

Electron impact ionization of amines using crossed electron-molecular beams

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Abstract. Ionization energy functions of triethyl amine, tri-*n*-propyl amine, N,N-dimethyl-benzenamine and N,N-diethyl-benzenamine, and appearance energy functions of major products of dissociative ionization have been measured using a high sensitivity crossed electron beam-molecular beam apparatus incorporating a quadrupole mass spectrometer and an on-line laboratory computer. The data obtained is useful in understanding the role of dopants in gas laser plasmas.

Keywords. Electron impact; ionization energy; appearance energy.

1. Introduction

An understanding of the gas phase chemistry of laser plasmas requires knowledge of ionization processes resulting from collisions of electrons with atoms and molecules. In order to produce a uniform discharge and to enhance the output power from electric discharge lasers, some polyatomic molecules, such as the amines, have recently been used as dopants in laser gas mixtures (Kline and Denes 1982). The introduction of amines results in the formation of large numbers of both parent ions as well as fragment ions due to electron impact. In some cases, the fragment ions are found to dominate the parent ions even at energies just above the threshold for ionization. This necessitates the measurement of ionization efficiency curves of the parent ion as well as the major fragment ions in making the right choice of dopants to be used in the lasers without inducing much dissociation. Recently, amine dopants have also been used in nitrogen lasers (Krishna Kumar and Mitra 1986).

In order to understand the atomic and molecular collision processes responsible for altering the plasma characteristics and excited state populations, accurate information on ionization energies (IE) of parent ions and appearance energies (AE) of fragment ions are essential. However, literature values show a large spread in IE data pertaining to such amines. For instance, in the case of N,N-dimethyl-benzenamine, reported IE values range from 7.10 to 7.92 eV (Levin and Lias 1982). Most of these measurements report the vertical IE (rather than the adiabatic values) which are of actual consequence in laser plasmas; these have been measured using either photoelectron spectroscopy or with photoionization techniques. AE data for most of the fragment ions of the amines are not available. Electron impact ionization near the threshold yields vertical IE and AE values (Field and Franklin 1957) and hence makes it a good choice for their determination.

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As there is a paucity of accurate electron impact data, high sensitivity experiments were conducted using a crossed electron beam-molecular beam apparatus incorporating a quadrupole mass spectrometer to determine IE, AE and ionization efficiency curves of some amines which may be of use in gas laser plasmas.

2. Experimental

The experimental apparatus used, shown schematically in figure 1, has been described extensively in recent publications (Mathur 1980; Maccoll and Mathur 1981; Mathur and Badrinathan 1984, 1986) and therefore, only the salient features pertaining to the present study are briefly mentioned here. A well-collimated beam of intensity $\sim 10^{-8}$ A, with an energy resolution of ~ 120 meV (full width at half maximum), intersects a molecular beam at right angles in a field free region enclosed by a highly transparent molybdenum wire mesh. Fast differential pumping in the collision zone yields a base pressure of 2×10^{-8} torr. Ions produced by electron impact which drift towards the mass spectrometer (in the direction of the molecular beam) are extracted by a weak three-element lens into a quadrupole mass spectrometer which has unit resolution at mass 300. The mass spectrometer is

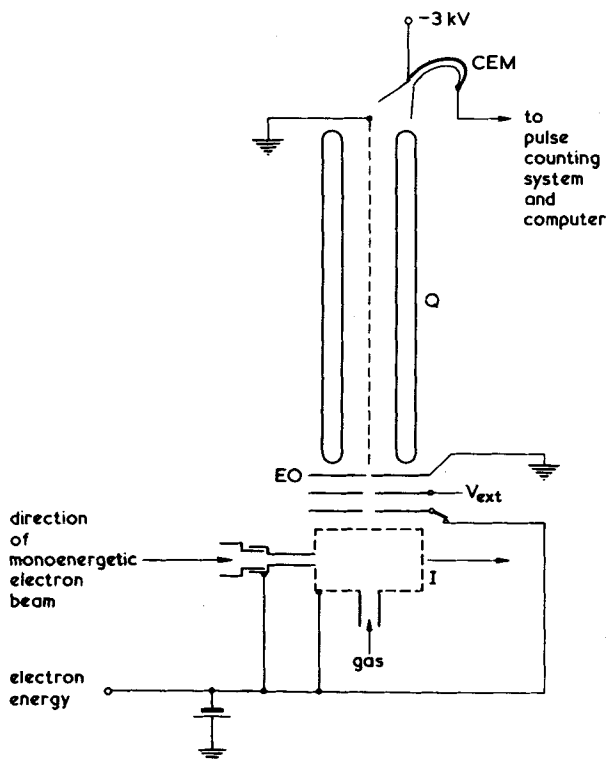


Figure 1. Schematic view of the experimental apparatus. I = collision zone, V_{ext} = ion extraction electrode, EO = ion entry orifice, Q = quadrupole mass filter rods, CEM = off-axis channel electron multiplier.

