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Cross sections for the production of N_2^+, $N^+ + N_2^{2+}$ and N^{2+} by electron impact on N_2

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Abstract. Cross sections for the production of N_2^+, $N^+ + N_2^{2+}$ and N^{2+} by electron impact on N_2 have been measured for an energy range from threshold to 1000 eV. These cross sections have been fitted to an empirical formula for future use in modelling various plasmas. Considerable differences from some previous data have been found.

1. Introduction

Collision of electrons with N_2 molecules can give rise to a wide variety of processes. Among them ionisation and dissociative ionisation play important roles in the Earth's ionosphere, aurora and in various electrical discharges where N_2 is used as a carrier gas (Märk and Dunn 1985). With this in mind it seems that the ionisation properties of this molecule should have been extensively studied and the cross section values over a wide electron impact energy range should have been known to a high degree of accuracy.

However, a look at the previously published literature shows that this is not true. All measurements performed up to 1962 reported cross section values for total ionisation (i.e. the cross section for the production of all ionic species resulting from direct and dissociative ionisation of N_2). The first such measurements were published by Tate and Smith (1932). Subsequently, total cross section values were reported by Hagstrum and Tate (1941), Stevenson and Hipple (1942), Lampe *et al* (1957), Cook and Peterson (1962), Rapp and Englander-Golden (1965) and Schram *et al* (1965, 1966).

Experiments on total ionisation measurements are relatively simple compared with those needed for the determination of partial (i.e. generation of N_2^+, N_2^{2+} etc) and dissociative (i.e. generation of N^+, N^{2+} etc) ionisation cross sections, mainly due to the need for mass/charge selection of individual ionised species. Therefore, data on cross section values for the partial and dissociative ionisation are not readily available. In the past, they have been measured by Cook and Peterson (1962) and Märk (1975). Daly and Powell (1966) measured the relative values of cross sections for the above species and normalised them to the total ionisation cross section values of Cook and Peterson (1962) and Tate and Smith (1932). Rapp *et al* (1965) reported cross section values for the production of N^+ and higher stages of ionisation for those ions which

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were born with kinetic energies greater than 0.25 eV. Subtraction of these cross sections from total ionisation cross sections (Rapp and Englander-Golden 1965) should give the values of cross sections for the generation of $N_2^+ + N_2^{2+}$. These cross sections were used by Halas and Adamczyk (1973) and Crowe and McConkey (1973) to normalise their relative measurements for partial and dissociative ionisation cross sections.

Cross sections for the production of N_2^+ near the threshold for ionisation have been obtained by Fox (1961) and Erhardt and Kresling (1967). These studies were done at higher electron energy resolutions to gain information on the thresholds for the various ionisation channels. Measurements have also been made on the kinetic energy and/or angular distributions of the fragment ions resulting from the dissociation of N_2. Noteworthy among them are Kieffer and Van Brunt (1967), Deleanu and Stockdale (1975), Crowe and McConkey (1975), Kollman (1975), Locht *et al* (1975) and Feldmeier *et al* (1983). Results of these measurements are important for deriving the values of cross sections for N_2^+ formation from the knowledge of total ionisation cross sections of Rapp and Englander-Golden (1965).

It is clear from the above that absolute values of cross sections for the production of N_2^+ have been measured in only two investigations (Cook and Peterson 1962, Märk 1975). Similarly, the values of cross sections for N^+ production have only been measured by Cook and Peterson (1962). As pointed out by Itikawa *et al* (1986), the previous data obtained by normalisation to Rapp and Englander-Golden's results may be in error because proper magnitudes of dissociative ionisation cross sections may not have been subtracted from the total ionisation cross sections. In addition, there may be error in the McLeod gauge pressure measurement by Rapp *et al* (1965). By taking these two corrections into account in an empirical way, Itikawa *et al* (1986) have recommended a set of cross sections for the production of N_2^+ and $(N^+ + N_2^{2+})$.

