

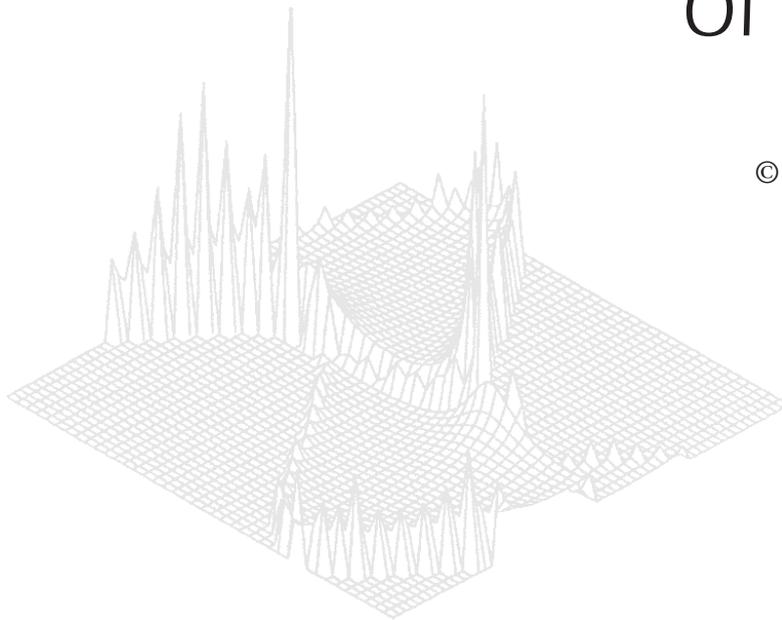
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## Diffusion of Excited Neutral Particles: Basic Studies and Potential Applications\*

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### *Abstract*

Recent experiments, carried out in highly pure samples of molecular nitrogen, have demonstrated the strong influence exerted by neutral, excited metastable states. The influence of the electronically excited, metastable  $N_2(A)$  state on the ionisation growth is demonstrated through observation of the diffusion phenomena associated with the spatial and temporal growth of ionisation. Evidence has also emerged demonstrating the existence of a second metastable particle influence. The diffusion time observed, however, is not consistent with it being due entirely to an electronically excited state such as the metastable  $N_2(a')$  state. Rather the observations suggest the possibility that intersystem crossings between the  $N_2(a')$ , the highly vibrationally excited  $N_2(X)$  states and the  $N_2(A)$  state may be responsible for the increased diffusion time and large molecular size. The possible relevance of these findings to applications such as plasma nitriding is canvassed.

### **1. Introduction**

Considerable effort has been devoted over many years to establishing the influence of diffusion and drift phenomena in determining the electronic and ionic behaviour of atomic and molecular gases. The successes of Crompton and his colleagues in removing many ambiguities in our understanding of the basic processes has ensured that a firm basis now exists for extending our knowledge to embrace the added complexities that intrude into situations where ionising events begin to dominate. Crompton was, of course, very much involved in the complexities of ionisation phenomena in the early fifties and, during a study leave from the University of Adelaide in 1953–4, undertook some collaborative investigations of static breakdown in uniform electric fields in the laboratories of F. Llewellyn Jones at Swansea. It was a time when controversy was rampant about the significance or otherwise of streamer phenomena in the pre-breakdown growth of ionisation. Investigations in both air and nitrogen had shown that the growth of ionisation prior and up to the setting of the breakdown criterion was in accord with the well-known Townsend relationship based on primary  $\alpha$  and secondary  $\omega/\alpha$  ionisation coefficients, even at  $pd$  values well in excess of the 200 Torr cm at which the streamer mechanism had been claimed to take over. In the circumstances, the need for precise determination of the values of  $\alpha$  and  $\omega/\alpha$  was clearly demonstrated and led to precise measurements of these

\* Dedicated to Professor Robert W. Crompton on the occasion of his seventieth birthday.

quantities in hydrogen (Crompton *et al.* 1955, 1956). Researches have moved on considerably since those pioneering days with increasing efforts being concentrated on improving our understanding of the complexities of sustained gas-discharge phenomena. The motivation for many of these studies has been the expected commercial benefits likely to emerge, and the rewards of such endeavours have been clearly demonstrated by the large variety of important gas lasers now available.

