Dissociation mechanisms in nitrogen discharges

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Received 19 December 2002; in final form 24 February 2003

Abstract

This work presents a theoretical and experimental investigation of the dissociation rate and $N(^4S)$ atom concentrations in a nitrogen DC discharge operating at gas pressures $p = 0.5$–4 Torr and discharge currents $I = 10$–80 mA. By comparing the measured and calculated atomic densities, the various mechanisms for production of $N(^4S)$ atoms are discussed and weighted. It is shown that electron impact dissociation controls nitrogen dissociation only at the lower pressures considered in this study. For $p \gtrsim 1$ Torr, dissociation proceeds essentially via reactions involving the long-lived metastable heavy-particles $N_2(X\ ^1\Sigma_g^+, v)$ and $N_2(A\ ^3\Sigma_u^+)$, such as $2N_2(X, 10 < v < 25) \rightarrow N_2(X) + 2N$ and $N_2(X, 14 \leqslant v' \leqslant 19) + N_2(A) \rightarrow N_2(X) + 2N$. For a gas temperature of 500 K, the rate coefficients for these two reactions are estimated to be of the order of 10^{-15} and 10^{-12} cm^3/s, respectively.
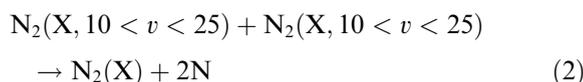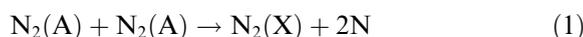© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

It is a well established fact that at pressures above ~ 1 Torr and for values of reduced electric field strength, E/N, typically below 8×10^{-16} V cm^2, the relatively high dissociation rate experimentally observed in a nitrogen glow discharge cannot be conveniently explained by electron impact dissociation only [1]. This has led several authors to propose a purely vibration-dissociation (V-D) mechanism by vibration–vibration (V-V) and vibration–translation (V-T) energy exchanges into a pseudo-level above the last vibrational level [2,3]. However, these studies have not considered at that time the deac-tivation of the vibrational levels at the wall of the container [4] nor the strong V-T exchanges in N_2–N collisions [5,6]. Therefore, the actual vibrational distribution function (VDF) of ground-state N_2 molecules is not high enough populated in the very high levels to allow V-D processes to be effective, so that dissociation should take place through a different mechanism.
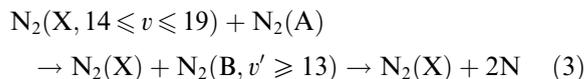
The need of an extra source of dissociation was recently stressed in [7–9], which have proposed, respectively, additional channels of dissociation according to reactions:

$$N_2(A) + N_2(A) \rightarrow N_2(X) + 2N \tag{1}$$

$$N_2(X, 10 < v < 25) + N_2(X, 10 < v < 25)$$
$$\rightarrow N_2(X) + 2N \tag{2}$$

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and

$$N_2(X, 14 \leqslant v \leqslant 19) + N_2(A)$$
$$\rightarrow N_2(X) + N_2(B, v' \geqslant 13) \rightarrow N_2(X) + 2N \quad (3)$$

Reaction (1) was abandoned soon later due to difficulties in the explanation of experimental data, but even though the problem of lack of nitrogen dissociation was clearly pointed out in [7]. Dissociation in reaction (3) takes place through the excitation of the pre-dissociative levels $N_2(B, v' \geqslant 13)$, as it is suggested in [10]. Notice that at $v \geqslant 20$ reaction (3) does not create $N_2(B, v')$ anymore, but instead the non-dissociative state $N_2(C)$ [10]. It is still worth to note that an important contribution to the total dissociation rate resulting from the excitation of levels $v' \geqslant 13$ in reaction (3) was also mentioned in [11].

In the present Letter we present a theoretical and experimental study of nitrogen dissociation in a N_2 DC glow discharge, operating at gas pressures $p = 0.5$–4 Torr and discharge currents $I = 10$–80 mA. In order to investigate the effect of reactions (2) and (3) in the total rate of dissociation, we have used a detailed kinetic model coupling in a self-consistent way the electron Boltzmann equation and the rate balance equations for the populations of the most important neutral and charged heavy-particles, which has already allowed to obtain an excellent agreement between theory and experiment in DC and HF nitrogen discharges in many situations [9,12–14]. The calculated densities of ground-state atomic nitrogen are compared with absolute measurements performed using the electron spin resonance (ESR) method.