As will be clear from the later part of this paper, the previously measured data for these cross sections widely differ from each other. Therefore, we undertook the present measurements. We expect higher accuracy in these measurements for the following reasons: (i) we have developed a relative flow technique (Orient and Srivastava 1983) which determines the values of cross sections in terms of accurately known cross sections for He (Bell *et al* 1983); (ii) a pulsed ion extraction technique has been employed which permits a complete collection of ions which are born with a considerable amount of kinetic energies; and (iii) the mass/charge dependent transmission efficiency of the entire system has been determined by utilising our relative flow technique and accurately known values of rare gas electron impact ionisation cross sections. For ease of application of the present values to the plasma modelling we have fitted the present cross sections to an empirical function (Bell *et al* 1983) using the chi squared minimisation technique (Srivastava and Nguyen 1987).

2. Apparatus and method

2.1. The apparatus

The apparatus is described in detail in two of our previous publications (Orient and Srivastava 1983, Krishnakumar and Srivastava 1988). A schematic diagram of the apparatus used for the present measurements is shown in figure 1. It consists of the following major components: a magnetically collimated pulsed electron gun, a pulsed ion extraction system, a quadrupole mass spectrometer, and electronic devices for data

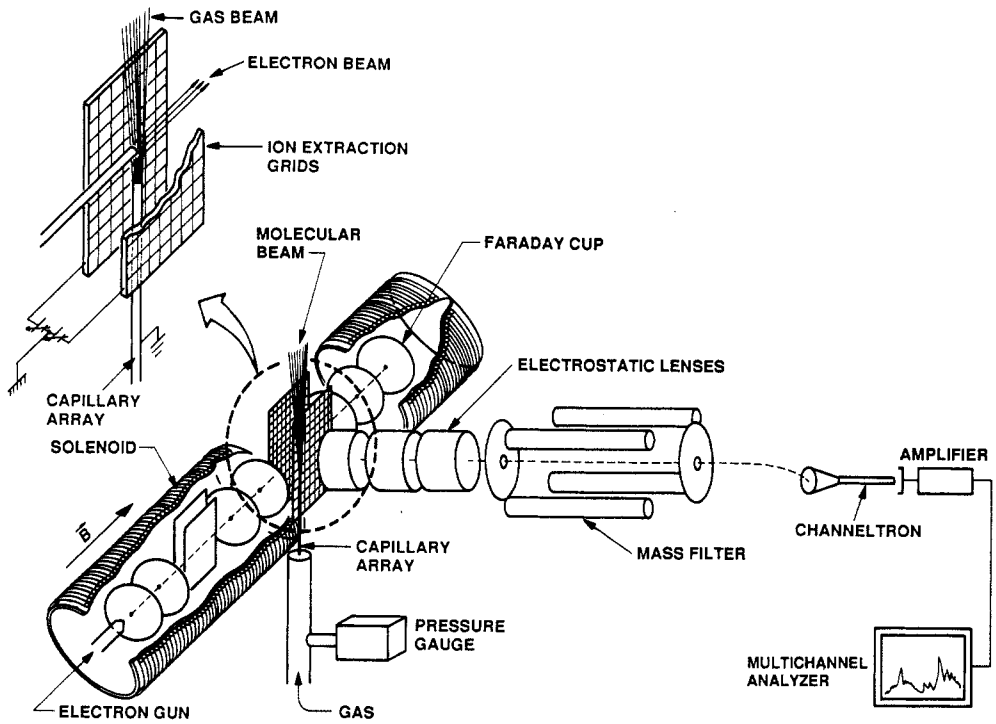

Figure 1. Schematic diagram of the apparatus.

acquisition. In the following a brief description of each of the above components is given.

2.1.1. Magnetically collimated pulsed electron gun. This gun produces a well defined magnetically collimated pulsed beam of electrons with rise time of the order of 10 ns or less and duration which can be varied from 100 ns to 1 ms or more. The energy of the beam can be continuously varied from 0 eV to 1 keV. Details on the gun are given in our previous publication by Khakoo and Srivastava (1984).

