Emission in the Ultraviolet–Visible Region produced by the Electron-impact Excitation of Polyatomic Molecules. Part 1. Amino-compounds

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The electron-impact induced optical emissions of a series of amino-compounds have been studied using single electron–molecule collision conditions. Various excited fragment radicals have been observed from all the amines, together with an excited molecular emission from non-aromatic tertiary amines. No electronically excited ionic states were observed. The formation of electronically excited neutral molecules is shown to occur by both electric-dipole allowed and electric-dipole forbidden excitation processes.

THE formation of optically fluorescing species by electron–molecule collisions occurs in flames, electrical discharges, plasmas, planetary ionospheres, and in mass spectrometry. The electron-impact excitation of atoms and small molecules has been thoroughly investigated.[1,2] There are, however, very few data available upon the emissions produced by electron impact upon polyatomic organic molecules.[3-5]

The electron-impact excitation process (1), occurring under single collision conditions, may involve transitions

$$e + M \longrightarrow e + M^* \qquad (1)$$

that are electric-dipole allowed or electric-dipole forbidden, or may be an electron exchange between the projectile electron and a molecular electron.[6] Thus some of the electronic states of M* populated by electron-impact may be forbidden by spin or symmetry conservation, and would not be observed under photon excitation. Another important difference between electron-impact excitation and photon excitation lies in the ' non-quantisation ' of the energy transfer process. A photon is either absorbed or not, and as such the energy transferred to the molecule has a very specific value, whereas for a single electron impact event the energy transferred may take any value from zero up to the kinetic energy of the impacting electron, subject to the availability of energy levels.

The excited molecule M* may subsequently fluoresce [reaction (2)], or undergo rearrangement and/or dissociation [reaction (3)], the products of which may themselves be capable of emitting fluorescence [reaction (4)].

$$M^* \longrightarrow M + h\nu_1 \qquad (2)$$

$$M^* \longrightarrow m_1 + m_2^* \qquad (3)$$

$$m_2^* \longrightarrow m_2 + h\nu_2 \qquad (4)$$

There will of course be a whole range of competing processes that do not lead to light emission, but these would not be observed using the present technique.

In general, each of the emission features will have fluorescence cross-sections which behave differently as the electron energy is changed. Monitoring both the threshold energies and the fluorescence cross-section excitation profiles provides information on the mechanisms of the particular excitation processes under study.

EXPERIMENTAL

The apparatus consists of a metal vacuum chamber, within which is a brass reaction chamber, length *ca.* 5 cm, maintained at ground potential. Electrons are produced by a directly heated thoriated tungsten filament, and accelerated into the field free reaction chamber by a potential variable up to 1 200 V. The electron beam is collimated by a system of slits and an axial magnetic field. After passage through the reaction chamber the electrons are collected at a trap; the beam current, measured at the trap, could be stabilised at any value up to 180 μA. Gas pressure in the reaction chamber was measured by a high sensitivity Pirani gauge, while the pressure in the main vacuum chamber was monitored with a Penning ionization gauge.

Fluorescence is viewed at right angles to the electron beam through a 25 mm diameter Spectrosil A window located at the mid-point of the reaction chamber, by an *f*/4 scanning monochromator fitted with a 1 200 lines mm^{-1} grating blazed at 300 nm. Spectra were recorded over the range 200—600 nm at a nominal bandpass of 1 nm, using an EMI 9601B photomultiplier tube and direct current amplifier. To reduce the level of scattered light from the hot filament, the inside of the reaction chamber was coated with a thin layer of colloidal graphite.

All the compounds studied were available commercially. After fractional distillation under vacuum, with retention of the middle third portion, the purities were better than 99.5% as determined by g.l.c. To prevent the possibility of thermal or photochemical reaction of the unsaturated compounds, the purified samples were stored in the dark under vacuum at 77 K.