A notable early success was the development of the nitrogen laser which generated intense radiation at  $\lambda = 337$  nm as a result of population inversion between the C and B states of the nitrogen molecule. Although the processes leading to inversion of the populations in the C and B states are now well established, there is much about the complexities of the nitrogen molecule that still remains obscure. Indeed it is our persistent lack of knowledge and understanding of the complexities of the nitrogen molecule that inhibits further commercial applications of nitrogen plasmas. An example of an important potential application is the harnessing of nitrogen plasmas to bring about dramatic changes to the surface properties of metals.

It is especially relevant to address these issues in the context of the many tributes to the extensive contributions made by Crompton and his colleagues, because one of the significant remaining aspects of the new studies is the positive identification of the neutral excited states of the nitrogen molecule and an accurate determination of the diffusive characteristics of those states that are important in modifying metal-surface properties. In addressing these new problems, the researches undertaken so far have demonstrated that traces of impurities can have an overwhelming influence on the behaviour of nitrogen plasmas (Ernest *et al.* 1986). The characteristics of the spatial growth of ionisation are radically affected by parts per million of gas impurities such as carbon monoxide and oxygen commonly found in commercial samples of iron and steel. Furthermore, the corresponding temporal growth of the ionisation is similarly affected. Perhaps of most significance in the context of diffusive phenomena, experiments have revealed contributions to the growth of ionisation from at least two neutral excited states of the nitrogen molecule (Haydon *et al.* 1996). One has been unambiguously identified as the metastable  $N_2(A)$  state, but uncertainty still surrounds a positive identification of the second metastable phenomenon (Fewell *et al.* 1996).

In contrast with the extensive studies of electronic and ionic diffusion phenomena, relatively little experimentation has been devoted to establishing the diffusive behaviour of the many excited neutral states of nitrogen. Given the expertise of Crompton and his colleagues with diffusion phenomena, the challenge posed by this complex molecule may perhaps attract them into this important environment. This overview attempts to provide the essential background to our existing knowledge and to highlight those aspects that need further study.

## 2. Diffusion Experiments on Neutral Metastable Particles

Investigations of neutral particle diffusion require different experimental procedures from those used for studies of charged particles such as electrons and ions. They have been described in detail elsewhere (Haydon *et al.* 1996) and are briefly summarised below.

The information required is obtained by observing the growth of ionisation under pre-breakdown conditions. This ensures steady-state conditions, the absence of any influence from space-charge effects and, in general, well-defined ionisation parameters that control both the spatial and the temporal growth of ionisation. The relevant diffusion information is obtained from observations of the temporal characteristics of the ionisation growth. Complementary spatial information is also required in order to monitor both the state of purity of the gas samples and any changes in the boundary surfaces that yield the electrons required to maintain the growth of ionisation.

The need to operate under pre-breakdown conditions imposes constraints on the facilities required to collect the temporal data. The electrons required to initiate the growth of ionisation must be generated by an external source of ultraviolet radiation. Furthermore, this source must be capable of being repetitively switched on and off so that a pulse of electrons can be released in a controlled manner from the boundary surface. The signal generated in this way is too weak to be subjected to analysis because it is contaminated by unacceptable noise levels. Signal averaging is necessary to reduce this noise influence. With appropriate facilities, however, extremely good averaged signals can be recorded for analysis.

The analysis of such data to obtain the fundamental diffusion time constant  $\tau$  must take into account the consequences of regeneration processes. These arise when metastable particles of sufficient energy arrive at the cathode and release new electrons which then initiate further avalanches of electrons and, in turn, create further metastable particles. The treatment of these regeneration processes has been addressed by Molnar (1951), and his approach has been extended to include the influence of more than one type of metastable particle (Haydon *et al.* 1996). Before further discussion of these complex analytical processes, it is essential to appreciate the experimental procedures that are required to record meaningful ionisation data.

A stainless steel ionisation chamber with an internal diameter of 182 mm was used to collect the required data. The ionisation gap consisted of two plane-parallel circular electrodes, fabricated from 'oxygen-free' copper, each of diameter 100 mm and with a circular edge profile of radius 5 mm. The electrode separation was adjustable and appropriate potential differences could be applied across the electrodes from a Fluke high voltage power supply. The ionisation current was initiated and maintained photoelectrically by irradiating the cathode with ultraviolet light from a small low-pressure mercury lamp. This was positioned below the lower electrode (Fig. 1), which had a 20-mm-diameter quartz disk set into it. By coating with an appropriately thin gold film, a significant fraction of the incident ultraviolet light could be transmitted to irradiate the upper, bulk copper, electrode. In this way either electrode could be selected as the cathode by choice of the polarity of the applied voltage. Furthermore, this technique avoids the electric-field distortions inevitably associated with the use of electrode perforations.

