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Nitrogen Atoms and Triplet States $N_2(B^3\Pi_g)$, $N_2(C^3\Pi_u)$ in Nitrogen Afterglow

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Résumé. — La fluorescence des états $N_2(B^3\Pi_g)$ et $N_2(C^3\Pi_u)$ est observée dans une post-décharge temporelle. Ces fluorescences sont dues à un repeuplement par la réaction de pooling entre états $N_2(A^3\Sigma_u^+)$. A partir d'un modèle cinétique, il est montré que le temps caractéristique de décroissance de l'état $N_2(C^3\Pi_u)$ dépend de la densité d'azote atomique. La densité d'atomes est déduite de la fluorescence observée pour des densités supérieures à $5 \times 10^{13} \text{ cm}^{-3}$. La densité atomique augmente avec la durée et l'intensité de l'impulsion.

Abstract. — The fluorescence of $N_2(B^3\Pi_g)$ and $N_2(C^3\Pi_u)$ states is observed in a time afterglow. This fluorescence is due to repopulation *via* pooling reaction of $N_2(A^3\Sigma_u^+)$ state. From a kinetic model, it is shown that the $N_2(C^3\Pi_u)$ characteristic decay time depends on the atomic nitrogen density. Atomic density is deduced from the observed fluorescence of $N_2(C^3\Pi_u)$ for density higher than $5 \times 10^{13} \text{ cm}^{-3}$. This density increases with pulse duration and current intensity.

1. Introduction

Low pressure nitrogen discharges are used in industrial reactors for nitriding metallic surfaces. The reactors are mainly working with d.c. discharges using samples as cathodes [1].

Process efficiency depends on the gas mixture. Nitride layer production is a function of the surface temperature [2]. In industrial reactor, the sample heating is due to ionic bombardment. The sample temperature is then adjusted with the electrical power injected in the reactor. So, the discharge drives the heating of the metallic sample and reactive nitrogen production. Unfortunately, with d.c. discharges, some arcs can occur and cause some damage on treated surfaces. In order to eliminate these arcs, some authors have studied nitriding in pulsed discharges [3] and in flowing afterglows [4]. In the flowing experiments, the reactive species are created upstream and blown downstream on the samples, out of the excitation zone. So, active nitrogen production is disconnected from the sample heating which can be controlled by an external device. In pulsed discharges, sample heating and active nitrogen production are done by the discharge as in d.c. conditions, but, pulsed mode limits arc production.

In flowing afterglow or pulsed discharges, the reactive gas is submitted during a short time to the discharge. In flowing afterglow this time is a function of the gas flow and the discharge length. In pulsed discharge this time is the pulse duration.

In order to understand the discharge temporal evolution and to obtain data for the optimization of atomic nitrogen production, it is important to know the characteristic times to populate and to relax electronic states and also the characteristic times of molecular nitrogen dissociation and reassociation.

In electrical discharges, molecular nitrogen dissociation occurs by two processes [5, 6] :

- direct electronic impact on the molecular ground state vibrational levels leading to a repulsive potential curve ;
- anharmonic pumping of higher molecular ground state vibrational levels by vibration-vibration and electron-vibration energy transfers leading to a vibrational pseudolevel above the last vibrational level of molecular ground state.

The characteristic time of the first process is on the order of the characteristic time of inelastic electronic collisions on molecules : about $1\text{ }\mu\text{s}$ at $P = 1\text{ Torr}$ for a mean electron energy equal to 1 eV . The second process is linked to the temporal evolutions of the molecular ground state vibrational distribution and the electron energy distribution function which are slow (characteristic time longer than 1 ms) [6].

Some atomic nitrogen density measurements have been performed by NO titration [7] or by V.U.V. optical absorption spectroscopy [8], mainly in flowing afterglows.

In this paper are presented measured $\text{N}_2(\text{C}^3\Pi_u)$ and $\text{N}_2(\text{B}^3\Pi_g)$ fluorescences in a time afterglow. These fluorescences are compared with the calculated ones, deduced from a kinetic model taking into account the coupling between $\text{N}_2(\text{A}^3\Sigma_u^+)$, $\text{N}_2(\text{B}^3\Pi_g)$ and $\text{N}_2(\text{C}^3\Pi_u)$ triplet states and the atomic density.