RESULTS AND DISCUSSION

Emission spectra were recorded under single collision conditions, *i.e.* the fluorescence intensity varied linearly with both the electron beam current and the gas pressure, as demonstrated in Figures 1 and 2. Spectra were routinely recorded at a pressure of *ca.* 2×10^{-5} Torr, an emission current of 150 μA, and an electron energy of 80 eV. All spectra reproduced here are uncorrected for the spectral response of the monochromator–photomultiplier combination. Unless otherwise specified, the identities of the emitting species were confirmed using the compilation of Pearse and Gaydon.[7]

The electron-impact excitation of ammonia has been studied by Bubert and Froben.[8] In Figure 3 is shown an ammonia fluorescence spectrum obtained using the present apparatus for comparison with the amino-com-

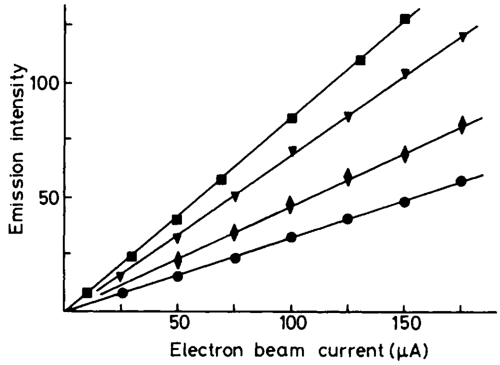

FIGURE 1 Linear dependence of fluorescence intensity in arbitrary units upon electron-beam current. ■ Molecular emission from triethylamine; ▼ H-Balmer (4 → 2) from monomethylamine; ◆ NH ($\tilde{A}^3\Pi - \tilde{X}^3\Sigma$, 0,0 Q-branch) from monomethylamine; ● CH ($\tilde{A}^2\Delta - \tilde{X}^2\Pi$, 0,0 Q-branch) from monomethylamine. All measurements carried out at an electron-beam energy of 80 V and a gas pressure of *ca.* 5 × 10^{-5} Torr

pounds. A series of Balmer lines, diminishing in intensity from $n = 4 \longrightarrow 2$ to $n = 9 \longrightarrow 2$, and a broad emission from *ca.* 400—600 nm due to excited NH_2 radicals ($\tilde{A}^2A_1 \longrightarrow \tilde{X}^2B_1$, the ammonia α band)[8,9] can be seen. The most intense feature in the spectrum is the 0,0 *Q* transition of NH $\tilde{A}^2\Pi \longrightarrow \tilde{X}^3\Sigma^-$ at 336 nm (note the change in sensitivity). The NH biradical is also produced in a singlet state[8-11] as evidenced by the $\tilde{c}^1\Pi \longrightarrow \tilde{a}^1\Delta$ and $\tilde{c}^1\Pi \longrightarrow \tilde{d}^1\Sigma$ emissions.

Substitution of a methyl group for a hydrogen atom leads to marked changes in the spectrum (methylamine, Figure 4). $NH_2(\tilde{A})$ emission is no longer observed, *i.e.* although NH_3 readily undergoes N–H fission to give $NH_2(\tilde{A})$, CH_3NH_2 does not undergo the analogous N–CH_3 fission. This is consistent with the N–H fission occurring *via* a quantum mechanical tunnelling mechanism which is not available to the N–CH_3 bond. Loss of CH_3 and H does occur to give NH($\tilde{A}^3\Pi$) but at a lower relative intensity compared with the rest of the spectrum. There is also a marked reduction in NH($\tilde{c}^1\Pi$) compared with NH($\tilde{A}^3\Pi$) in going from NH_3 to CH_3NH_2. Presumably process (5) is much more favourable in ammonia[9,10] than the corresponding process (6) is in monomethylamine.

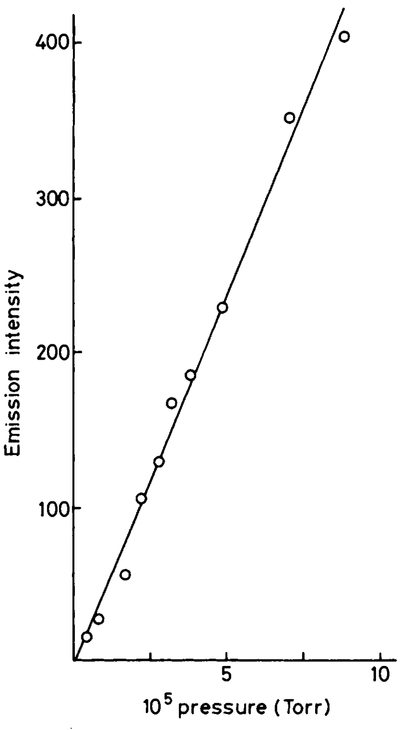

FIGURE 2 Linear dependence of fluorescence intensity upon pressure for the molecular emission produced from triethylamine at an electron-beam current of 150 μA and an electron-beam energy of 80 V