controlled by a laboratory computer which accomplishes on-line multiple scanning of electron beam energy and synchronous storage of ion intensities in the computer memory. The use of quadrupole mass spectrometer has the advantage of high ion transmission efficiency. Ions are detected by an off-axis channel electron multiplier which prevents detection of spurious signals due to photons and fast neutral metastables.

The electron energy scale for all the IE and AE values reported here was calibrated by admixing small amounts of argon ($IE = 15.76 \text{ eV}$) for which IE is well established. This is necessary to take into account the energy differences which arise due to contact potentials and other field inhomogeneities in the collision zone. To obtain good signal to noise ratio in the threshold region for ionization, signal averaging is done over at least 100 scans in the electron energy range from 5 to 20 eV. The system was stabilized and checked for drift over the time taken for data acquisition, which was found to be negligible. Typical threshold ionization efficiency curves pertaining to N,N-dimethyl-benzenamine and argon are shown in figure 2. The method of establishing ionization thresholds is discussed in the context of our present data in the following section.

3. Results and discussion

Electron-impact mass spectra and ionization efficiency curves have been measured for triethyl amine, tri-*n*-propyl amine, N,N-dimethyl-benzenamine and N,N-diethyl-benzenamine. Typical mass spectra obtained at an electron impact energy of 20 eV are shown in figure 3 whilst figures 4–7 illustrate threshold IE curves for molecular ions and AE curves for the major dissociative fragmentation ions. For the sake of clarity, only the range from threshold energy to a few eV is plotted taking

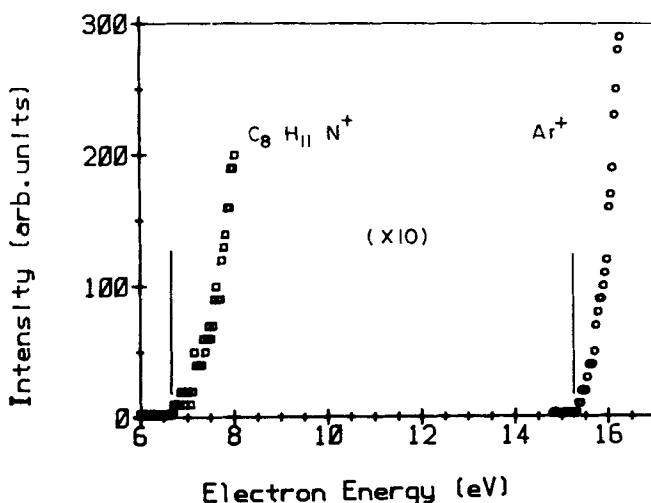


Figure 2. Typical threshold ionization efficiency curves of the $C_8H_{11}N^+$ molecular ion and Ar^+ calibrant gas for a mixture containing N,N-dimethyl-benzenamine and argon. The electron energy scale is as read from a 41/2 digit voltmeter. Vertical solid lines mark the threshold energies.