All investigations were carried out at room temperature and at gas pressures between 0.3 and 20 Torr as measured with a Texas-Instruments fused-quartz Bourdon gauge, accurate to  $\pm 0.01$  Torr. The gas used was Matheson research-grade nitrogen, which has a total impurity content of not greater than 5 ppm. A vitally important aspect of all the experimental work was the need to undertake

extensive outgassing procedures. When using copper and gold-film electrodes, the ionisation chamber and associated stainless steel vacuum accessories were subjected to prolonged outgassing at temperatures  $\sim 200^\circ\text{C}$  for periods of some three to four weeks. This ensures that the pre-breakdown discharges established between the electrodes are not influenced by any remaining contaminants released by the stainless steel ionisation chamber. Dramatic changes in the characteristics of the ionisation growth were observed as a consequence of these procedures.

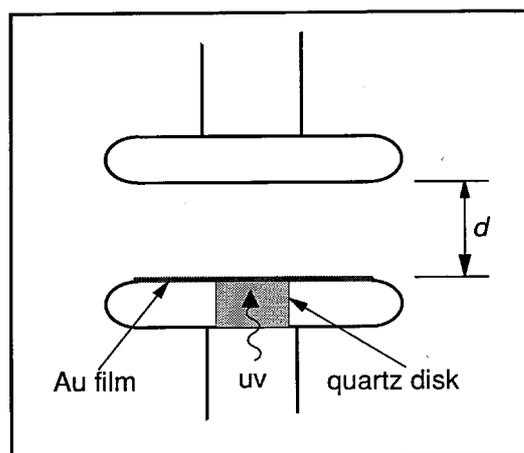
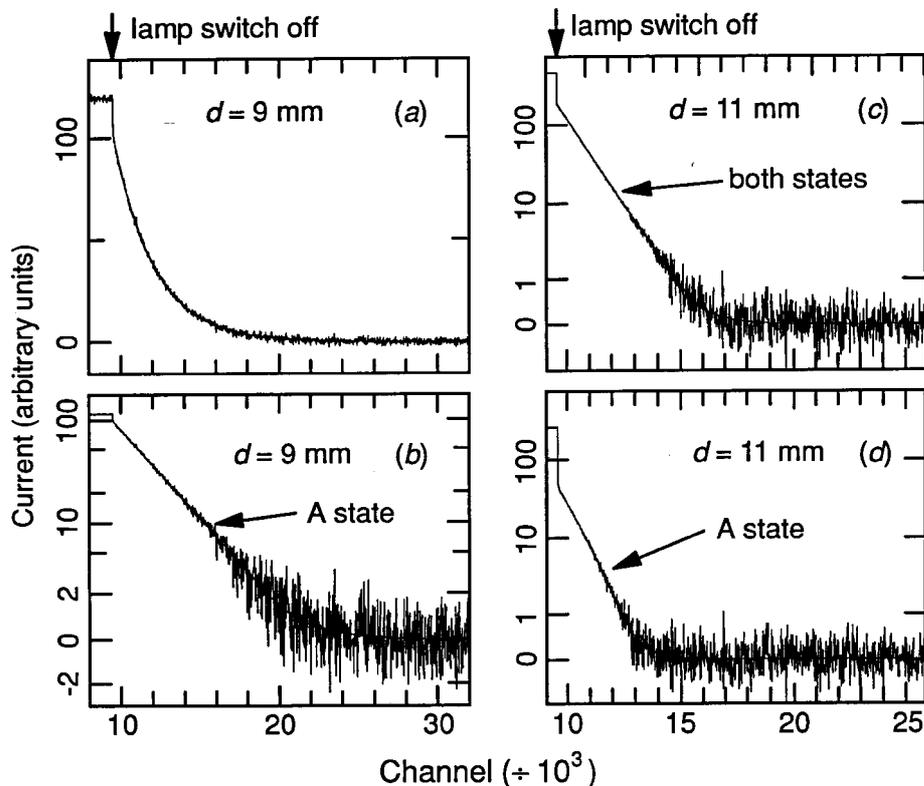


Fig. 1. Schematic diagram of the electrode configuration in the ionisation chamber.