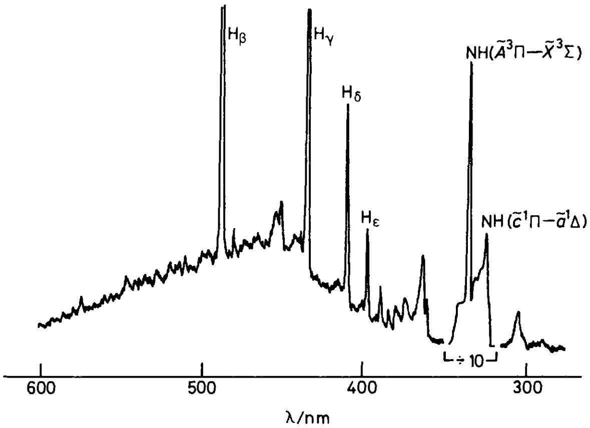

FIGURE 3 Fluorescence spectrum observed during the electron-beam excitation of ammonia. Electron energy 80 V, electron-beam current 150 μA, ammonia pressure 5 × 10^{-5} Torr. The features labelled Hβ *etc.* are members of the H-Balmer series. Note that the main NH bands are recorded at one tenth the sensitivity of the remainder of the spectrum. The broad band at 400—600 nm is NH_2 ($\tilde{A}^2A_1 - \tilde{X}^2B_1$) emission

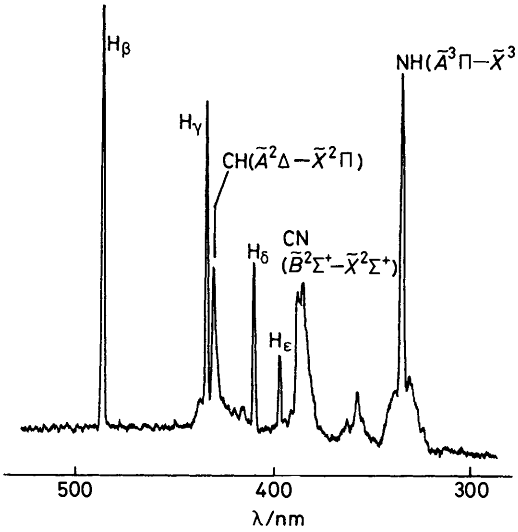

FIGURE 4 Fluorescence spectrum observed during the electron-beam excitation of monomethylamine. Electron energy 80 V, electron-beam current 150 μA, monomethylamine pressure 5 × 10^{-5} Torr. Bands due to H, CH, CN, and NH can be identified

$$NH_3 \longrightarrow NH(\tilde{c}^1\Pi) + H_2(\tilde{X}) \qquad (5)$$

$$CH_3NH_2 \longrightarrow NH(\tilde{c}^1\Pi) + CH_4(\tilde{X}) \qquad (6)$$

With di- and tri-methylamine (Figure 5) there is a large reduction in intensity of emission from NH($\tilde{A}^3\Pi$) compared with monomethylamine. The fact that the excited imino radical is observed in the excitation spectrum of trimethylamine shows that rearrangement processes are occurring.