The organization of this article is as follows. Next section briefly presents the details about the experimental procedure used in this work. Section 3 contains the indications relative to the kinetic modeling. The results are presented and discussed in Section 4, while last section summarizes the main conclusions.

2. Experiment

The measurements were performed in a flow system using the setup described in [15,16]. Briefly, the discharge was produced in a S-52 glass cylindrical tube with inner radius $R = 7.5$ mm. The gas flow rate was measured by a capillary rotameter calibrated at atmospheric pressure and room temperature. The electric field sustaining the discharge was measured by the voltage of current compensation in a circuit of two cylindrical probes, each of diameter of 20 μm. The gas temperature at the positive column axis and the wall temperature were determined using a copper–constantan thermocouple. The concentration of ground-state $N(^4S)$ atoms was determined by electron spin resonance (ESR), using a RE1301 radio spectrometer. The atomic nitrogen ESR spectrum consisted of three symmetric equidistant lines of equal intensity and was registered for a magnetic field intensity $H_0 = 3100$ Oe. The absolute concentrations of $N(^4S)$ were determined with an uncertainty of less than 40%. The main plasma parameters corresponding to the conditions of the present investigation can be found in [8], and the reader should refer to [8,15,16] for further details on the experiments.

3. Kinetic model

The theoretical study was conducted using a self-consistent model for a nitrogen DC discharge. The detailed description of the model can be found in [12]. Shortly, we solve the homogeneous electron Boltzmann equation using a two-term expansion in spherical harmonics, coupled to a system of kinetic master equation describing the creation and destruction of the most important neutral and charged heavy-particles, namely the vibrational levels of ground state molecules, $N_2(X\ ^1\Sigma_g^+, v)$, the most important electronically excited states, $N_2(A\ ^3\Sigma_u^+,\ B\ ^3\Pi_g,\ C\ ^3\Pi_u,\ a'\ ^1\Sigma_u^-, a\ ^1\Pi_g,\ w\ ^1\Delta_u)$, ground-state $N(^4S)$ and excited $N(^2D, ^2P)$ atoms, and N_2^+ and N_4^+ ions. The kinetics of the metastable atomic species $N(^2D, ^2P)$, not considered in [12], is taken into account in the same way as in [17]. The reduced electric field sustaining the discharge is obtained from the requirement that in steady-state conditions the total ionization rate must compensate exactly the loss of electrons by ambipolar diffusion and electron–ion

recombination, under the assumption of a quasi-neutral plasma. As discussed in [12], new electrons are created by direct and stepwise electron impact ionization, as well as from the associative reactions $N_2(A) + N_2(a') \rightarrow N_4^+ + e$ and $N_2(a') + N_2(a') \rightarrow N_4^+ + e$. Of course reactions (2) and (3) were added to the kinetic scheme presented in [12,17] and were considered in this work.

The input parameters for the model are the usually externally controlled ones, gas pressure p, tube radius R and discharge current I. The value of the gas temperature can be calculated as described in [18], but for simplicity it was used here as an input parameter as well. It is still worth to note that we have used the constant value $\gamma = 10^{-3}$ for the probability of recombination of $N(^4S)$ atoms at the wall. This approximation is well justified by the measurements of γ reported in [8] for the conditions of this investigation, which did not exhibit any significant dependence of the recombination probability with the pressure (and thus with the wall temperature).

It should be emphasized that the present theoretical model has proved already to be a powerful predictive tool. In effect, it has been used in many different situations with excellent results in what concerns its predictions, such as the calculations of E/N and of the concentrations $[N_2(A\,^3\Sigma_u^+)]$ and $[N_2(B\,^3\Pi_g)]$ in nitrogen DC discharges [12], of E/N and the concentrations $[N_2(A\,^3\Sigma_u^+)]$ and $[N_2(C\,^3\Pi_u)]$ in N_2–O_2 DC discharges [13], of the gas temperature in nitrogen surface-wave discharges [14], and very recently of $[N_2(A\,^3\Sigma_u^+)]$, $[N_2(B\,^3\Pi_g)]$, $[N_2^+(B\,^2\Sigma_u^+)]$ and of the electron density in a nitrogen afterglow [9,19]. That being so, even if the concentrations of $N_2(A\,^3\Sigma_u^+)$ and of $N_2(X\,^1\Sigma_g^+, v)$, which are of interest for reactions (2) and (3), have not been measured in this work, they are determined accurately from the present calculations.