2.1.2. Pulsed ion extraction system. It is known in general that ionic fragments are formed with considerable amounts of kinetic energy. In order to extract these species completely from the collision region and to focus them at the entrance aperture of a quadrupole mass spectrometer (such as the one employed in the present experimental set-up), one needs a high extraction voltage between the grids shown in figure 1. To estimate the magnitude of this voltage we carried out trajectory calculations by utilising the SIMION program (EGG-cs-7233 Rev. 2 prepared by EG&G Idaho Inc, PO Box 1625, Idaho Falls, ID 83415, USA). Figure 2 shows the trajectories of ions which are born with 5 eV kinetic energy and travel isotropically away from the collision region. The calculations took into account the magnetic field of 100 G present along the axis of the solenoid shown in figure 1. Our calculations show that for the present type of extraction system a field of 50 V cm^{-1} between the grids should be employed. However, this field will affect the electron beam. In order to avoid this situation we developed a pulsed method of extraction. It was first used by Fox *et al* (1955) and later by Foner

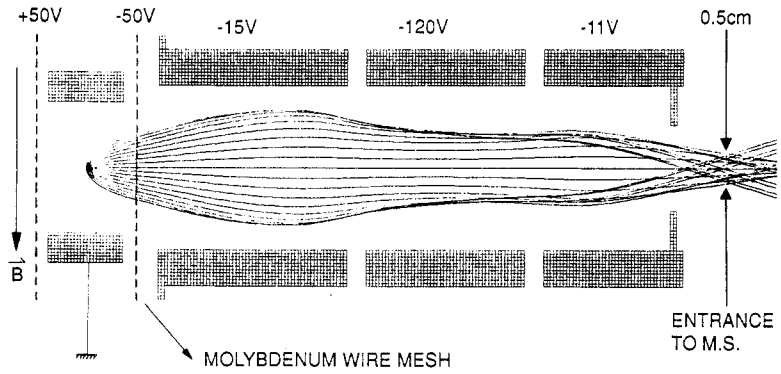

Figure 2. Trajectories of ions through the electrostatic lenses for ions born with 5 eV kinetic energy and immersed in a magnetic field of 100 G along the axis of the solenoid.

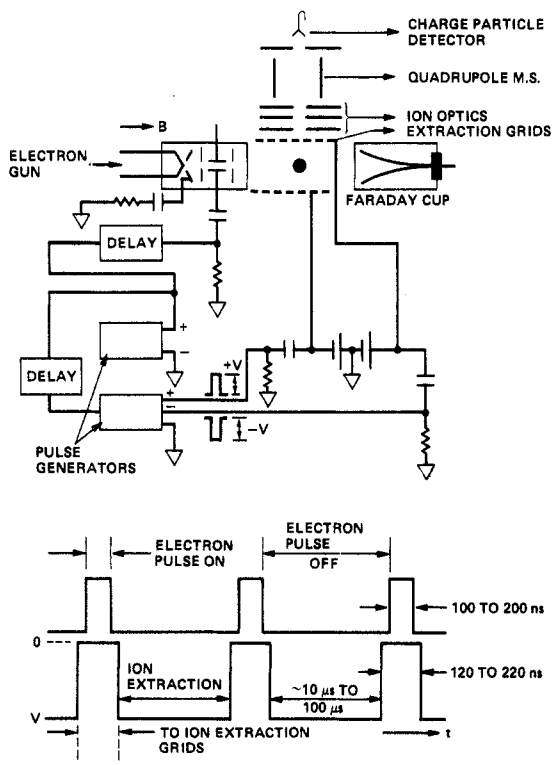

Figure 3. Schematic diagram showing the pulsing scheme.

and Nall (1961). The pulsing scheme is shown in figure 3. The procedure for extracting positive ions from the collision region is as follows. First, the grid close to the electrostatic lenses (figure 3) is biased by −50 V with respect to ground for extracting positive ions. Then a +50 V pulse of 120 to 220 ns width is applied. This reduces the voltage on the extraction grid to zero (ground potential) during the time interval of the pulse. A few nanoseconds later an electrical pulse of about 5 to 10 V in magnitude and width varying from 100 to 200 ns (narrower in width than the pulse applied to the extraction grid) is applied to the electron gun. This enables the electron gun to transmit to the collision region a collimated pulsed beam of electrons. Thus, during the collision time of the electron pulse with the target molecules the collision region remains at the ground potential. However, right after the ions are formed, as a result of the collision, they are extracted out of the collision region by −50 V on the grid.