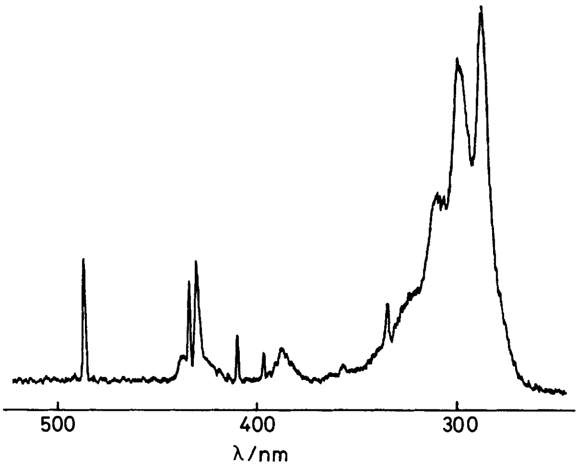

FIGURE 5 Molecular fluorescence observed during the electron-beam excitation of trimethylamine. Electron energy 80 V, electron-beam current 150 μA, trimethylamine pressure 5 × 10^{-5} Torr. Weak bands due to H, CH, CN, and NH can also be seen (see Figure 4)

All compounds containing C and H, with the notable exception of pyridine, produce emission from CH($\tilde{A}^2\Delta$) together with Balmer lines from electronically excited hydrogen atoms. The di- and tri-methylamines show a reduced ratio of Balmer line emission to CH($\tilde{A}^2\Delta$) compared with monomethylamine. This implies that the excitation cross-section for production of an excited H atom from the amino-group is larger than for removing an excited H atom from the methyl group.

CN($\tilde{B}^2\Sigma^+ \longrightarrow \tilde{X}^2\Sigma^+$) emission is observed with most of the compounds studied, although being most important in the case of methylamine. Thus the extensive sequential decomposition required to eliminate a CN fragment is more probable when hydrogen atoms, rather than alkyl groups, are being lost.

Trimethylamine exhibits a strong emission band at *ca.* 280—350 nm. This emission can be attributed to the electronically excited molecule, similar bands having been observed with other tertiary amines during electric discharge [12] and photo-excitation.[13,14] The excitation process is thought to involve formation of a Rydberg state $n = 3$ from the $n = 2$ highest occupied molecular orbital (a_1 symmetry in C_{3v} group). This MO is not a non-bonding lone pair, but has some N–H and H–H (in NH_3) bonding character and is primarily responsible for the pyramidal structure of amines. Excitation of an electron from this MO to a Rydberg level results in a planar geometry with considerable ' umbrella ' vibrational excitation.[15] In the case of tertiary amines the lifetime of the excited state is sufficiently long for fluorescence to be observed. Fluorescence is not observed with primary or secondary amines, the lifetime of the excited state being much reduced by predissociation of an H atom. This is assumed to occur by a quantum mechanical tunnelling process,[13] a channel that is not available in tertiary amines.

All the tertiary amines studied, *i.e.* trimethyl- and triethyl-amine, *N*-methylpyrrolidine, 1-azabicyclo[2.2.2]-octane (quinuclidine), and 1,4-diazabicyclo[2.2.2]octane (DABCO), emitted molecular fluorescence. *N*-Methylpyrrole, although it contains a tertiary nitrogen atom, gave no molecular emission. Its electron impact fluorescence spectrum is similar to that of pyrrole itself, showing only H, CH, CN, and NH fragment fluorescence. The lack of molecular fluorescence may be due to the incorporation of the ' lone-pair ' electrons in the aromatic-like sextet. Pyridine exhibited only very weak CN fragment emission, with no detectable molecular emission. However, it has been shown [16] that the photo-excited pyridine molecule fluoresces with a quantum yield of only 10^{-5}, with radiationless processes dominating in this molecule; therefore the lack of molecular emission is not unexpected.

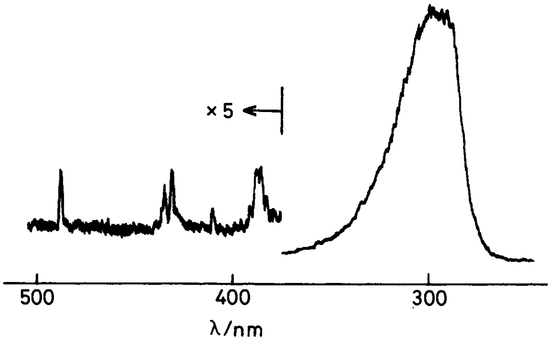

FIGURE 6 Molecular fluorescence observed during the electron-beam excitation of *N*-methylpyrrolidine. Electron energy 80 V, electron-beam current 150 μA, *N*-methylpyrrolidine pressure 4 × 10^{-5} Torr. Note the increased sensitivity used to record the H, CH, and CN bands

