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Charged Particle Transport in Gaseous Nitrogen at Intermediate E/N using the Voltage Transient Method

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Abstract

A pulsed swarm of charged particles crossing an inter-electrode gap under the influence of an applied electric field E will produce a pulsed current in the external circuit which, when integrated over time, will result in a transient voltage pulse, the shape and magnitude of which is characteristic of the number and type of charged particles. This voltage transient technique has been used to investigate a gas discharge in nitrogen gas at values of E/N (the ratio of applied electric field to gas number density), such that ionisation is non-negligible. The voltage transients have been subjected to a theoretical analysis, which has previously been reported, which includes not only cathode and anode image terms but also both electron and ion diffusion terms. Electron transport parameters are reported for $E/N \leq 350$ Td ($1\ \text{Td} = 10^{-17}\ \text{V cm}^2$). Data are also obtained for the drift velocities and diffusion coefficients of the ions operative within the nitrogen discharge. An estimate is obtained for the collisional decay rate of N_2^+.

1. Introduction

Measurements of charged particle transport parameters in pure swarm experiments relevant to a gas discharge have been, almost exclusively, restricted to the electron coefficients whilst ion transport has been studied by experiments in which known ions are injected into a swarm drift tube. Intermediate E/N (the ratio of applied electric field to gas number density) may be defined as that region over which ionisation is non-negligible but in which equilibrium still exists. Here the role of ions in a gas discharge is at least as important as that of the electrons. In nitrogen this region may be considered to range from 80 Td to approximately 700 Td. Further, in some gases, of which nitrogen is an example, these ions can undergo chemical reactions such that the ion which contributes most to the discharge is not necessarily the ion which was initially formed by direct electron-molecule collision. Since the different ions can have vastly different mobilities and diffusion coefficients, the behaviour of a pulsed discharge will be dependent upon the nature of the ions present, on the relative abundances of each and on the way in which these vary with time. It is thus important to the present study of pulsed swarms at intermediate E/N to evaluate these ion parameters along with the corresponding electron data.

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It is now well established that electron transport parameters and rate coefficients are dependent upon the type of experiment used to measure them, i.e. a steady state Townsend (SST) discharge, a pulsed Townsend (PT) discharge or a time of flight (TOF) experiment. These differences have been discussed in detail by Tagashira *et al.* (1977) and by Blevin and Fletcher (1984). Further, any analysis of the experimental data from the SST or PT experiments must include the correct electrode boundary conditions. This is not so crucial in those TOF experiments in which the data are taken remote from electrode boundaries (e.g. Blevin *et al.* 1976, 1978; Fletcher and Reid 1980), since in these experiments the effect of the non-equilibrium region near the cathode can be allowed for by using difference methods.

In a previous paper the authors reported a series of experiments using a pulsed Townsend system to measure electron transport parameters with a full data analysis including all image and diffusion terms (Purdie and Fletcher 1989). The work described in that paper was restricted to low E/N since the intention was to test the validity of the data analysis. At such low values of E/N it would not be expected that appreciable differences are evident between the results obtained from the different types of experiment since the differences are a measure of the effect of ionisation (or attachment if this is relevant) on each type of discharge.

The present paper describes the extension of that work to the intermediate range of E/N. In this region ionisation becomes appreciable and the type of experiment used to measure the transport parameters is important (Tagashira *et al.* 1977). Since ions are now present in the discharge, their role can also be investigated.

In the present work ions were found to contribute significantly to the voltage transient for values of $E/N \geq 100$ Td. In order to correctly analyse an experimental voltage transient which has a significant ion component it is necessary to know which of the four possible nitrogen ion species might be present in the discharge in the operative range of E/N.

Formation of the two primary ions N_2^+ and N^+ by direct electron–molecule collision occurs according to the reactions

$$N_2 + e \rightarrow N_2^+ + 2e, \tag{1}$$

$$N_2 + e \rightarrow N^+ + N + 2e. \tag{2}$$

Ionisation of molecular nitrogen by reaction (1) is considered to be the dominant process since the first ionisation potential (i.e. to give ground state N_2^+ ions) is 15·6 eV (Field and Franklin 1957) whereas reaction (2) is a dissociative ionisation with the lowest ionisation potential being 24·3 eV (Kieffer and Van Brunt 1967; Saporoschenko 1965). In a nitrogen discharge in which E/N is less than 350 Td it is highly unlikely that significant numbers of electrons will be present with energies above 35 eV. Data of Rapp and Englander-Golden (1965) (quoted by Kieffer and Dunn 1966) indicate that the integrated cross section from threshold to 35 eV for the dissociative ionisation, reaction (2), is of the order of 0·5% of that for direct ionisation, reaction (1). It is therefore reasonable to assume that the overwhelmingly dominant primary ion will be N_2^+.