4. Results and discussion

The calculations were done for three values of the discharge current, $I = 20$, 50 and 80 mA, in the pressure range $p = 0.5$–4 Torr. The values of the gas temperature T_g used in the model were taken

from the experiment [8], and vary approximately between 330 and 680 K.

In order to investigate the effect of reactions (2) and (3) on nitrogen dissociation, different series of calculations were realized by testing several values for the corresponding rate coefficients, hereafter denoted by k_2 and k_3, respectively. Figs. 1–3 show the measured and calculated concentrations of ground-state $N(^4S)$ atoms for the three values of I considered here, when different assumptions are made. Thus, curves (A) correspond to $k_2 = k_3 = 0$, so that dissociation takes place only by electron
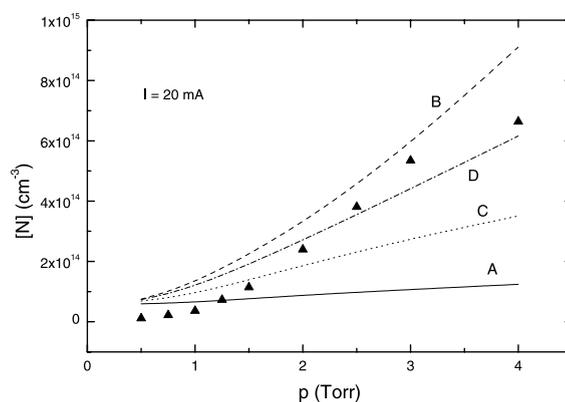

Fig. 1. Measured (points) and calculated (curves) concentrations of ground-state $N(^4S)$ atoms, for $I = 20$ mA and the following values of the rate coefficients of reactions (2) and (3): (A) $k_2 = k_3 = 0$; (B) $k_2 = 7.5 \times 10^{-15}$ cm^3/s and $k_3 = 0$; (C) $k_2 = 0$ and $k_3 = 6.5 \times 10^{-11} \exp(-1765/T_g)$ cm^3/s; (D) $k_2 = 3.5 \times 10^{-15}$ cm^3/s and $k_3 = 4.5 \times 10^{-11} \exp(-1765/T_g)$ cm^3/s.

Fig. 2. The same as in Fig. 1, but for $I = 50$ mA.

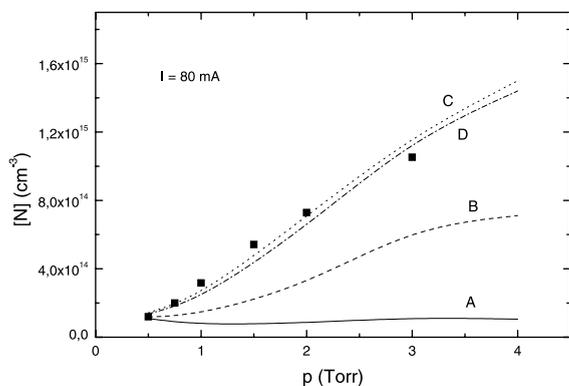Fig. 3. The same as in Fig. 1, but for $I = 80$ mA.

Fig. 4. Relative contribution of the different dissociation channels to the total dissociation rate, for $I = 20$ mA (———) and $I = 80$ mA (- - -): (A) $e + N_2 \rightarrow e + N + N$; (B) $N_2(X, v) + N_2(X, v) \rightarrow N_2 + N + N$, mechanism (2); (C) $N_2(X, v) + N_2(A) \rightarrow N_2 + N + N$, process (3).