2.1.3. Quadrupole mass spectrometer. The various ions, after extraction from the collision region, are analysed by a quadrupole mass spectrometer. It is well known that the transmission efficiency of such a mass filter depends upon the mass to charge ratio of the ion and, in most situations, changes with the experimental conditions. Therefore, the transmission efficiency must be measured each time data on cross sections are obtained. We utilised a method described in detail by Orient and Srivastava (1983) and Krishnakumar and Srivastava (1988).

Briefly, the method employs rare-gas atoms (He, Ne, Ar, Kr and Xe) for which accurate values of electron impact ionisation cross sections are known (Krishnakumar and Srivastava 1988). The energy of the incident electron beam is fixed to some value E_0. Then the above mentioned gases are flowed through the capillary array individually. For each gas the transmitted intensity of singly charged ions is subsequently measured. In an ideal case, the ratios of intensities of transmitted ions should be equal to the ratios of their respective ionisation cross sections. However, in practice they are not the same. Therefore, by comparing the two, normalisation factors are obtained.

2.1.4. Electronic devices for data acquisition. Ions transmitted through the mass spectrometer are detected by a charged particle detector. This detector converts the detected ions into electrical pulses. These pulses are subsequently amplified by a fast amplifier which changes each pulse into a TTL pulse. This pulse is then fed to a multichannel analyser (MCS). The MCS records the TTL pulses as a function of the incident electron beam's energy. In the present experiment 1024 channels of the MCS were employed.

2.2. The method of normalisation

Thus, by utilising the above described instrumentation and procedure the intensity of each ion as a function of incident electron energy was obtained. Absolute values of cross sections were then determined by the relative flow technique (Srivastava *et al* 1975) which was subsequently modified and improved by Orient and Srivastava (1983) and Krishnakumar and Srivastava (1988). Details on the method of normalisation can be found in those publications. In the following it is briefly described.

First, a beam of He atoms was produced by flowing He gas through the capillary array (figure 1). The excitation function curve (a plot of intensity of ions as a function of electron impact energy) for the generation of He^+ was obtained. The He beam was then replaced by a beam of N_2 molecules and, as before, excitation function curves for the generation of N_2^+, $N^+ + N_2^{2+}$ and N^{2+} were recorded. The ratio of the two

excitation function curves (i.e. the ratio of their intensity of nitrogen ions to the helium ions) is directly proportional to the ratio of respective cross sections and is given by the following relation:

$$\sigma_N(E_0) = \sigma_{He}(E_0)\frac{I_N(E_0)}{I_{He}(E_0)}\left(\frac{M_{He}}{M_N}\right)^{1/2}\frac{F_{He}}{F_N}\frac{K(M_{He})}{K(M_N)} \tag{1}$$

where E_0 is the energy of the colliding electron, $\sigma_N(E_0)$ and $\sigma_{He}(E_0)$ are cross sections for ionisation, M_N and M_{He} their masses, F_{He} and F_N their flow rates and $K(M_N)$ and $K(M_{He})$ are the mass/charge dependent transmission efficiencies of the apparatus. The procedures for obtaining the values of F_{He}/F_N and $K(M_N)$ are given by Krishnakumar and Srivastava (1988). Thus by utilising the accurately known values of σ_{He} (Bell *et al* 1983) the values of σ_N for N_2^+, $N^+ + N_2^{2+}$ and N^{2+} were determined by the help of equation (1).

It is estimated that the relative shapes of the excitation function curves are obtained with an accuracy of ±5%. The errors in the normalised values are accurate to within ±8%. This number has been arrived at by considering the uncertainties in the measurement of flow rates, mass transmission efficiencies (equation (1)) and the values of σ_{He} cross sections. Further details on the method of error estimation can be found in a publication by Krishnakumar and Srivastava (1988).

3. Results and discussion

Present results are compared with the available experimental data in figures 4 and 5. Cross section values for selected electron impact energies are given in table 1. In the following the various results are discussed.