Formation of secondary ions can result in the appearance of other nitrogen ions during the course of the discharge pulse. For example, N_3^+ ions can be produced by

$$N^+ + 2N_2 \rightarrow N_3^+ + N_2\,, \tag{3}$$

$$N_2^+ + N_2 \rightarrow N_3^+ + N\,. \tag{4}$$

Reaction (3) requires the presence of N^+ which has been shown not to be produced significantly as a primary ion. Also it is a three-body reaction, which further makes it unlikely at the lower pressures used in the present experiments (2 to 10 Torr), though this reaction may contribute to the presence of N_3^+ at the higher gas pressures ($\approx$100 Torr), which implies low E/N, particularly if some other reaction provides a source of atomic nitrogen. Reaction (4) requires the N_2^+ ion to be an excited species and would be favoured by a long-lived state. McDaniel (1964) reported metastable N_2^+ as having a lifetime of $5{\cdot}3$ μs. Since this excited ion requires an appearance potential of $22{\cdot}28$ eV, reaction (4) would be favoured by high E/N.

The production of N_4^+ ions can occur by the reaction

$$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2\,. \tag{5}$$

This three-body reaction is also favoured by high pressure (low E/N). Moseley *et al.* (1969) found that this reaction has a very large rate constant ($5{\cdot}0\times10^{-29}$ cm^6 s^{-1} at thermal energies) which decreases with increasing E/N. McKnight *et al.* (1967) found that the reverse of reaction (5) increases rapidly for increasing E/N above 150 Td.

From the above discussion it would appear that it is possible that all nitrogen ion species can occur in a discharge, but that at low E/N little N^+ will be present and most of the N_2^+ produced by direct ionisation will be rapidly converted to N_4^+. Since the formation of N_3^+ requires an excited N_2^+ ion, this species also would not be anticipated at low E/N. At higher E/N the reverse of reaction (5) will ensure that little if any N_4^+ will occur, but metastable N_2^+ will be possible leading to the appearance of N_3^+ by reaction (4). Further, at high E/N, direct ionisation of atomic nitrogen produced by reaction (4) may result in N^+ which may be reinforced by a contribution from reaction (2). The results of Fletcher and Blevin (1981), however, indicate that the presence of the atomic ion will not be appreciable for $E/N \leq 600$ Td, well beyond the scope of the present work.

2. Experimental Apparatus

The experimental apparatus used for the present experiments was almost identical to that discussed by Purdie and Fletcher (1989). The drift gap was between 15 cm diameter stainless steel electrodes, the separation of which was variable over the range 0–5 cm. The initial electron swarm was released from the cathode by the incidence of a $3{\cdot}5$ ns u.v. light pulse and the resulting current pulse was integrated in the cathode circuit with an integration time of the order of $0{\cdot}01$ s. A unit gain charge-sensitive preamplifier was used to match the impedances and the resulting voltage pulse was detected and measured by means of a LeCroy

8828 Transient Digitiser. The transients were displayed and stored using an AT-type personal computer running LeCroy Catalyst software. This computer was on-line to Mainframe Prime 750 and Encore computers which were used for data analysis and curve fitting.

The drift tube was evacuated by a turbomolecular pump backed by a rotary pump to a base pressure of the order of 10^{-7} Torr. In the present work the pressure of the 99·9995% ultra-high purity gas tended to be lower than in the previous work so that higher values of E/N could be achieved. For measurement of these lower pressures, an extra 0–10 Torr Baratron pressure gauge was fitted to augment the previous high pressure head.