For most of the tertiary amines, the molecular fluorescence consisted of an unstructured band (see for example Figure 6). In comparison trimethylamine (Figure 5) and DABCO (Figure 7) both showed evidence of vibrational fine structure. This structure has been observed previously by Halpern [17,18] under photo-excitation. It has been inferred that the excited states of both trimethylamine and DABCO must have a rigidity which is not present in the other tertiary amines studied. Halpern [19] has speculated that when trimethylamine is in the near planar excited state, the methyl groups are hindered towards rotation. The excited state thus becomes more rigid, which in turn leads to a stricter adherence to the vibronic selection rules than occurs in a much more flexible excited state such as triethylamine. In DABCO the ' lone-pair ' orbitals on the two nitrogen atoms can combine either in phase, $n(+)$, or out of phase, $n(-)$. The higher energy Rydberg atomic orbitals located on the nitrogen are also expected to interact either through space or through the intervening bonds [20-22] to give symmetric and antisymmetric combinations. These interactions would be expected to increase the rigidity of the DABCO molecule.

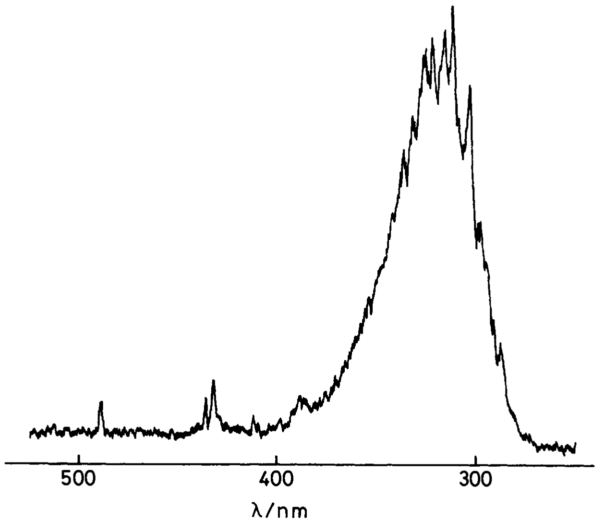

FIGURE 7 Molecular fluorescence observed during the electron-beam excitation of 1,4-diazabicyclo[2.2.2]octane (DABCO). Electron energy 80 V, electron-beam current 150 μA, DABCO pressure 6 × 10^{-5} Torr

A further series of measurements were carried out on trimethylamine, triethylamine, *N*-methylpyrrolidine, and quinuclidine, involving the determination of the threshold energies required for production of the molecular fluorescence, together with the excitation functions from threshold up to 180 eV. For these measurements the molecular emission was monitored at the maximum in the emission band (near 300 nm) with the monochromator bandpass set to 10 nm. The electron energy scale was calibrated using excitation of the $\tilde{C}^3\Pi_u \longrightarrow \tilde{B}^3\Pi_g$ transition of molecular N_2, the threshold energy and energy for maximum intensity being known.[23] For triethylamine, the emission threshold was also obtained by a photoexcitation method, using a Perkin-Elmer MPF-3L fluorimeter and a gaseous triethylamine sample. The threshold for molecular emission occurred at 282 ± 3 nm (4.38 ± 0.04 eV). The spectral distribution of the fluorescence, using excitation at 255 nm, was almost identical to that observed in the electron impact experiments. From these measurements we conclude that trimethylamine, *N*-methylpyrrolidine, and quinuclidine have threshold energies of 4.6 ± 0.1 eV and triethylamine a threshold energy of 4.4 ± 0.1 eV. These low values for the threshold energies confirm that the emission must involve the ground state as the lower level, and cannot be between two electronically excited states.