2. Experiment

The experimental device is shown in Figure 1. The discharge is produced by a high voltage pulsed generator, in a pyrex tube of 50 cm length and 1.5 cm internal diameter. A weak nitrogen flow keeps the gas in high purity condition without pressure gradient. Flowing conditions are adjusted by a needle valve upstream and a throttle valve downstream. The pressure gradient is measured by two gauges : a pirani gauge upstream and a capacitance gauge downstream. In order to improve nitrogen cleanliness and purity, the tube is heated at $200\text{ }^\circ\text{C}$ and a d.c. discharge is maintained with a high gas flow during one hour before the experiments, then the tube is pumped down to 10^{-6} torr by a diffusion pump.

The pulse duration is adjusted by a master pulse generator which is also used as trigger. The pulse duration can be fixed from $25\text{ }\mu\text{s}$ to 5 ms and repetition rate from 10 Hz to 100 Hz . The rise time and fall time of the pulse are about $1\text{ }\mu\text{s}$.

The light emitted is observed along the tube axis through a MgF_2 window. Wavelength selection is carried out by a 64 cm focal monochromator (HRS2 Jobin Tvon). Behind the monochromator exit slit, the light is detected with a side-on photomultiplier (R943-02 Hamamatsu), sensitive in the 160 nm to 930 nm range. The photomultiplier output signal is amplified with a fast preamplifier (Stanford Research System SR440) connected to a multi-channel scaler (SR430) for time resolved photons counting. The photons counting is done over 6 k (6144) channels each 160 ns wide.

Data are transferred to a PC computer to be analyzed.

In the visible and in the near U.V. range the more intense observed bands of the neutral molecules [9] are the first positive system :

Fig. 1. — Experimental set up. D.T. : discharge tube, N.V. : needle valve, T.V. : throttle valve, P.G. : pirani gauge, C.G. : capacitance gauge, P.U. : pumping unit, M. : monochromator, P.M. : photomultiplier, A. : amplifier, M.T. : master trigger, H.V.P.G. : high voltage pulse generator, M.A. : multichannel analyzer.

and the second positive system :

We have checked that the fluorescence decay time is independent of the $\text{N}_2(\text{C}^3 \Pi_u)$ vibrational level. We have experimentally observed that the $\text{N}_2(\text{C}^3 \Pi_u)$ fluorescence is more intense for the upper vibrational levels than for the $v=0$ level. Then we choose the transition which gives the more intense fluorescence :

which is emitted at 326.8 nm.

In the afterglow, the fluorescence of $\text{N}_2(\text{B}^3 \Pi_g)$ could be due to atomic recombination [10] :

The coefficient for this process is $k_{\text{N}-\text{N}}^{\text{B}} = 2.4 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$ [10]. In the lower part of our pressure range this effect is negligible, but can be important for pressures higher than a few torr. In order to minimize the contribution of the recombination, we observe the lower vibrational level of $\text{N}_2(\text{B}^3 \Pi_g)$. Atomic reassociation can give fluorescence on the vibrational levels lower than $v' = 11$ after vibration-vibration transfers. We can suppose that this effect does not occur in the early afterglow.

Because of the wavelength range of our optical device, the lower observable vibrational level of $\text{N}_2(\text{B}^3 \Pi_g)$ is $v' = 2$. The more intense transition is :

which is emitted at $\lambda = 775.4 \text{ nm}$.

3. Experimental Results

Figure 2a presents the $\text{N}_2(\text{C}^3 \Pi_u)$ emission for $P = 0.2 \text{ Torr}$ and a long pulse duration $d = 700 \mu\text{s}$. In the post-discharge, a fast decay mainly due to radiative losses is observed. Following this fast decay, a weak fluorescence can be seen. Figure 2b shows $\text{N}_2(\text{C}^3 \Pi_u)$ emission for higher pressure $P = 0.9 \text{ Torr}$ and a shorter pulse duration $d = 50 \mu\text{s}$. In these conditions, the fluorescence becomes more important.