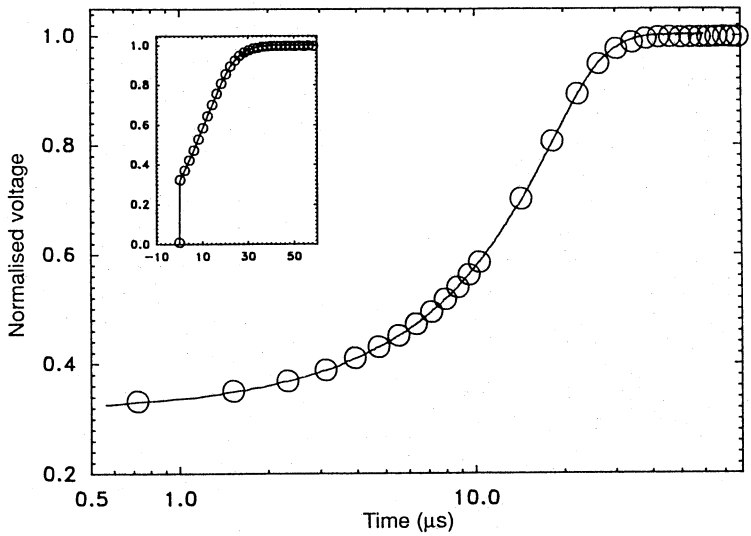

Fig. 1. Typical voltage transient showing the fitted theoretical curve with the experimental data superimposed. For clarity only one in 50 of the experimental points is shown.

3. Data Fitting

A typical voltage transient showing both the electron and ion components is shown in Fig. 1 with time on a logarithmic scale to accentuate the electron contribution. Full details of the analysis and the method of data fitting are given in Purdie and Fletcher (1989). Briefly, the first estimate of the electron drift velocity is obtained from the time to the first knee of the transient while the ion transit time is estimated from the final curve before saturation. Other initial parameters such as the various diffusion coefficients, the ionisation coefficient and the N_2^+ decay rate were estimated, hopefully, to within an order of magnitude. These first values were then put into equations (10) and (12) of Purdie and Fletcher (1989) and the theoretical transient was compared with the experimental data on the computer screen. The parameters in the theoretical transient were then changed progressively until a good fit was obtained between prediction and experiment. Such a fit is shown in Fig. 1 where the curve is the theory and the circles are the experimental data. In practice 4096 experimental points make up any one transient. For clarity, only one point in 50 is shown below $t < 10$ μs and only one in every 200 for $t > 10$ μs. The uniqueness of the final set of swarm

parameters was checked by attempting to fit the experimental data with other sets of coefficients. It was found that, while sections of the transient could be fitted in this way, 'incorrect' data tended to distort other parts of the curve. Only one set of values, at any one E/N, was ever found to provide a good fit over the whole transient.

The analysis used in the present work (Purdie and Fletcher 1989) incorporates both image terms and ion diffusion. Neglect of either of these simplifies the analysis and speeds the fitting technique and it is found that a good fit between theory and experiment can still be obtained. However, if the image terms are neglected a discrepancy in the ion drift velocity, of the order of 7% compared with the data from the full analysis, is evident at $E/N = 200$ Td, rising to about 12% at $E/N = 300$ Td. The ion diffusion coefficients show a corresponding discrepancy of less than 5% throughout the E/N range. Clearly, if the ion diffusion terms are ignored the ion diffusion coefficients cannot be obtained. Hence, throughout the work described here, all terms were included in the analysis.

4. Results

During the entire course of this work experimental voltage transients were recorded within the swarm energy range $3 \leq E/N \leq 350$ Td over a pressure range of $2 \leq p \leq 50$ Torr. The results at low E/N (no or negligible ionisation), however, have been published previously (Purdie and Fletcher 1989) and hence the present discussion is limited to the intermediate E/N regime in which ionisation is significant, *viz.* $80 \leq E/N \leq 350$ Td.