The excitation functions determined for trimethylamine, triethylamine, *N*-methylpyrrolidine, and quinuclidine all had qualitatively similar shapes; those of trimethylamine and *N*-methylpyrrolidine are shown in Figure 8. It can be seen that the excitation function rises from threshold rapidly to a sharp maximum, and then falls to an intermediate value at higher electron energies. For comparison we show in Figure 9 two excitation functions of states of N_2. Excitation of the $N_2(\tilde{C}^3\Pi_u)$ state from ground state $N_2\,(\tilde{X}^1\Sigma^+{}_g)$ is an electric-dipole forbidden process, and the excitation function is typical of a forbidden process.[24] A sharp maximum is reached soon after threshold, and the function then falls to a low value at higher voltages. Excitation of the $N_2{}^+(\tilde{B}^2\Sigma^+{}_u)$ ionic state is a fully allowed process, and the excitation function rises only slowly from threshold and passes through a very broad maximum at higher voltage. The shape of the tertiary amine excitation functions indicate that there must be contributions from both allowed and forbidden processes in the excitation of the molecular fluorescence.

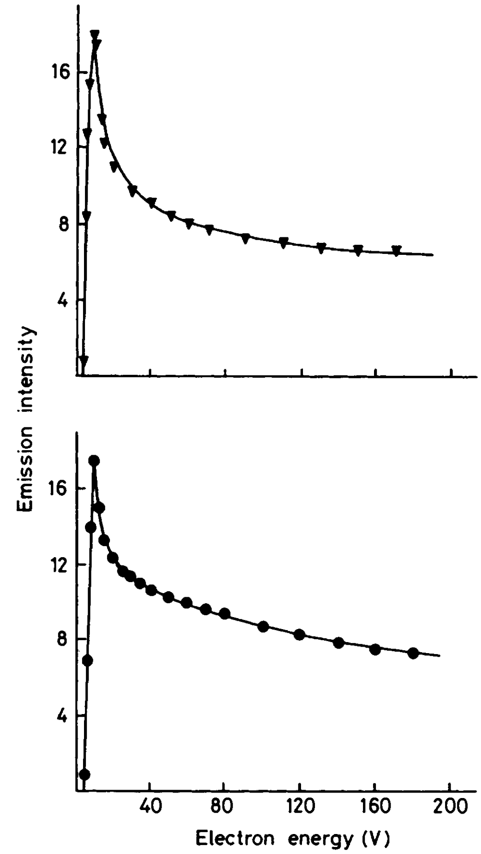

FIGURE 8 Excitation functions for molecular emission from (▼) *N*-methylpyrrolidine and (●) trimethylamine at an electron-beam current of 10 μA and a pressure of *ca.* 5 × 10^{-5} Torr (emission intensity in arbitrary units)

Parker and Avouris,[25] in multiphoton excitation studies on DABCO, have concluded there is an allowed photon absorption, $\tilde{X}^1A'_1[n(+)] \longrightarrow \tilde{B}^1E'[3p_{x,y}(+)]$, with an adiabatic threshold at 253 nm (4.94 eV), and a weak forbidden absorption, $\tilde{X}^1A'_1[n(+)] \longrightarrow \tilde{A}^1A_1$, $[3s(+)]$ with a threshold at 279 nm (4.44 eV). When DABCO is excited to the $\tilde{B}$ state, there is a fast non-radiative transfer $\tilde{B} \longrightarrow \tilde{A}$, followed by $\tilde{A} \longrightarrow \tilde{X}$ fluorescence which is observed at 280—350 nm.

Our electron impact excitation data are entirely consistent with these conclusions. At electron energies close to threshold it is the $\tilde{X} \longrightarrow \tilde{A}$ transition that is being excited. Although this transition gives only a weak photon absorption, under electron-impact, where the optical selection rules do not apply, it is primarily responsible for the excitation at energies within *ca.* 10—15 eV of threshold. At much higher electron energies the cross-section for this process will become small.