The significant outcome of these procedures was the clear demonstration that two slowly diffusing metastable states are active in controlling the growth of ionisation. Furthermore, the action of one of these slowly diffusing states is markedly altered by the presence of carbon monoxide. Since CO is commonly outgassed by stainless steel, it is important for these experiments to reduce the outgassing rate in the ionisation chamber as much as possible, and this was clearly achieved by the outgassing procedures described above. The spatial ionisation-growth curves obtained with the new procedures have been reported by Ernest *et al.* (1986).

For the temporal measurements, the current decay following lamp switch off was monitored rather than current growth following switch on. This was to avoid instrumental effects caused by the uv lamp exhibiting a jitter of about 0.5 ms when switching on. Tests without gas in the chamber show that the output of the lamp consistently falls to zero within  $20\ \mu\text{s}$  of switch off. This  $20\ \mu\text{s}$  decay time is a convolution of the intrinsic decay time of the lamp with the RC time constant of the system, and is easily fast enough for our purposes.

The complexities associated with the analysis of the temporal data have been explained in detail elsewhere (Haydon *et al.* 1996). The main features and difficulties can be most simply appreciated by reference to Fig. 2. (Note that, of the panels in Fig. 2, only Fig 2a is plotted on a linear scale.) The data in Figs 2a and 2b were obtained at a smaller electrode separation  $d$ , and hence further from breakdown, than the data in Figs 2c and 2d. In Figs 2a and 2b,



**Fig. 2.** Typical decay-of-current traces showing (a, b) a single exponential component and (c, d) multiple exponential components for pre-breakdown discharges in  $N_2$  at a reduced electric field  $E/N = 283$  Td, a reduced gas pressure  $p_0 = 5$  Torr and the electrode separations  $d$  indicated. The time scale on the abscissa is  $8 \mu\text{s}$  per channel. The full curves show computer fits to the data. (a) Signal averaged data on a linear scale. (b, c) Semi-logarithmic plots after baseline subtraction. (d) Semi-logarithmic plot of the data in (c) with the second-state component also subtracted. In panels (b–d), a linear scale is used in the lower parts of the figures to accommodate the negative values arising in the subtractions because of noise. The scale switches between logarithmic and linear at an ordinate value of (b) 2.0, (c, d) 1.0. The linear scale is chosen to preserve slopes across the position at which the scale switches.

only one metastable particle is contributing to the ionisation growth. The decay rate of the exponential shown in Fig. 2b is consistent with it being caused by diffusion of molecules in the  $N_2(A)$  state through the background of ground-state molecules. Close to breakdown in very pure nitrogen, the current decay is more complex, exhibiting several exponential components. An example is given in Figs 2c and 2d, where panel (c) shows a semi-logarithmic plot of the current-decay trace following baseline subtraction. The behaviour is basically, but not exactly, exponential. When the dominant exponential component is subtracted, a second exponential component is revealed (Fig. 2d), and more complex behaviour is seen near the time of lamp switch off. A detailed discussion of these characteristics has been given elsewhere (Haydon *et al.* 1996). For the purposes of this overview of metastable particle diffusion, it is necessary to note simply that the exponential

component dominating Fig. 2*d* has a decay time corresponding to diffusion of the  $N_2(A)$  state. The component dominating Fig. 2*c* is due to a second slowly diffusing metastable particle. Of particular interest now is identity of this second metastable particle.

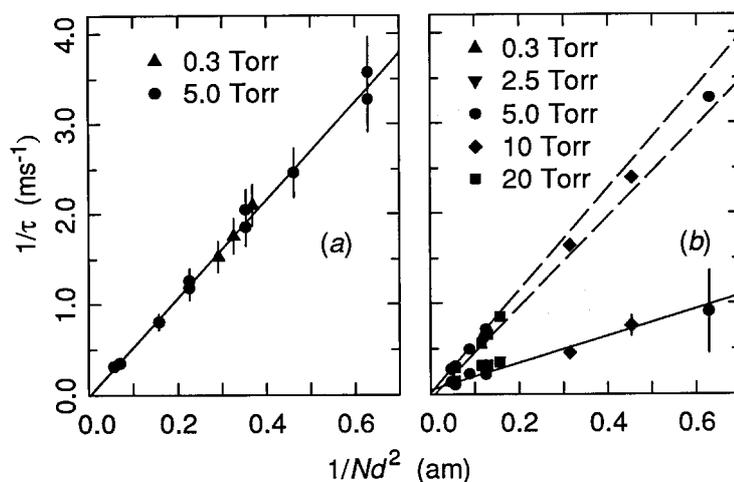
Some information toward this goal is obtained by examining the variation in temporal diffusion behaviour with variation in gas pressure and electrode separation. To extract this information, a computer program was written to fit exponentials, baseline and other features of the data, based on a standard function-minimisation package (James and Roos 1975). Fitting multiple exponentials to noisy data can be ill-conditioned when the time constants of the exponentials are parameters to be fitted (e.g. Acton 1970). Without any constraints on the parameters being fitted, a wide range of parameter values can give essentially equally good fits. Fortunately, information from the single-component traces can be used to assist in fitting the multi-exponential cases. Full details of the procedures have been described elsewhere (Haydon *et al.* 1996). Briefly, a sufficient number of cases showing the  $N_2(A)$  state only have been investigated to determine the diffusion coefficient  $D_m$  and the quenching rate  $G$  for this species. This enables the fundamental metastable diffusion time  $\tau$  to be determined for the  $N_2(A)$  state, using