(a) Electron Swarm Parameters

At any one combination of E/N, gas pressure and electrode separation a voltage transient was obtained with a time resolution of 5 ns per point. If necessary a further transient would be obtained at a larger time per point in order

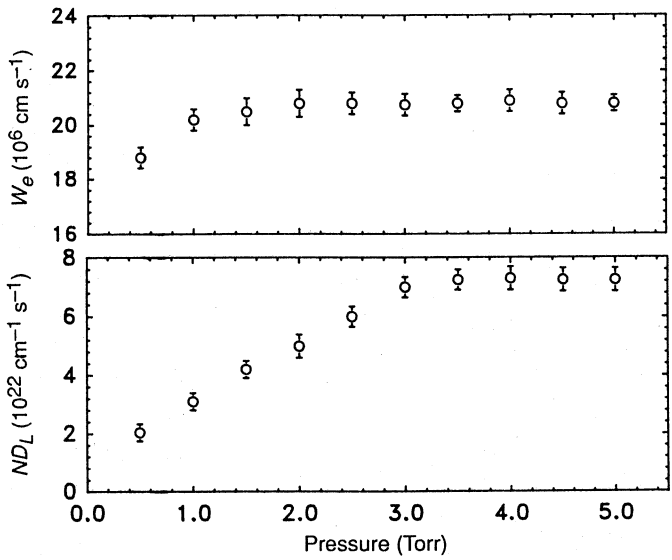

Fig. 2. Electron drift velocity and diffusion coefficient as a function of gas pressure. The gap separation is 4·0 cm and $E/N = 200$ Td.

to include the ion contribution out to saturation. Each transient was fitted using the method given above.

One of the main concerns in any study of electron and ion swarms is to ensure that the swarm is in equilibrium with the external electric field, i.e. that the charged particle transport parameters are constant across the inter-electrode gap. Hence at $E/N = 200$ Td transients were obtained at a gap separation of 4 cm over a pressure range of 0·5 to 5·0 Torr. From these data the apparent values of the electron drift velocity W_e and the electron longitudinal diffusion coefficient ND_L were calculated. These are shown in Fig. 2. It is clear that, in general, the diffusion coefficient achieves a pressure-independent value for $pd \geq 12$ cm Torr, while the electron drift velocity appears to become constant at values of $pd \geq 6$ cm Torr. This is explicable when it is noted that the drift velocity is dependent upon $\epsilon^{-\frac{1}{2}}$ (where ϵ is the electron energy) and hence is dominated by low energy electrons which might be expected to come into equilibrium quickly, while the diffusion is proportional to $\epsilon^{\frac{1}{2}}$ and is therefore equally determined by the whole distribution function.

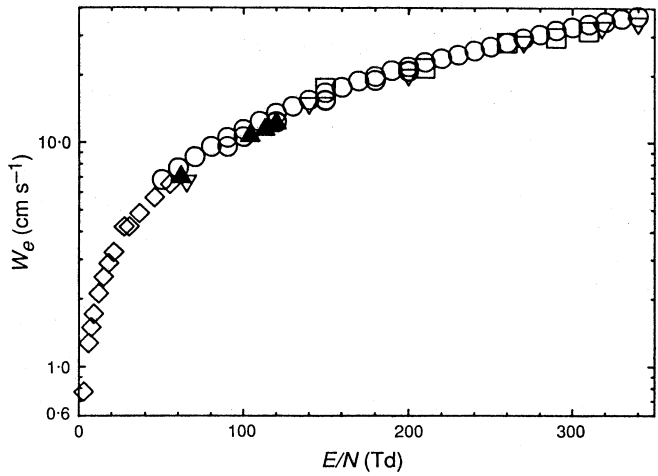

Fig. 3. Electon drift velocity as a function of E/N in nitrogen: ○, present results; ◇, Lowke (1963); ▲, Prasad and Smeaton (1967); □, Wedding *et al.* (1985); ▽, Fletcher and Reid (1980).

Values of the electron drift velocity as a function of E/N are presented in Fig. 3 where they are compared with previous values [some of the data from Purdie and Fletcher (1989) at low E/N are included for completeness]. The value of pd which can be used at any given value of E/N is limited by the breakdown potential but, as may be seen from Fig. 2, all the drift velocity data are obtained at values of pd above that at which W_e becomes pd independent, *viz.* at $pd \geq 6$ cm Torr. As may be seen the data agree well at low E/N with those of Lowke (1963) using a shutter method and at high E/N with Fletcher and Reid (1980) using the photon flux technique. Agreement between data from three different techniques lends support to the results.

In Fig. 4 the present values of ND_L versus E/N are compared with the previous data of Fletcher and Reid (1980) and of Wedding *et al.* (1985).