impact; curves (B) show the best case considered when only dissociation by reaction (2) is added to electron impact dissociation, with $k_2 = 7.5 \times 10^{-15}$ cm³/s and $k_3 = 0$; curves (C) illustrate the reverse effect, when additional dissociation occurs only via reaction (3), for $k_2 = 0$ and $k_3 = 6.5 \times 10^{-11}$ exp $(-1765/T_g)$ cm³/s, with T_g in K; curves (D) show the conjoint effect of reactions (2) and (3) and were obtained for $k_2 = 3.5 \times 10^{-15}$ cm³/s and $k_3 = 4.5 \times 10^{-11} \exp(-1765/T_g)$ cm³/s, which corresponds to the best case considered in the present study. The exponential factor $\exp(-1765/T_g)$ corresponds to an average value of the energy difference between the energy levels involved in reaction (3). Curves (A) in these figures strikingly confirm that electron impact dissociation alone cannot explain the degree of dissociation experimentally observed. Further inspection of Figs. 1–3 show that dissociation through the mechanism (2) could explain the measured atomic concentrations for $I = 20$ mA, but does not give satisfactory results at higher discharge currents (curves B). On the other hand, dissociation in process (3) has the opposite behavior, providing a good description of the atomic nitrogen yield only at the higher values of I (curves C). Finally, the coupled effect of both dissociation mechanism provides a good comparison between the measured and calculated values for all the conditions considered in this work (curves D).

The indications obtained by the analysis of the previous figures are quantified in Fig. 4, which depicts the relative contribution of the various dissociation mechanisms to the total dissociation
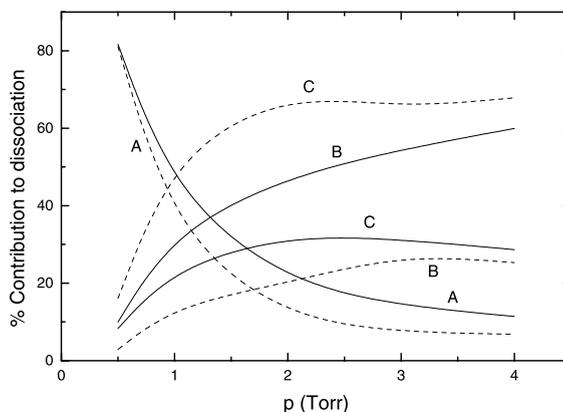
rate, for $I = 20$ mA (full curves) and $I = 80$ mA (dashed curves), calculated for the conditions of curves D from the previous figure. The different labels correspond to the contributions of electron impact dissociation $e + N_2 \rightarrow e + N + N$ (curves A), dissociation according to reaction (2) (curves B), and dissociation via process (3) (curves C). This figure reveals that dissociation of N_2 by electron impact is the major source of atomic nitrogen only at pressures below ~ 1 Torr. For higher values of the pressure, the dissociation processes (2) and (3) start to be effective, their contribution to dissociation reaching values as high as 90%.

The correctness of the present calculations can be checked by comparing the self-consistently calculated and the measured values for the reduced electric field at the discharge axis, shown in Fig. 5 for the three values of I under analysis. The agreement between the theoretical predictions and the experimental values is good in all cases. It can be seen that at the same pressure the values of E/N change only slightly with the discharge current. Therefore, the different behavior of the dissociation mechanisms (2) and (3) in regard to I exhibited in Fig. 4 cannot be attributed to any differences in E/N. On the contrary, the vibrational temperature T_V of ground-state molecules increases with the discharge current. For instance,

at $p = 1$ Torr T_V raises from $T_V \simeq 4750$ K at $I = 20$ mA to $T_V \simeq 7020$ K at $I = 80$ mA, while these values are changed to 4240 K and 6203 K at $p = 4$ Torr. At almost constant E/N, these differences in T_V significantly modify the shape of the electron energy distribution function, favoring the excitation of the metastable state $N_2(A\ ^3\Sigma_u^+)$ at high T_V [20] and, consequently, dissociation according to reaction (3). This is the reason why this later mechanism is more effective at higher values of I.
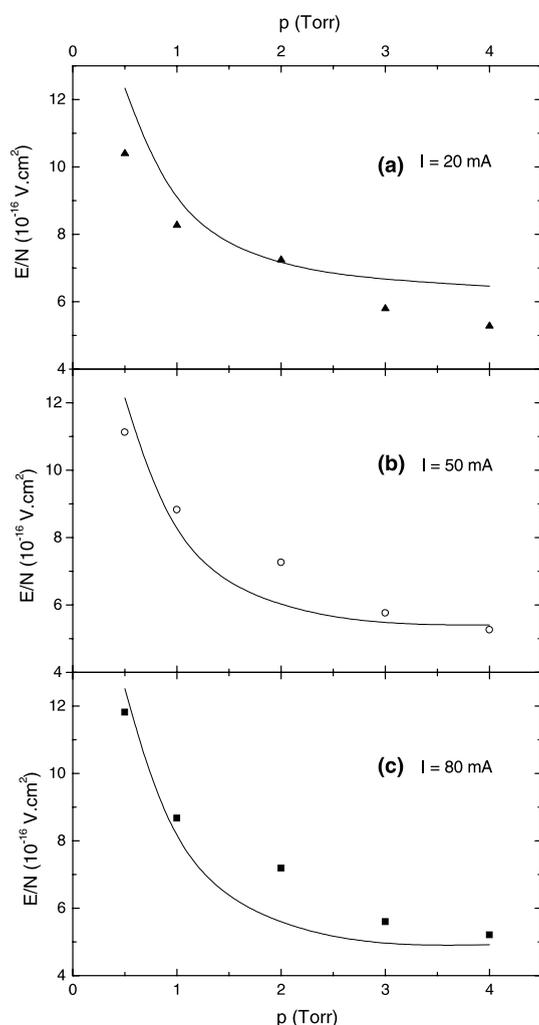