$$\frac{1}{\tau} = \frac{\pi^2 D_m N}{Nd^2} + G, \quad (1)$$

where  $N$  is the gas number density and  $d$  the separation of the electrodes.

As explained elsewhere (Haydon *et al.* 1996), the complexities of more than one metastable particle contributing to the ionisation growth can be severe. The general relationship between  $\tau$  and  $T$  has a complex form [see equation (9) of Haydon *et al.* 1996] and even the above  $1/\tau$  value cannot be converted straightforwardly into a characteristic current-decay time  $T$  without knowing whether there is significant interaction between other  $\tau$  values. The more widely these are separated the smaller the interaction between them and in many cases successive approximation is feasible. Restriction to such cases yields the results summarised in Fig. 3.

Estimation of the uncertainties in both the single-component and multi-component trace analysis has been considered in detail elsewhere (Haydon *et al.* 1996). The essence of the procedure adopted for the multi-component traces was to fix the characteristic decay time of the exponential component attributed to the  $N_2(A)$  state at that value determined from the single-component analysis. Although, in principle, traces showing more than two exponentials can introduce unmanageable complexities, it is possible to select cases in which the fast terms are sufficiently weak and have decay times sufficiently different from those of the two slow components that a meaningful  $\tau$  value can be established for the slowest component. A good example of such conditions is shown in Figs 2*c* and 2*d*. The values for the diffusion coefficients of the two slowly diffusing metastable particles were established as  $D_m N = 551 \pm 25 \text{ am}^{-1} \text{ s}^{-1}$  and  $158 \pm 17 \text{ am}^{-1} \text{ s}^{-1}$  respectively. (Note that  $1 \text{ am} = 10^{-16} \text{ cm}$ .) This unambiguously identifies the first as the  $N_2(A)$  state, but the identification of the second remains an intriguing mystery.



**Fig. 3.** Diffusion plots for (a) the A state and (b) the second slowly diffusing state of  $N_2$ . The reciprocal of the fundamental characteristic diffusion time  $\tau$  is plotted against the reciprocal of the product of the gas number density  $N$  and the square of the electrode separation  $d$ . The broken lines in (b) are the uncertainty limits of the A-state determinations from (a). The results of fitting are shown as the full lines; these give (a)  $D_m N = 551 \pm 25 \text{ am}^{-1} \text{ s}^{-1}$ ,  $G = < 20 \text{ s}^{-1}$ , and (b)  $D_m N = 158 \pm 17 \text{ am}^{-1} \text{ s}^{-1}$ ,  $G = 50 \pm 16 \text{ s}^{-1}$ . (Note:  $1 \text{ am} = 10^{-16} \text{ cm}$ .)

### 3. Diffusion Studies and Particle Identification

A variety of procedures is available to help identify neutral excited particles generated in gas discharges. Penning ionisation is useful in mixtures containing inert gas atoms, especially helium and neon. Laser-induced perturbation of excited states generated in the discharge can also modify the plasma behaviour and so provide reliable identification of the excited state itself. In some cases, the simpler procedure of observing the effects of trace impurities can provide useful information. The first experiments of this kind were reported by Haydon and Williams (1973). Their observations demonstrated the very strong influence of impurities, accumulated gradually over periods of several weeks, on the spatial variation of the secondary ionisation coefficient  $\varpi(d)$ .