In order for reliable diffusion data to be obtained pd must be greater than 12 cm Torr which means that with a 4 cm gap separation a minimum gas pressure of 3 Torr must be used. This, combined with breakdown, limited the E/N range for valid data to below 200 Td. Also shown in Fig. 4 are ND_L data taken at higher E/N, for which pd was below the critical value. Both previous sets of data were obtained at pd values well below the critical value and as expected they fall dramatically below the present data taken at $pd = 8$ cm Torr, which in turn fall below an extrapolation of the present high pd results. We thus believe that many of the previously published diffusion data are in error because of this effect and that diffusion data at $E/N \geq 150$ Td will not only be E/N dependent but also pd dependent.

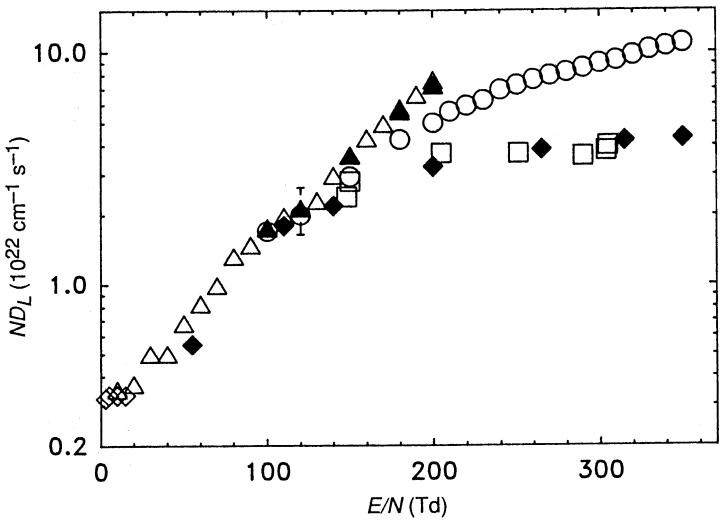

Fig. 4. Electron diffusion coefficients as a functon of E/N in nitrogen: ◇, $p = 50$ Torr; △, $p = 10$ Torr; ▲, $p = 5$ Torr; ○, $p = 2$ Torr; □, Wedding *et al.* (1985); ◆, Fletcher and Reid (1980).

Fig. 5 shows the present ionisation coefficient data. It is found in practice that the leading edge of the voltage transient is critically dependent upon α/p, so giving a very sensitive measure of ionisation. At low E/N, moderately high gas pressures could be used ($10 \leq p \leq 50$ Torr) giving a pd in excess of 40 cm Torr. At these values of pd any cathode non-equilibrium effects are negligible and the values of α/p are observed to be pressure independent. At higher E/N (≥ 180 Td), the pressure range used was lower ($2 \leq p \leq 10$ Torr). In this latter case the α/p values measured at constant E/N were found to be higher at the lower gas pressures by as much as 20%, indicating that the cathode non-equilibrium was no longer a negligible proportion of the swarm gap. Hence only data below $E/N = 200$ Td are presented.

(b) Ion Swarm Parameters

Initial attempts to fit the ion component of the voltage transient using a single ion contribution met with total failure. Similarly the data could not be fitted

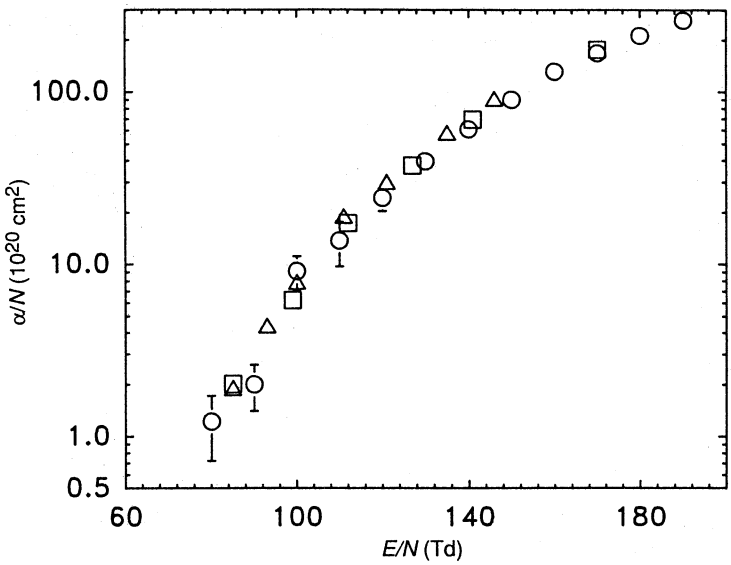

Fig. 5. Primary ionisation coefficient versus E/N in nitrogen: ○, present data; △, Daniel and Harris (1970); □, Haydon and Williams (1976).