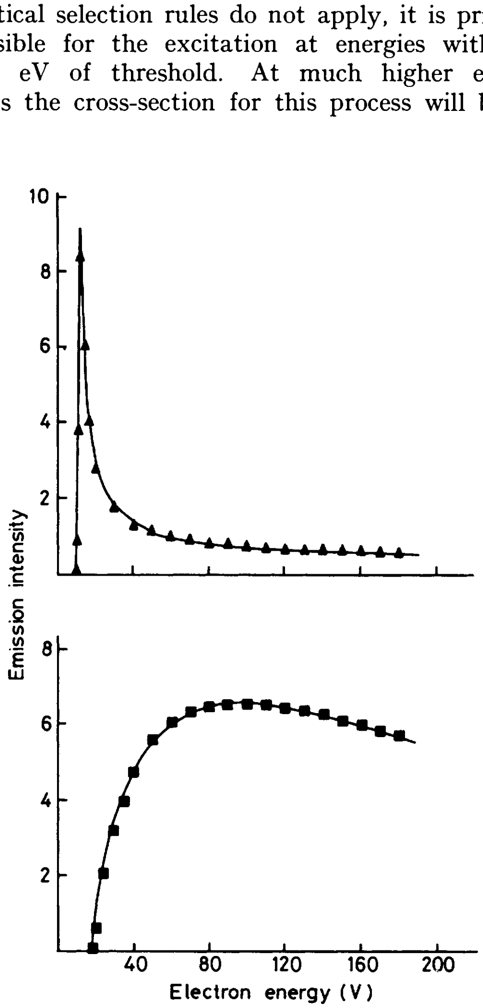

FIGURE 9 Excitation functions for states of N_2 at an electron-beam current of 50 μA and a pressure of *ca.* 2×10^{-5} Torr. ▲ N_2 ($\tilde{C}^3\Pi_u$), monitored as $\tilde{C}^3\Pi_u - \tilde{B}^3\Pi_g$ emission at 337 nm. ■ N_2^+ ($\tilde{B}^2\Sigma^+$), monitored as $\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Sigma_g^+$ emission at 391.4 nm (emission intensity in arbitrary units)

Electron-impact will also excite the optically allowed process $\tilde{X} \longrightarrow \tilde{B}$. The threshold for this process is only *ca.* 0.5 eV higher than that for the $\tilde{X} \longrightarrow \tilde{A}$ process.[25] This excitation makes only a small contribution to the total cross-section near threshold, due to the much slower increase with voltage, although at the higher electron energies it becomes the dominant process. Thus the total fluorescence excitation function shows the sharp peak at low energy characteristic of a forbidden process, together with a significant cross-section at higher energy characteristic of an allowed process. There is no evidence either from the present work, or from previous photoexcitation studies,[17,18,25] for $\tilde{B} \longrightarrow \tilde{X}$ fluorescence in tertiary amines. Presumably the non-radiative $\tilde{B} \longrightarrow \tilde{A}$ conversion is the faster process, and it is the $\tilde{A} \longrightarrow \tilde{X}$ molecular fluorescence that is always observed.

Relative cross-sections for excitation of molecular fluorescence from the tertiary amines have also been determined. These were determined at an electron energy corresponding to the maximum in the excitation function for each respective amine, where the most important process is the $\tilde{X} \longrightarrow \tilde{A}$ optically forbidden excitation. Values of 0.16, 0.34, 0.80, and 1.0 were obtained for quinuclidine, triethylamine, *N*-methylpyrrolidine, and trimethylamine, respectively. Halpern[19] has shown that the photoexcited gas-phase fluorescence quantum yields for all these compounds are near unity. Thus the differences in the electron-impact induced fluorescence for these compounds must reflect differences in the efficiency of the $\tilde{X} \longrightarrow \tilde{A}$ excitation process, which is in competition with alternative channels leading to, for example, ionised species or electronic ground state neutral fragments. These alternative channels become of increasing importance in the larger cyclic molecules. If the same exercise is carried out at high electron energies, in the range 100—150 eV, where the $\tilde{X} \longrightarrow \tilde{B}$ transition should be the dominant process, the values of relative cross-section obtained, *viz.* 0.08, 0.33, 0.77, and 1.0 are not significantly different.

