scissions of at least two skeletal bonds. Particularly, in the case of aniline and pyridine, the cleavage of the stable ring must take place.

Nitrobenzene. A typical emission spectrum of nitrobenzene under electron-impact excitation in the 200—600 nm region is shown in Fig. 6. The impact voltage was 200 V, and the electron beam current was 1 mA in this measurement. There are pronounced bands of CO and CO^+; they were assigned as in the cases of anisole[10] and phenol,[24] as will be shown below. The emission bands at 283—331 nm were assigned to the progression, $v'=0$, of the third positive system ($b^3\Sigma$–$a^3\Pi$) of CO; those at 219—247 nm, to the progressions, $v'=0$, 1, 2, of the first negative system ($B^2\Sigma$–

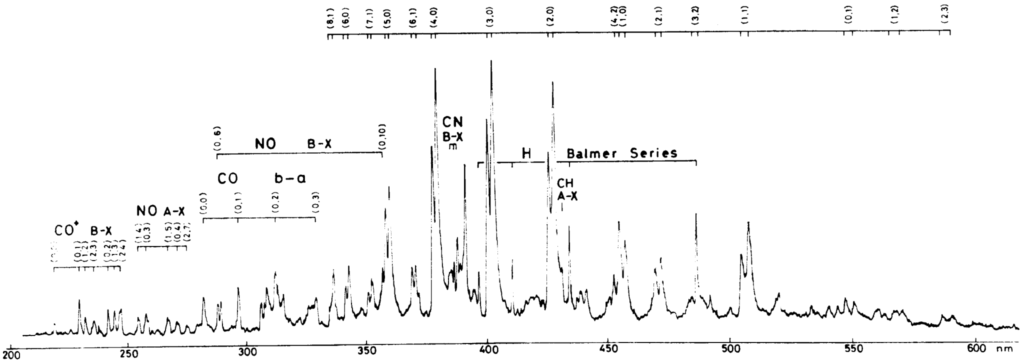

Fig. 6. Emission spectrum of nitrobenzene by controlled electron impact. Impact voltage 200 V, electron beam current 1 mA.

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

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

22) M. Toyoda, T. Ogawa, and N. Ishibashi, unpublished.

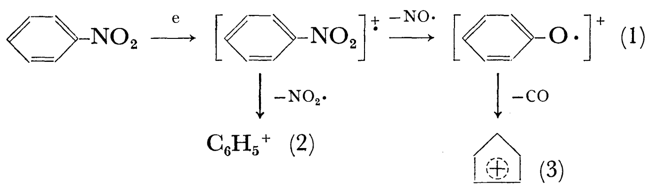
23) T. J. Cook and D. H. Levy, *J. Chem. Phys.*, **57**, 5059 (1972).

24) M. Tsuji, T. Ogawa, and N. Ishibashi, unpublished.

X$^2\Sigma$) of CO$^+$, and the characteristic doublet bands at 335—590 nm, to the progressions, $v''=0$, 1, 2, of the comet-tail system (A$^2\Pi$-X$^2\Sigma$) of CO$^+$. The relative emission intensities of the main progression of this comet-tail system of nitrobenzene agree with those of CO by 200 eV impact.[25)] The bands at 255—276 nm were assigned to the sequences with $\Delta v=-3$, -4 of the NO γ system (A$^2\Sigma$-X$^2\Pi$), and those at 289 and 359 nm, to the (0,6) and the (0,10) bands of the NO β system (B$^2\Pi$-X$^2\Pi$). Other bands were assigned to the H, CH, and CN bands observed on benzonitrile and anilines.

It is concluded from the linear relationships between the emission intensities and the electron beam current that H, CH, and NO species are produced by one-electron processes. Meanwhile, the emission intensities of CO and CO$^+$ species are found to be proportional to about 1.2 powers of the electron beam current. Thus, the production of these species is not a simple one-electron process, and it seems that positive ions of some kind are involved, as in the case of the CN produced from anilines. Since the energy of the b$^3\Sigma$ state of CO is larger than the first ionization potential of nitrobenzene, it seems that the CO species are produced through some superexcited states.

It should be noticed that there is no direct carbon-oxygen bond in the nitrobenzene molecule. The pressure of the collision chamber is so low that no recombination between carbon and oxygen atoms may occur. Meanwhile, from the analysis of the mass spectrum,[26)] it was suggested that the decomposition of nitrobenzene proceeded as is shown below;



The mass spectrum was measured in order to compare the relative intensities of these peaks. The intensities of the fragment peaks, (1), (2), and (3), relative to the parent peak were found to be 0.32, 2.55, and 0.37 respectively. The fragment species of CO and CO$^+$ may be produced through the positive ions, as has been described above.