using two ion species which are both formed simultaneously during the electron transit. The discussion presented above indicates that the primary ion produced by electron–molecule collision must be the N_2^+ ion. Once this is produced it can undergo reaction (4) to give N_3^+, and reaction (5) to give N_4^+. Since, as discussed in Section 1, reaction (5) is much more probable, particularly at lower E/N, a model was formulated in which N_2^+ is produced by direct ionisation and then decays exponentially with time to produce N_4^+. The fitting program was thus adapted to include two contributions from equation (12) of Purdie and Fletcher (1989), one of which decreased as $\exp(-\tau)$ and one which increased at the same rate. The time constant τ for the decay of N_2^+ to N_4^+ then became an extra variable. With this model good fits were obtained for the whole transient in the range $100 \geq E/N \geq 300$ Td. The possibility of reaction (4) occurring to produce N_3^+ ions was tested by setting up a computer model in which N_2^+ decayed to both N_4^+ and N_3^+ in some ratio. No agreement could be obtained using this model, whatever ratio was used, for $E/N \leq 300$ Td. Only when E/N exceeded 300 Td was there any evidence of the production of N_3^+, with the proportion of N_3^+ increasing rapidly from zero at $E/N = 300$ to 55% of all secondary ions at $E/N = 350$ Td. No evidence was seen for the existence of N^+ throughout the range of E/N studied which is consistent with the conclusions of Fletcher and Blevin (1981).

Fig. 6 shows the drift velocity for the N_2^+ and the N_4^+ ions as a function of E/N. The only value of the drift velocity which could be measured for the N_3^+ ion was at $E/N = 350$ Td for which the value was $22{\cdot}5\times10^4$ cm s^{-1}. These data are substantially in agreement with the results of Saporoschenko (1965) and of Moseley *et al.* (1969) who injected mass-identified ions into a gas discharge. From

the present work, however, the time constant for the decay of N_2^+ is obtained. These data are given in Fig. 7.

5. Conclusions

The present work has shown that the voltage transient technique is a useful method for studying not only electron swarms but also for obtaining details

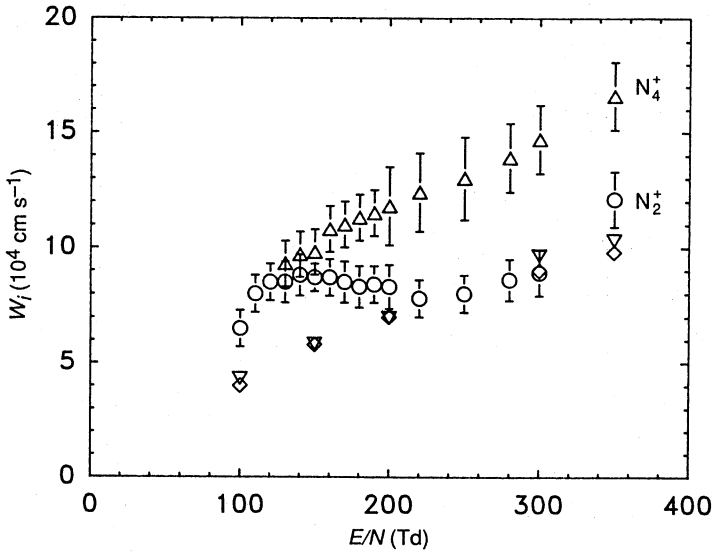

Fig. 6. Drift velocity of ions present in a nitrogen discharge as a function of E/N: ○ present N_2^+ data; △ present N_4^+ data; ▽ N_2^+ data of Moseley *et al.* (1969); ◇ N_2^+ data of Saporoschenko (1965).