Figures 3a and 3b present typical normalized $\text{N}_2(\text{C}^3 \Pi_u)$ fluorescence in semilogarithmic plots. In the former, we see that the fluorescence characteristic time becomes shorter as the pulse duration d increases. The later one shows that the fluorescence becomes shorter as the discharge current increases. In both figures, it can be seen that the fluorescence can be correctly described by a monoexponential decay. So, we use a non linear regression in order to fit experimental fluorescences by a function on the form :

Fig. 2. — a) Typical record for $\text{N}_2(\text{C}^3 \Pi_u, v' = 4)$ emission. $P = 0.2 \text{ Torr}$, $d = 700 \mu\text{s}$. b) Typical record of $\text{N}_2(\text{C}^3 \Pi_u, v' = 4)$ emission. $P = 0.9 \text{ Torr}$, $d = 50 \mu\text{s}$.

Fig. 3. — a) Normalized post-discharge $N_2(C^3\Pi_u, v'=4)$ fluorescence for several pulse duration values. $P = 0.2$ Torr, $I = 100$ mA. b) Normalized post-discharge $N_2(C^3\Pi_u, v'=4)$ fluorescence for several discharge current values. $P = 0.9$ Torr, $d = 50$ μ s.

$$[N_2(C^3\Pi_u)](t) = C \exp(-\nu t).$$

The influence of pulse duration and discharge current on the $N_2(C^3\Pi_u)$ decay frequency ν is shown in Figures 4a and 4b.

Figure 5 shows a comparison between normalized $N_2(B^3\Pi_g)$ and $N_2(C^3\Pi_u)$ measured fluorescences in the same experimental conditions. Emission from $N_2(B^3\Pi_g)$ presents a fast decay in the early afterglow. It is important to notice that the characteristic decay times of both states reach the same value in the far afterglow. This last point has been observed by de Benedictis *et al.* in R.F. pulsed discharge in He- N_2 mixture [11]. They analyzed the $N_2(B^3\Pi_g)$ fluorescence as the sum of three exponential decays. The slowest one has the same characteristic decay time as $N_2(C^3\Pi_u)$.

4. Modeling

$N_2(C^3\Pi_u)$ radiative lifetime is equal to 37 ns [9]. Consequently, an emission from this state during the post discharge can only be explained by gain processes.

The excitation of $N_2(C^3\Pi_u)$ and $N_2(B^3\Pi_g)$ by electronic collisions from molecular ground state require electron energy respectively equal to 11.1 eV and 7.4 eV. In the afterglow, the electron density and the mean energy of electrons decrease [12]. In this work, we assume that in the afterglow, the tail of the electrons energy distribution function is no more populated enough in order to obtain a significant excitation of triplet states. Some long life species are present in the afterglow. These species are mainly the vibrational levels $N_2(X^1\Sigma_g^+, w)$ of the molecular ground state, atomic ground state $N(^4S)$ and molecular metastable state $N_2(A^3\Sigma_u^+)$. We suppose that molecules $N_2(X^1\Sigma_g^+, w)$ cannot directly repopulate $N_2(B^3\Pi_g)$ and $N_2(C^3\Pi_u)$ states but can play an important role in a stepwise process [13]. Concerning $N_2(A^3\Sigma_u^+)$, the only radiative transitions are the Vegard Kaplan bands [9]. These transitions are forbidden and then the radiative losses can be neglected in comparison with

Fig. 4. — a) Experimental $N_2(C^3\Pi_u, v'=4)$ decay frequency versus pulse duration for several pressure values. $I = 300$ mA. b) Experimental $N_2(C^3\Pi_u, v'=4)$ decay frequency versus discharge current for several pulse duration values. $P = 0.5$ Torr.

the other loss processes. The main loss processes for $N_2(A^3\Sigma_u^+)$ are the diffusion to the wall [15] and quenching by atoms. Effective lifetime of this state is typically of some milliseconds for pressure about one Torr. Because of its long lifetime, $N_2(A^3\Sigma_u^+)$ is probably the main source of $N_2(B^3\Pi_g)$ and $N_2(C^3\Pi_u)$ production via pooling reactions.