For the nitrogen plasma of our present studies, we took the trace-impurity route in the early studies. Attention was focused on the properties of the well-known long-lived  $N_2(a')$  state, which is known to be readily populated by electron impact. A short study leave, spent in Crompton's laboratories, provided an opportunity to join with Malcolm Elford to document the sensitivity of the nitrogen pre-breakdown discharge to small levels of common impurities such as CO. The ionisation behaviour changed dramatically. Only very small (parts per million) levels of CO were necessary, whereas gases such as hydrogen and neon had little influence on the ionisation behaviour (Ernest *et al.* 1986). The tentative suggestion that the  $N_2(a')$  state might be responsible for the dramatic increase in ionisation in highly pure samples was subsequently thrown into doubt by Piper (1987), who measured a large self-quenching coefficient for the  $N_2(a')$  state. Later, extensive, precise measurements and careful analysis yielded new

information on the changes in the secondary ionisation coefficients caused by the impurity effects (Ernest 1991).

The extensive diffusion experiments on the second state, shown in Fig. 3, provided convincing evidence that any mechanism involving *only* the  $N_2(a')$  state must be excluded. This is simply because the much lower diffusion coefficient implies a significantly larger size than that of molecules in the  $a'$  state. Various possibilities involving other excited states and dimer states have been considered elsewhere (Fewell *et al.* 1996). Our conclusion is that the second diffusion mechanism most likely involves highly vibrationally excited states of the  $N_2$  electronic ground state. If such states are to contribute to electron emission from the cathode surface, then they must reach the surface with energy in excess of 5 eV (i.e. populated at vibrational levels  $v \geq 20$ ). Furthermore, the small diffusion coefficient suggests a larger effective radius than for A state molecules. It is well established that molecular size increases with increasing vibrational excitation (e.g. Kang and Kunc 1991). Indeed, nitrogen molecules in X,  $v \sim 38$  states are probably more than 50% larger than molecules in the  $N_2(A)$ ,  $v = 0$  state (Fewell *et al.* 1996).

The other constraint imposed on the slowly diffusing state was that it shows very low self-quenching in addition to having a long radiative lifetime. Low- $v$  states can be quenched by exchange of vibrational quanta with ground-state molecules, but anharmonicity renders this increasingly ineffective as the value of  $v$  increases. This arises because the spacing between neighbouring vibrational levels is about 150 meV near  $v = 35$  compared with the excitation energy of 289 meV for the  $v = 1$  state. This difference is sufficient to significantly suppress vibration–vibration exchange for high- $v$  states, and so these may well have long effective lifetimes. On the other hand, vibration–translation energy exchange becomes more likely as the value of  $v$  is increased because of the falling interstate energy gap. A detailed analysis (Fewell *et al.* 1996) suggests that there may be a range of vibrational quantum numbers around  $v = 25$  in which collisional relaxation is slow enough that the states are sufficiently metastable to account for the experimental findings.

#### 4. Mechanisms for Population of Vibrationally Excited Ground States

Electron impact will populate electronically excited states, but this is not an efficient mechanism for direct excitation of high- $v$  states. The highest vibrational state observed by electron impact is  $v = 17$ , with a peak excitation cross section of only  $2.4 \times 10^{-22}$  cm<sup>2</sup> (Allen 1985). This is a factor of  $4.3 \times 10^{-7}$  lower than the cross section for excitation of the  $v = 1$  state. Thus, one-step electron impact excitation cannot provide an adequate population of highly vibrationally excited states. Furthermore, spatial growth of current experiments rule out population by multiple electron impacts (Fewell *et al.* 1996).

An alternative mechanism relies on collision-induced transfer of population from any state that can be easily excited by electron impact. Such a state is the  $N_2(a')$  state, which was originally thought to be acting independently of other interactions. It has a peak excitation cross section  $\sim 10^{-17}$  cm<sup>2</sup>. Since the predicted excitation energy of the  $N_2(X)$ ,  $v = 38$  state is very close to the excitation energy of the  $N_2(a')$ ,  $v = 0$  state, a collision between the latter excited state and background gas molecule could lead to transfer of energy from the