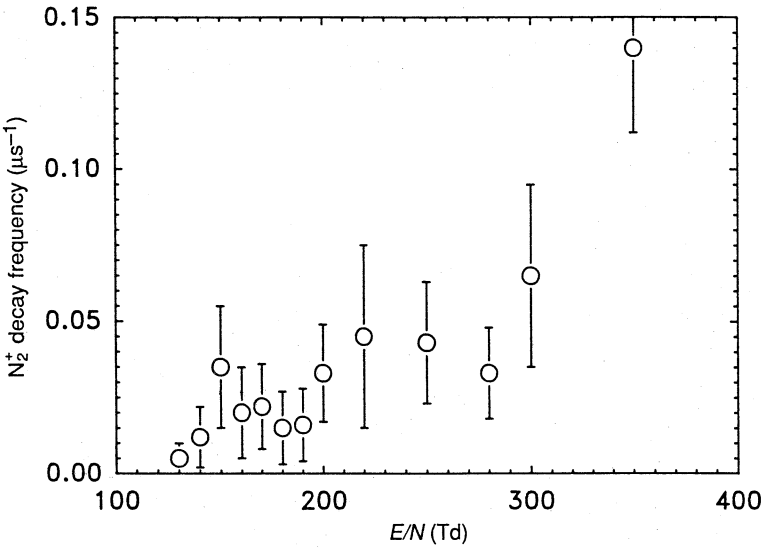

Fig. 7. Decay rate of the N_2^+ ion in a nitrogen discharge.

of the behaviour of the various ion components of the swarm. Since the ion chemistry operating within the swarm will have a marked influence on the overall behaviour of the swarm it is important to know not only which ions are present at any time but how they vary with time. Other techniques used to measure ion types and concentrations, e.g. the extraction of the ions through an aperture in the cathode, have been criticised by Skullerud and Holmstrom (1985). The present method, while being far more indirect than the extraction technique, is immune to these objections.

It is clear that the apparent measured values of the transport parameters of the various swarm components can be affected by non-equilibrium regions within the swarm and that such non-equilibrium affects the swarm parameters to different degrees, with the ionisation and the diffusion coefficients being the most sensitive and the drift velocities the least. The apparent variation of α/p with pd could well explain the difficulty of various previous workers to agree on ionisation coefficients at high E/N.

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References

Blevin, H. A., and Fletcher, J. (1984). *Aust. J. Phys.* **37**, 593.
Blevin, H. A., Fletcher, J., and Hunter, S. R. (1976). *J. Phys.* D **9**, 1671.
Blevin, H. A., Fletcher, J., and Hunter, S. R. (1978). *J. Phys.* D **11**, 1653
Daniel, T. N., and Harris, F. M. (1970). *J. Phys.* B **3**, 363.
Field, F. H., and Franklin, J. L. (1957). 'Electron Impact Phenomena and the Properties of Gaseous Ions' (Academic Press: New York).
Fletcher, J., and Blevin, H. A. (1981). *J. Phys.* D **14**, 27.
Fletcher, J., and Reid, I. D. (1980). *J. Phys.* D **13**, 2275.
Haydon, S. C., and Williams, O. M. (1976). *J. Phys.* D **9**, 523.
Kieffer, L. J., and Dunn, G. H. (1966). *Rev. Mod. Phys.* **38**, 1.
Kieffer, L. J., and Van Brunt, R. J. (1967). *J. Chem. Phys.* **46**, 2728.
Lowke, J. J. (1963). *Aust. J. Phys.* **16**, 115.
McDaniel, E. W. (1964). 'Collision Phenomena in Ionized Gases' (Wiley: New York).
McKnight, L. G., McAfee, K. B., and Sipler, D. P. (1967). *Phys. Rev.* **164**, 62.
Moseley, J. T., Snuggs, R. M., Martin, D. W., and McDaniel, E. W. (1969). *Phys. Rev.* **178**, 240.
Prasad, A. N., and Smeaton, G. P. (1967). *Brit. J. Appl. Phys.* **18**, 371.
Purdie, P. H., and Fletcher, J. (1989). *J. Phys.* D **22**, 759.
Rapp, D., and Englander-Golden, P. (1965). *J. Chem. Phys.* **43**, 1464.
Saporoschenko, M. (1965). *Phys. Rev.* **139**, A352.
Skullerud, H. R., and Holmstrom, S. (1985). *J. Phys.* D **18**, 2375.
Tagashira, H., Sakai, Y., and Sakamoto, S. (1977). *J. Phys.* D **10**, 1051.
Wedding, A. B., Blevin, H. A., and Fletcher, J. (1985). *J. Phys.* D **18**, 2361.

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