3.1. N_2^+

Figure 4 shows our results using a full curve. The most recent measurements are those of Märk (1975) and are shown by full circles. It is obvious that the differences between the two measurements are large over the entire electron impact energy range both in absolute magnitudes and relative shapes. Märk's data show a rapid decrease in cross section as the electron impact energy increases beyond 110 eV. An extrapolation of his results to higher energies shows a substantial difference from all other previous measurements. As mentioned in the previous section, the normalised values of present cross sections are estimated to be accurate to within ±8%. However, the relative shape of the excitation function curve is accurate to within 5%. The error bars are indicated in the figure. In addition, Märk's excitation function shows a sharp change in the slope at about 70 eV electron impact energy. This apparent structure indicates the possibility of the opening of new ionisation channels around this energy. However, no such structure is discernible in any previously reported data. Since the cross sections for the production of N_2^+ are about four times higher than for the production of $N_2^{2+} + N^+$, this structure should be evident in Rapp and Englander-Golden's (1965) total ionisation cross section data. Furthermore, in the present measurements, although the accuracy of the relative shape over the entire electron impact energy range (0–1000 eV) is 5%, in the small energy range ($\Delta E_0 \simeq 30$ eV) this accuracy is better than ±1% and is only limited by the statistical fluctuations in the counting rate. Therefore, the present data for N_2^+ should show this structure around 70 eV electron impact energy.

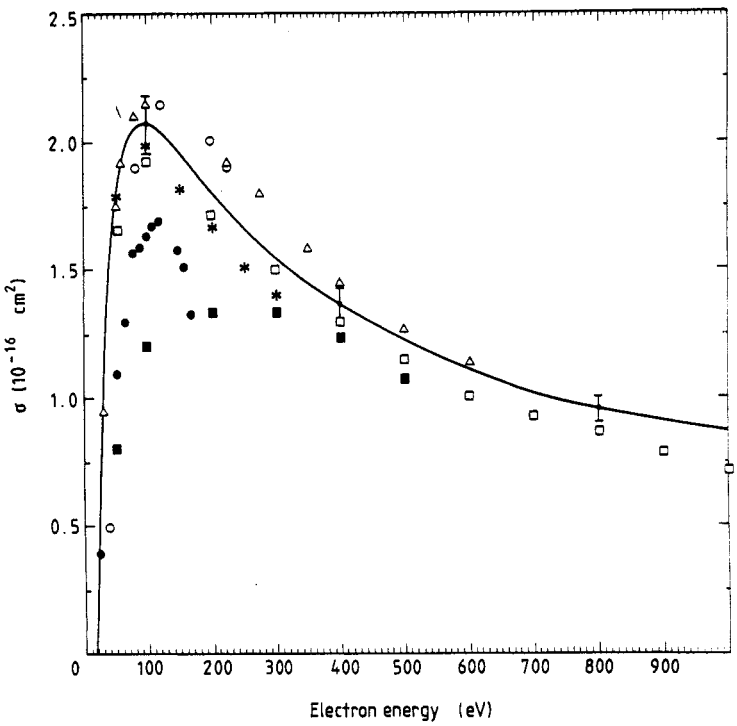

Figure 4. Cross sections for the production of N_2^+ as a function of electron impact energy. ■, Cook and Peterson (1962); ○, Daly and Powell (1966; normalised to Tate and Smith, Cook and Peterson); △, Halas and Adamczyk (1972, normalised to Rapp *et al*); *, Crowe and McConkey (1973, normalised to Rapp *et al*); ●, Märk (1975); □, Rapp and Englander-Golden's data recommended by Itikawa *et al* (1986); ——, present.