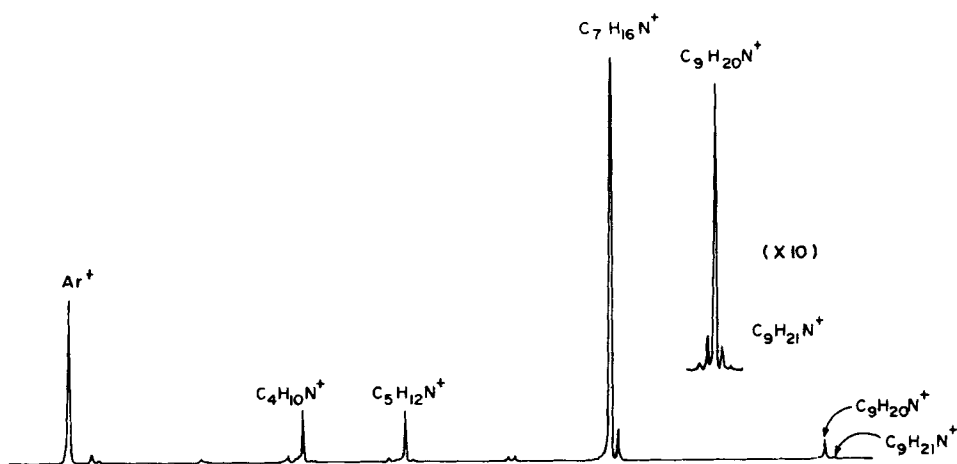


Figure 3. Mass spectrum of tri-*n*-propyl amine and argon mixture at an electron impact energy of 20.0 eV.

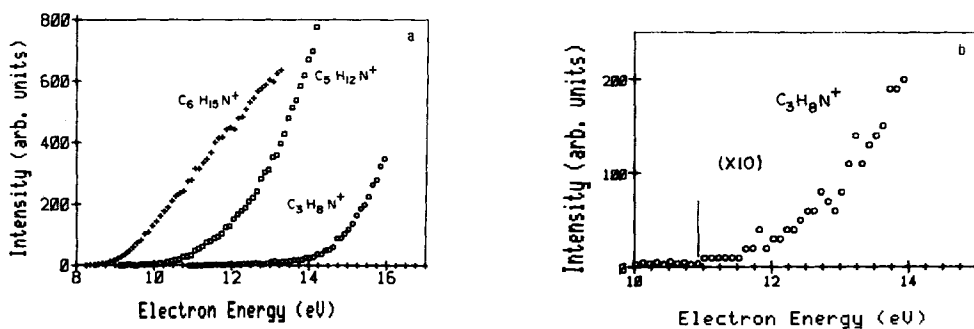


Figure 4. (a) Ionization efficiency curves near the threshold of the molecular and some major fragment ions of triethyl amine. (b) Threshold region of $C_3H_9N^+$ fragment ion at 10 times greater sensitivity shows pronounced tailing of the AE function.

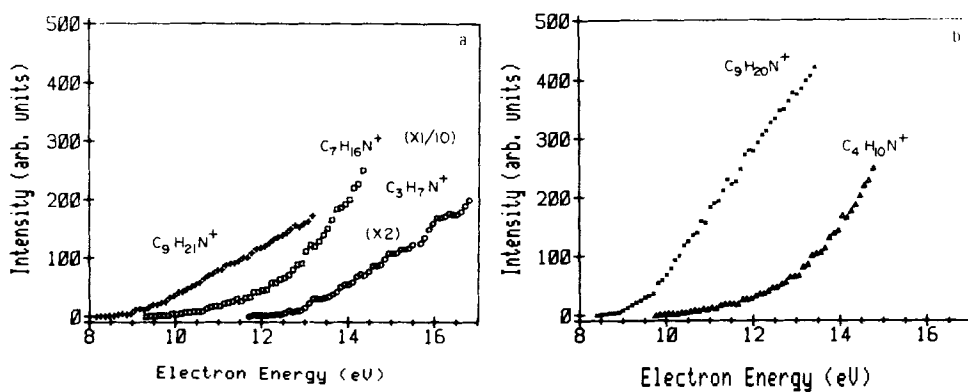


Figure 5. (a) Ionization efficiency curves of tri-*n*-propyl amine and its fragment ions $C_7H_{16}N^+$ and $C_3H_7N^+$. (b) AE functions for $C_9H_{20}N^+$ and $C_4H_{10}N^+$.

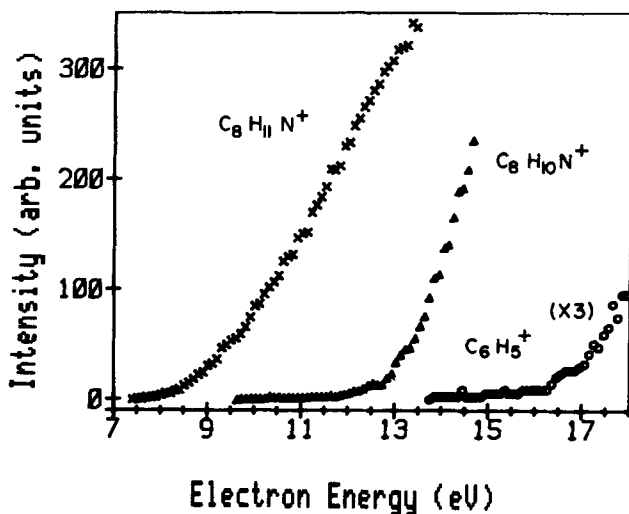


Figure 6. Ionization efficiency curves of N,N-dimethyl-benzenamine and its fragment ions.