Nitrobenzene exhibited no emission of the parent molecule in the present study, as was found in the case of the excitations by photons and by discharge.[1)] This is partly due to the fast intersystem crossing processes, since the lowest excited level is the *n* nonbonding orbital. Another reason for this is the dissociation of the carbon-nitrogen bond, as was pointed out by Lewis and Calvin.[11)] The relative intensity of the phenyl cation peak to the parent one was measured as 2.55 for nitrobenzene, while those for benzonitrile[27)] and chlorobenzene[9)] were reported to be 0.056 and 0.68 respectively. This indicates that the cleavage of the carbon-nitrogen bond can easily take place. Thus, it is concluded that the spin-orbit interaction and the predissociation of the parent molecule prevent the appearance of the band of the parent molecule under electron-impact excitation.

Concluding Remarks. Benzonitrile, aniline, and *N,N*-dimethylaniline were found to show the emission bands of the transitions from the lowest excited singlet state to the ground state of the parent molecules. The appearances and the positions of these bands do not change appreciably when the impact energy changes between 60—300 eV. It may be concluded that the molecules receive enough excess energy even though the exciting energy is 60 eV.

A pronounced feature of the electron-impact excitation is that the optically-forbidden singlet-triplet transition may be allowed. However, such a transition could not be observed under 60—300 eV electron-beam excitation in the present study, and the observed spectra are similar to those of optical excitation because the parent molecules are excited only to the singlet states. Meanwhile, in the energy loss spectrum of benzene, optical selection rules hold for 200—300 eV electrons,[28)] while three singlet-triplet transitions were observed in addition to three singlet-singlet transitions under low energy electron impact[29)] (13.6 and 20.0 eV). Thus, it is expected that a singlet-triplet transition will be observed when the impact energy is lowered to the near threshold value in the present method, although several experimental difficulties have to be overcome.

The first ionization potentials of benzene, benzonitrile, aniline, *N,N*-dimethylaniline, and nitrobenzene have been reported to be 9.56,[30)] 10.09,[30)] 8.32,[30)] 7.51,[31)] and 10.18[30)] or 10.26[31)] eV respectively. All these values are smaller than the excitation energy of the hydrogen atom (13.32 eV for the Balmer line H$_\varepsilon$); the first ionization potential of nitrobenzene is also smaller than the excitation energy of the CO b$^3\Sigma$($v'=0$) state (10.38 eV).[32)] It is concluded that hydrogen atoms are produced in the dissociative excitations of benzonitrile, aniline, and nitrobenzene, as has been shown before, and that these dissociative processes probably proceed through superexcited states. It seems that the superexcited states also play an important role in the production of the CO from nitrobenzene and other fragment species.

The emission intensities of the line of H$_\gamma$ relative to the (0,0) band of CH and the ratios of the H atom to the CH group in these molecules are shown in Table 1. This comparison is valid because the emission intensities of H and CH are proportional to the electron beam current and also to the gas pressure of the collision

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25) J. M. Ajello, *J. Chem. Phys.*, **55**, 3158 (1971).

26) H. Buzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day Inc., San Francisco (1967).

27) A. Cornu and R. Massot, "Compilation of Mass Spectral Data," Heyden & Son Ltd. (1967).

28) A. Skerbele and E. N. Lassettre, *J. Chem. Phys.*, **42**, 395 (1965).

29) J. P. Doering, *ibid.*, **51**, 2866 (1969).

30) G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

31) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, **1968**, 22.

32) G. Herzberg, "Spectra of Diatomic Molecules," D. Van. Nostrand, Princeton, N. J. (1950), p. 520.

Table 1. The ratios of H to CH in the molecules and the emission intensities of the line of H_γ relative to the (0,0) band of CH
Impact voltage: 200 V

Compounds	Estimated intensities H/CH	Emission intensities[a] H/CH
C_6H_6	1(6/6)	1.55 ± 0.08[b]
C_6H_5CN	1(5/5)	1.54
$C_6H_5NO_2$	1(5/5)	1.48
C_6H_5F	1(5/5)	1.55[c]
$C_6H_5NH_2$	1.4(7/5)	$2.09 (=1.49 \times 1.4)$

a) Intensities were measured in peak height and the slitwidth used was 300 μm.
b) Ref. 8.
c) Ref. 9.

chamber as has been shown in the cases of benzene[8] and fluorobenzene.[9] It should be noticed that the numbers of the second column and those of the third column correspond very well within the limits of experimental error. Therefore, the probabilities of the production of the excited H and CH species, whose fragmentation processes are competitive ones, are found to be almost equal in these simple benzene derivatives. In the case of aniline, it seems that the production of excited hydrogen atoms from the hydrogens in the NH_2 group and in the benzene ring is almost equally probable. These results may imply that similar super-excited states are involved in the collision with electrons with energy of 200 eV for the fragmentations of H and CH, whatever the substituents of the benzene ring are.

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