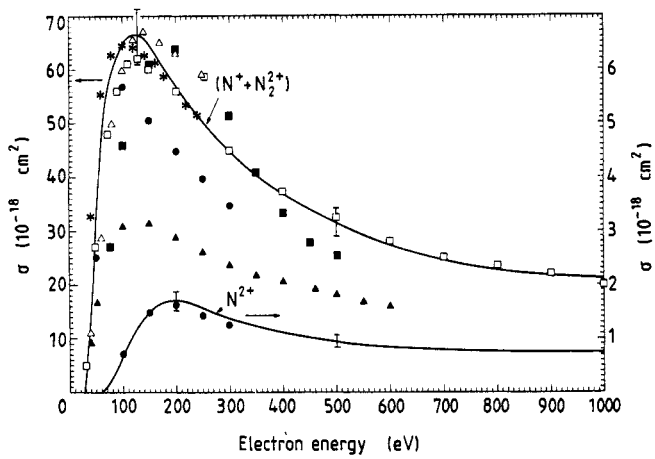

Figure 5. Cross sections for the production of $(N^+ + N_2^{2+})$ and N^{2+} as a function of electron impact energy. ■, Cook and Peterson (1962); □, Rapp *et al* (1965); *, Daly and Powell (1966); △, Peresse and Tuffin (1965, their data are multiplied by a factor 5 here); ●, Crowe and McConkey (1973); ▲, Halas and Adamczyk (1973); ——, present. Data for N^{2+} should be read on the right Y axis.

Table 1. Partial and dissociative ionisation cross sections for the production of various ionised species by electron impact on N_2.

E_0 (eV)	$\sigma(N_2^+)$ (10^{-16} cm^2)	$\sigma(N^+ + N_2^{2+})$ (10^{-18} cm^2)	$\sigma(N^{2+})$ (10^{-18} cm^2)
20	0.25	—	—
30	1.06	2.4	—
40	1.60	14.8	—
50	1.78	31.6	—
60	1.95	46.8	—
70	2.04	54.7	0.08
80	2.07	59.0	0.24
90	2.09	62.3	0.46
100	2.08	64.4	0.64
110	2.07	65.7	0.87
120	2.06	66.2	1.08
130	2.04	66.3	1.23
140	2.01	65.8	1.39
150	1.99	64.7	1.51
160	1.95	63.2	1.55
170	1.93	61.6	1.63
180	1.89	60.2	1.67
190	1.86	58.7	1.70
200	1.83	57.4	1.69
210	1.80	56.9	1.68
220	1.77	54.5	1.66
230	1.74	53.0	1.62
240	1.71	51.7	1.58
250	1.68	50.5	1.55
300	1.55	44.8	1.38
350	1.45	40.3	1.23
400	1.37	37.0	1.11
450	1.29	33.4	1.02
500	1.23	31.6	0.95
550	1.18	29.2	0.89
600	1.12	27.2	0.85
650	1.07	25.7	0.81
700	1.03	24.3	0.77
750	0.99	23.3	0.74
800	0.97	22.7	0.72
850	0.94	22.0	0.71
900	0.90	21.2	0.70
1000	0.86	21.0	0.70

No such structure is seen. Märk's method of normalisation is similar to the present one. He used a cross section value of 2.75×10^{-16} cm^2 for the production of Ar^+ from Ar by electron impact at 110 eV for the purpose of normalisation. This value agrees very well with our recent measurements (2.50×10^{-16} cm^2; Krishnakumar and Srivastava 1988). Therefore, differences between Märk's and the present data cannot be attributed to the method of normalisation. In our view Märk's ion extraction system suffers from focusing problems which lead to discrepancies in the relative shape of the excitation function curve. Also shown in figure 4 are the corrected values of Rapp and Englander-Golden's (1965) data as recommended by Itikawa *et al* (1986), measurements of Crowe and McConkey (1973, 1975), Halas and Adamczyk (1972) (both utilised Rapp and

Englander-Golden's data for normalisation) and Daly and Powell (1966) who used Tate and Smith's (1932) values for normalisation. All of these results agree with the present ones within the combined error limits of the various measurements. However, there is a large disagreement with the values reported by Cook and Peterson (1962). Their technique employed a crossed molecular beam and electron beam collision geometry and measured the flux of the molecular beam, scattered current of ions, and electron beam current. Thus, it provided absolute values of cross sections. Any error in the measurement of above mentioned quantities will be reflected in the absolute cross section values. However, even the relative shape of their excitation function does not agree with the present results.