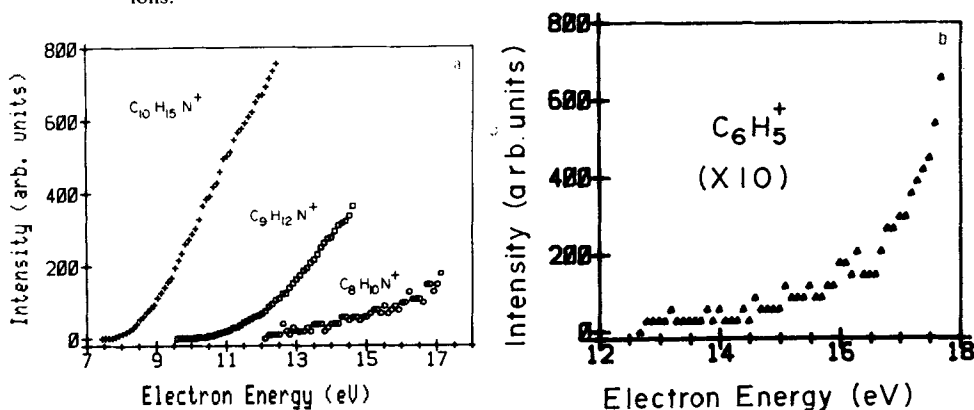


Figure 7. (a) Ionization efficiency curves of N,N-diethyl-benzenamine and its fragment ions $C_9H_{12}N^+$ and $C_8H_{10}N^+$. (b) AE functions for $C_6H_5^+$.

every tenth data point stored in the computer memory. It can be seen from figure 3 that at electron energies as low as 15 eV the intensity of fragment ions is much more than the intensity of molecular ions except in the case of N,N-dimethyl-benzenamine. Tri-*n*-propyl amine stands out with a two-orders of magnitude difference in intensity between the fragment ion $C_7H_{16}N^+$ and the molecular ion $C_9H_{21}N^+$. In all the molecular species studied, the positive charge is localised on the heteroatom. Consequently, following ionization, nitrogen becomes isoelectronic with carbon. This can result in the formation of an sp^2 -hybridised nitrogen structure with an unpaired electron which may lead to a π -bond with the electron situated on the carbon atom being ejected as a result of the cleavage of the β -bond.

Most of the earlier values of IE and AE that have been reported rely on either the semilog plot technique or the linear extrapolation technique of determining onsets. In the semilog plot technique, the logarithm of the ion current, usually normalized at 50 eV impact energy, is plotted as a function of electron energy for the sample

and also for a reference gas whose ionization energy is known accurately. The resulting curves, in general, show approximately linear and parallel sections at about 1 to 0.5% of the ion currents at 50 eV impact energy and the differences in the ionization or appearance energies are given by the separation of the curves along the energy axis. In the linear extrapolation method, the ionization efficiency curves are plotted upto a few eV above the threshold. The curve above the threshold, which is taken to be approximately linear, is extrapolated to the energy axis. The intercept is taken as the IE or AE. Both these methods fail to take into account the shape of the curve near the threshold. Any curvature in the ionization efficiency curve is assumed to be solely due to the high energy tail of the electron energy distribution. However, even in experiments that are carried out using monoenergetic electron beams with an energy width as low as 30 meV, pronounced 'tailing' of threshold IE and AE curves (extending over several eV in certain cases) is found to occur (Maccoll and Mathur 1981). Curvature at the threshold is not due only to the contribution from the high energy part of the electron energy distribution; other physical factors such as the threshold behaviour of the ionization cross-section, reaction competition (in the case of fragment ions) as well as instrumental factors such as detection sensitivity, signal to noise ratio and ion residence time in the interaction region must also be taken into account when considering thresholds and inelastic onsets. Neither the semilog plot technique nor the method of linear extrapolation can yield accurate onset information in cases where some of the above factors result in a pronounced tailing of the AE curves.