Fig. 5. Measured (points) and calculated (lines) values of the reduces electric field as a function of pressure, for $I = 20$ mA (a), 50 mA (b) and 80 mA (c).

5. Conclusions

In this Letter we have conducted a study on the dissociation mechanisms in low-pressure nitrogen discharges. In agreement with previous observations by several authors [1,7–9], it has been clearly demonstrated that dissociation by direct electron impact, $e + N_2 \rightarrow e + N + N$, cannot explain alone the relatively high atomic nitrogen yield measured experimentally for $p \gtrsim 1$ Torr.

It has been shown that if the ionization degree is high enough to ensure a relatively important value for the vibrational temperature of nitrogen molecules, the increased formation of metastables $N_2(A\ ^3\Sigma_u^+)$ makes dissociation through reaction (3), $N_2(X, 14 \leqslant v \leqslant 19) + N_2(A) \rightarrow N_2(X) + N_2(B, v' \geqslant 13) \rightarrow N_2(X) + 2N$, a major source of $N(^4S)$ atoms. The rate coefficient for this process was estimated in a limited range of T_g, being of the order of 10^{-12} cm^3/s at $T_g = 500$ K. It should be noted that this reaction is known to be very efficient in the excitation of the lower v' levels. In fact, the rate coefficient for excitation of levels $v' \leqslant 12$ in collisions between $N_2(X, 5 \leqslant v \leqslant 14)$ and $N_2(A)$ metastables is accepted to be close to 2×10^{-11} cm^3/s [12,21], so that the value estimated here for k_3 seems very reasonable.

At low discharge currents dissociation by the mechanism (3) does not provide a good explanation of the experimental results. In this case it has been shown that the measurements can be explained by considering an additional source of dissociation, described by equation (2) and rewritten here, $N_2(X, 10 < v < 25) + N_2(X, 10 < v < 25) \rightarrow N_2(X) + 2N$, which is effective under conditions of low ionization degree. Although this reaction furnishes the conciliation between the model predictions and the experimental data for low I, written as it is it seems a relatively unlikely process, so that it probably represents a sequence of other reactions. One possibility is that reaction (2) corresponds to a two step mechanism, like, for example, $2N_2(X, v > 16) \rightarrow N_2(X) + N_2(a')$, followed by $N_2(X, v \geqslant 7) + N_2(a') \rightarrow N_2(X) + N_2(a, v' \geqslant 6) \rightarrow N_2(X) + N + N$. The first of these reactions is considered in [22], with a rate of 10^{-15} cm^3/s, while the second one is quite similar to reaction (3) proposed in this work. However, the direct excitation of the states $N_2(B\ ^3\Pi_g, v')$ and

$N_2(a\ ^1\Pi_g, v')$ in the predissociative levels $v' \geqslant 13$ and $v' \geqslant 6$, respectively, with subsequent dissociation of these states is also possible. For example, reaction $2N_2(X, v > 13) \rightarrow N_2(X) + N_2(B)$ is reported in [10,22] with a rate coefficient of $10^{-15}\ cm^3/s$.

Of course the problem of dissociation in nitrogen discharges at $p \gtrsim 1$ Torr remains open. In the line of the suggestions resulting from the present investigation, future efforts should concentrate in a more accurate determination of the rate coefficient k_3, including its temperature dependence, and in the elucidation of what actual mechanisms are involved in dissociation at low values of I.

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