Conclusions.—When subjected to electron-impact excitation, aliphatic tertiary amines exhibit strong molecular fluorescence, with a threshold energy for production of the emission of *ca.* 4.5 eV. At electron energies a little above threshold the amines undergo an $\tilde{X} \longrightarrow \tilde{A}$ forbidden Rydberg excitation, with $\tilde{A} \longrightarrow \tilde{X}$ fluorescence then being observed. At high electron energies, this forbidden excitation becomes less important, and is replaced by an $\tilde{X} \longrightarrow \tilde{B}$ fully allowed excitation. This is followed by a rapid $\tilde{B} \longrightarrow \tilde{A}$ internal conversion and $\tilde{A} \longrightarrow \tilde{X}$ fluorescence.

All the compounds studied also produced electronically excited neutral fragments, although cyclic compounds showed much less fragmentation than acyclic compounds. Formation of electronically excited ionic species was not observed for any of the compounds studied, thus predissociation to ground state fragments may be the faster reaction channel for these species.

We thank Professor B. G. Gowenlock for his interest and encouragement, and one of us (H. P. F.) would like to thank Heriot-Watt University for financial assistance during the course of this work.

[1/1565 *Received*, 8*th October*, 1981]

REFERENCES

[1] H. S. W. Massey and E. H. S. Burhop, 'Electronic and Ionic Impact Phenomena,' Oxford University Press, Oxford, 1969, vol. I, p. 169.

[2] J. M. Ajello, *J. Chem. Phys.*, 1971, **55**, 3158, 3169.

[3] D. E. Donohue, J. A. Schiavone, and R. S. Freund, *J. Chem. Phys.*, 1977, **67**, 769.

[4] C. I. M. Beenakker and F. J. de Heer, *Chem. Phys.*, 1974, **6**, 291.

[5] M. Tsuji, T. Ogawa, Y. Nishimura, and N. Ishibashi, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2432.

[6] Y.-K. Kim and M. Inokuti, *Phys. Rev. A*, 1971, **3**, 665.

[7] R. W. B. Pearse and A. G. Gaydon, 'The Identification of Molecular Spectra,' Chapman and Hall, London, 1976, 4th edn.

[8] H. Bubert and F. W. Froben, *J. Phys. Chem.*, 1971, **75**, 769.

[9] H. Okabe and M. Lenzi, *J. Chem. Phys.*, 1967, **47**, 5241.

[10] K. Fukui, I. Fujita, and K. Kuwata, *J. Phys. Chem.*, 1977, **81**, 1252.

[11] M. Kawasaki and I. Tanaka, *J. Phys. Chem.*, 1974, **78**, 1784.

[12] A. N. Fletcher, H. P. Richter, and J. L. Jernigan, *Appl. Phys.*, 1976, **11**, 175.

[13] C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.*, 1971, **8**, 77.

[14] A. M. Halpern, J. L. Roebber, and K. Weiss, *J. Chem. Phys.*, 1968, **49**, 1348.

[15] A. D. Walsh and P. A. Worsop, *Trans. Faraday Soc.*, 1961, **57**, 345.

[16] I. Yamazaki, K. Sushida, and H. Baba, *J. Chem. Phys.*, 1979, **71**, 381.

[17] A. M. Halpern, *Chem. Phys. Lett.*, 1970, **6**, 296.

[18] A. M. Halpern and R. M. Danziger, *Chem. Phys. Lett.*, 1972, **16**, 72.

[19] A. M. Halpern, *Mol. Photochem.*, 1973, **5**, 517.

[20] P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 1969, 4025.

[21] E. Heilbronner and K. R. Muszkat, *J. Am. Chem. Soc.*, 1970, **92**, 3818.

[22] R. Hoffman, A. Imamura, and W. J. Hehre, *J. Am. Chem. Soc.*, 1968, **90**, 1499.

[23] T. G. Finn, J. F. M. Aarts, and J. P. Doering, *J. Chem. Phys.*, 1972, **56**, 5632.

[24] H. S. W. Massey, 'Electronic and Ionic Impact Phenomena,' Oxford University Press, Oxford, 1969, vol. II, p. 956.

[25] D. H. Parker and P. Avouris, *J. Chem. Phys.*, 1979, **71**, 1241.