We have attempted to circumvent some of the problems of onset determination by adopting the vanishing current method. We employ a single particle counting technique to determine the minimum energy at which ionization or fragmentation occurs. For such a method to be feasible, the using of the channel electron multiplier in a pulse-output mode and employment of multiple scanning techniques is mandatory.

The IE and AE of some major fragments have been determined for triethyl amine, tri-*n*-propyl amine, N,N-dimethyl-benzenamine and N,N-diethyl-benzenamine and are given in table 1. The present results agree closely with the vertical IE determined by photoelectron spectroscopy.

The ionization onset results from ejection of a single electron from the b_1 or b_1 -like π orbitals which are contributed either from the substituent groups' n or π orbitals, or alternately, from the benzene e_{1g} π orbitals. HeI photoelectron angular distributions have been measured by Kobayashi (1978) and others (Sell and Kuppermann 1978) and the β asymmetry parameter has been determined from the first photoelectron band in N,N-dimethyl-benzenamine as well as for the corresponding π bands of the reference compound trimethyl amine and the first band in benzene. Reasonably close correspondence is observed for β values obtained for the lowest energy thresholds in N,N-dimethyl-benzenamine and the substituent group, indicating that electron ejection is most probably from one of the π orbitals of the substituent groups attached to the benzene ring in the compounds investigated in the present study.

Though there are only a few results to compare with for AE values, the results reported earlier in literature are higher than the present work. This can be attributed to the linear extrapolation or semilog technique that earlier workers have used, which does not take into account the shape of the ionization efficiency

Table 1. Ionization energy and appearance energy of major fragment ions.

	IE or AE (eV)	
	Present work	Earlier work
$C_6H_{15}N^+$	8.27 ± 0.11	8.08 (V) [PE] ^b 8.19 \pm 0.05 (V) [PE] ^b
$C_5H_{12}N^+$	9.16 ± 0.12	11.48 [EI] ^b
$C_3H_8N^+$	10.93 ± 0.05	-
$C_9H_{21}N^+$	8.17 ± 0.05	8.04 \pm 0.3 (V) [PE] ^b 7.23 [PI] ^a
$C_9H_{20}N^+$	8.41 ± 0.09	-
$C_7H_{16}N^+$	9.33 ± 0.17	-
$C_4H_{10}N^+$	9.75 ± 0.13	-
$C_3H_7N^+$	11.72 ± 0.27	-
$C_8H_{11}N^+$	7.42 ± 0.05	7.45 (V) [PE] ^b 7.51 (V) [PE] ^a
$C_8H_{10}N^+$	9.64 ± 0.29	10.75 \pm 0.05 [PI] ^a 10.56 \pm 0.05 [PI] ^b
$C_6H_5^+$	9.88 ± 0.1	15.7 \pm 0.1 [EI] ^a
$C_{10}H_{15}N^+$	7.44 ± 0.07	7.51 (V) [PE] ^a 7.20 (V) [PE] ^b
$C_9H_{12}N^+$	9.61 ± 0.04	-
$C_8H_{10}N^+$	12.12 ± 0.04	-
$C_6H_5^+$	12.68 ± 0.06	-

^a Rosenstock *et al* 1977; ^b Levin and Lias 1982; PE: photoelectron spectroscopy; PI: photoionization; EI: electron impact.

curve near the threshold, and to the high sensitivity of the instrument which has been used in the present experiments.

Our present data indicates that in the case of ionization of the parent molecules, the resulting IE curves have a fairly sharp and structureless onset. In the case of fragment ions, on the other hand, the threshold AE function generally exhibits fairly pronounced tailing, which extends over a range of upto 3 eV in some cases. In the case of the phenyl positive ion formation some distinct structure is also observed about 2 eV above the initial onset. This is possibly indicative of the existence of a low-lying excited state of the fragment ion, though lack of spectroscopic information precludes specific identification of the electronic configuration of such a state at present.

We have attempted to estimate the cross-sections for ionization and dissociative ionization by considering the electron flux in the interaction zone as well as the number density of neutral molecules. Our estimates indicate cross-sections in the 10^{-16} to 10^{-17} cm² range, although the uncertainties involved in determining the above mentioned parameters are extremely large (\approx 50%). Furthermore, IE and AE curves could not be reliably determined over an extended energy range due to electron-optical constraints in the present experimental configuration.

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