$N_2(a')$  state to the  $N_2(X)$ ,  $v = 38$  state. Closer examination (Fewell *et al.* 1996) of the available literature indicates the possibility that the  $N_2(X)$ ,  $v = 38$  state may have an energy within a few meV of the  $v = 0$  state of  $N_2(a')$ . Some doubt surrounds the various estimates of the respective energies and it would clearly be of considerable interest if such uncertainties could be removed. In pursuing this line of reasoning, a further intriguing possibility suggests itself. Another close resonance exists between the  $N_2(X)$  and  $N_2(A)$  states at  $N_2(X)$ ,  $v = 27$  and  $N_2(A)$ ,  $v = 1$  so that a reverse exchange of energy may occur, transferring the  $N_2(X)$  state back to the metastable A state. Such a mechanism would effectively show a significant decrease in the diffusion coefficient because the diffusing particle would then exist for part of its life as a larger entity, moving more slowly through the gas environment. The transfer of energy back to the A state removes any difficulties about how the electrons are released from the cathode surface. In this interpretation, the longer diffusion time is merely a consequence of the energy residing in several different excited states, with one of the states having a significantly larger size and therefore diffusing more slowly. It should be pointed out that intersystem crossings similar to those involved in the above discussion have been observed in CO (Lavollée and Tramer 1979) and  $O_2$  (Bednarek *et al.* 1994). In the case of nitrogen, such crossings might occur during the interaction with the electrode surface. Further investigation of such a possibility needs to be undertaken.

### 5. Possible Implications for Commercial Nitriding

The uncertainties that have now come to light about the interpretation of the ionising behaviour of pure nitrogen are not only of interest at the fundamental level but almost certainly have relevance to the success of commercial applications. From this second point of view, identifying the second state is not such an important consideration. It is sufficient to have phenomenological data on its properties: how its presence affects a discharge or plasma and what interactions it undergoes with surfaces exposed to the plasma.

One important application involves the nitriding of metal surfaces, especially of iron and steel. Nitriding has been undertaken over many years by subjecting the specimens to conventional high temperature heat treatment in nitrogen-dominated atmospheres. More recently, interest has concentrated on exposing the specimens to either dc or rf plasmas. Such techniques look promising, but there is, as yet, no clear understanding of the precise mechanisms involved in the nitriding process. Henrion and his colleagues have recently undertaken optical diagnostic studies of dc pulsed plasmas in order to determine the most favourable conditions for surface treatment (Hugon *et al.* 1996; Henrion *et al.* 1992). The creation and loss processes of states such as  $N_2^+(B)$ ,  $N_2(C)$ ,  $N_2(A)$  and  $N_2(X)$  have been extensively studied. Ricard *et al.* (1990) have also studied the species active in microwave postdischarges used for surface nitriding. For many years, it has been realised that highly vibrationally excited states may be important in dc nitriding plasmas (Ricard *et al.* 1988).

In the light of our own researches on the ionisation behaviour of nitrogen, we are presently investigating a variety of possible processes and mechanisms. All of our investigations revealing the existence of several diffusion processes have been undertaken with electrodes made of copper and gold. Highly pure nitrogen

and extensive outgassing procedures at temperatures  $\sim 200^\circ\text{C}$  were essential, and the phenomena were regularly observed in ionisation chambers constructed of stainless steel. Replacing the copper electrode with a stainless steel specimen was not expected to unduly modify the outcomes, especially as the same outgassing procedures were adopted. Surprisingly however, the second diffusion mechanism was quenched in the presence of the stainless steel electrode (Baldwin *et al.* 1997). In commercial applications involving nitriding, the specimens are always held at temperatures  $\sim 500^\circ\text{C}$ . The precise reasons for having to do so are not yet clear and further investigations on this point are in progress.

## 6. Conclusion

This brief review demonstrates the important role played by the diffusion of neutral excited metastable particles in determining the ionisation behaviour of pure molecular nitrogen. Their importance has emerged through the application of careful and precise experimentation, so characteristic of the extensive investigations into the diffusive behaviour of charged particles by Crompton and his colleagues. In retrospect, it is not surprising that any attempts in the 1950s to undertake precise experiments in air and nitrogen were not likely to succeed. Although hydrogen appeared likely to yield more significant fundamental information, history has shown that, even with this much simpler molecule, nature's secrets are not revealed without extensive, careful and precise investigations.

Crompton and his colleagues have made considerable progress in unravelling the subtleties controlling the diffusion of charged particles. Now that the causes of the complex behaviour of nitrogen are gradually coming to light, an extension of the Crompton philosophy needs to be applied to establish the precise mechanisms involved in both the gas and surface influences. This should add substantially to our chances of success in pursuing new and potentially important applications.

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