3.2. $N^+ + N_2^{2+}$

As mentioned earlier N^+ and N_2^{2+} cannot be distinguished mass spectroscopically because in a mass spectrum both will appear at the same position. In order to overcome this problem Halas and Adamczyk (1972) employed an ingenious method which utilised the isotopic molecule $N^{14}N^{15}$ so that the doubly charged parent ion appears at mass number 14.5 instead of at 14. They measured the ratio N^+/N_2^{2+} and N_2^+/N_2^{2+} for electron impact energies ranging from 50 to 600 eV. At an electron impact energy of 100 eV these ratios are 9.55 and 73.47, respectively. Subsequent measurements by Märk (1975) show an N_2^+/N_2^{2+} ratio of 52.8 at an electron impact energy of 107.5 eV. Both results show that N_2^{2+} cross sections are about two orders of magnitude less in comparison with those for N_2^+ and about one order of magnitude less in comparison with the cross sections for the production of N^+. Therefore, the cross sections for N^+ production reported here will have, at most, 10% contribution from the N_2^{2+}.

The sums of N^+ and N_2^{2+} cross sections are presented in table 1 and are compared with previous measurements in figure 5. It is clear from this figure that the present results are in good agreement with the data of Rapp *et al* (1965) and Daly and Powell (1966). However, differences are rather large with respect to the values reported by Crowe and McConkey (1973, 1975), Peresse and Tuffin (1967), and Halas and Adamczyk (1973). It is surprising that although Crowe and McConkey's results for N_2^+ (normalised to Rapp *et al* data) agree with the present ones within the combined error limits it is not so for N^+. This may be due to errors caused by inaccuracies either in the measurement of mass transmission efficiency of the quadrupole mass spectrometer employed by them or the ion extraction system. It has been shown by Märk (1985) that the latter source of error is serious if proper care is not taken to eliminate it. The differences with others (Halas and Adamczyk 1973, Peresse and Tuffin 1967) can also be attributed to the same sources of error. The results of Cook and Peterson (1962) agree with the present ones only in a very small range (between 150 and 350 eV) of energies. The differences are rather large at low energies.

3.3. N^{2+}

The only other measurement on the cross section for the production of N^{2+} by electron impact on N_2 are those of Crowe and McConkey (1973, 1975). They are shown in figure 2 along with the present ones. It is clear from the figure that there is excellent agreement between the two. These cross sections are about two orders of magnitude less than those for N_2^+ and are shown in table 1.

For ease of future use of the cross sections in modelling various plasmas, we have parametrised them according to the following relation which has the same form as used by Bell *et al* (1983):

$$\sigma_N(E) = \frac{1}{IE}\left[A \ln\left(\frac{E}{I}\right) + \sum_{i=1}^{N} a_i \left(1 - \frac{I}{E}\right)^i\right] \tag{2}$$

where A and a_i are coefficients obtained by fitting to the experimental data, I is the ionisation potential of the respective species, E the electron impact energy, i determines the number of terms and N is needed to fit the experimental data. Details on the fitting procedure are given by Srivastava and Nguyễn (1987) and the values of coefficients pertaining to present results are presented in table 2.

Table 2. Parameters (in units of 10^{-18} cm^2) defined in equation (2) after fitting it to the present values of cross sections by the χ^2 minimisation method. The fitted values agree with the experimental data with ±10%.

Species	A	a_1	a_2	a_3	a_4	a_5	a_6
N_2^+	5.265 40 $\times 10^5$	−6.667 07 $\times 10^5$	1.268 02 $\times 10^6$	−5.022 30 $\times 10^6$	8.020 12 $\times 10^6$	−6.131 93 $\times 10^6$	1.610 17 $\times 10^6$
$N^+ + N_2^{2+}$	3.048 55 $\times 10^4$	−2.482 31 $\times 10^4$	−2.875 64 $\times 10^4$	9.992 295 $\times 10^4$	3.462 40 $\times 10^5$	2.071 19 $\times 10^3$	−3.396 41 $\times 10^4$
N^{2+}	7.569 95 $\times 10^4$	−8.563 69 $\times 10^4$	1.180 78 $\times 10^5$	−6.929 50 $\times 10^5$	1.331 52 $\times 10^6$	−8.995 37 $\times 10^5$	0

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