Fig. 5. — Experimental fluorescences of $N_2(C^3\Pi_u, v'=4)$ and $N_2(B^3\Pi_g, v'=2)$ for $P = 0.9$ Torr, $I = 100$ mA and $d = 50$ μ s. Comparison with calculated fluorescences for corresponding initial conditions. In this calculation the reaction R7 is neglected and $[N] = 2.8 \times 10^{13} \text{ cm}^{-3}$

According to these remarks, we assume that $N_2(C^3\Pi_u)$ state is coupled with $N_2(B^3\Pi_g)$, $N_2(A^3\Sigma_u^+)$, $N_2(X^1\Sigma_g^+)$ and $N(^4S)$ by the following reactions :

- $N_2(B^3\Pi_g)$ and $N_2(C^3\Pi_u)$ radiative transfers :

- $N_2(A^3\Sigma_u^+)$ pooling reactions :

- $N_2(A^3\Sigma_u^+)$ quenching by atoms :

- $N_2(B^3\Pi_g)$ quenching by molecules :

- collisional transfer :

- $N_2(A^3\Sigma_u^+)$ diffusion to the wall :

$$\text{frequency } \nu_D \quad R8.$$

If a Bessel radial profile is assumed, the diffusion frequency is $\nu_D = D_A / \lambda^2$ where D_A is the diffusion coefficient and λ the diffusion length equal to $R/2.4$ if R is the tube radius.

The diffusion coefficient of $N_2(A^3\Sigma_u^+)$ has been measured for a pressure of 1 Torr at 300 K [15]: $D_A = 155 \pm 9 \text{ cm}^2 \text{ s}^{-1}$ (for $v = 0$).

The pooling reaction R3 is the only production process for $N_2(C^3\Pi_u)$ in the afterglow and this state is lost only by radiative emission R2.

The rate coefficients for all the collisional reactions are presented in Table I. These coefficients have been used for all the electronic states without vibrational discrimination. As we have seen previously, no vibrational dependence of $N_2(C^3\Pi_u)$ fluorescence is observed. For the radiative processes R1 and R2, we can then suppose that the vibrational level $v = 0$ for $N_2(B^3\Pi_g)$ and $N_2(C^3\Pi_g)$ are relevant to describe the fluorescence of these states. So, for the radiative loss we have considered the radiative lifetimes i.e. [9]:

$$\tau_1 = 37 \text{ ns} \quad \text{for} \quad N_2(C^3\Pi_u, v' = 0)$$

$$\tau_4 = 8.9 \text{ ns} \quad \text{for} \quad N_2(B^3\Pi_g, v' = 0) .$$

Table I. — Rate coefficients used in the kinetics of $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$ and $N_2(C^3\Pi_u)$ states.

Reaction	Rate coefficient	Reference
R3	$k_{A \rightarrow A}^C \approx 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	[22]
R4	$k_{A \rightarrow A}^B \approx 7.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	[23]
R5	$k_{A \rightarrow N} = 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	[24]
R6	$k_Q \approx 2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	[25]
R7	$k_{A \rightarrow X}^B = 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	[26]
R8	$\nu_D = \frac{1.74 \times 10^3}{P \text{ (Torr)}} \text{ s}^{-1}$	[15]

In the kinetic model, these processes are described by the transition probabilities :

$$A_1 = \frac{1}{\tau_1} \quad \text{and} \quad A_4 = \frac{1}{\tau_4}$$

The population of $N_2(B^3 \Pi_g, v=0)$ and $N_2(A^3 \Sigma_u^+, v=0)$ by radiative cascade depends on the vibrational distribution of the upper electronic state which is not known. Therefore, only the radiative transition between the more populated levels which are the $v=0$ levels is taken into account. The transition probabilities are [9] :

$$A_3 = 1.39 \times 10^7 \text{ s}^{-1} \quad \text{for} \quad N_2(C^3 \Pi_u, v'=0) \rightarrow N_2(B^3 \Pi_g, v''=0)$$

$$A_2 = 6.25 \times 10^4 \text{ s}^{-1} \quad \text{for} \quad N_2(B^3 \Pi_g, v'=0) \rightarrow N_2(A^3 \Sigma_u^+, v''=0) .$$

The time evolution of densities of the three triplet states is then described by the following equations :

$$\begin{cases} \frac{\partial [N_2(A)]}{\partial t} = A_2 [N_2(B)] - k_{A-A} [N_2(A)]^2 - [N_2(A)](v_D + k_{A-N} [N]) \\ \quad - k_{A-X}^B [N_2(A)] [N_2(X, w \geq 6)] \\ \frac{\partial [N_2(B)]}{\partial t} = k_{A-A}^B [N_2(A)]^2 + A_3 [N_2(C)] + k_{A-X}^B [N_2(A)] [N_2(X, w \geq 6)] \\ \quad - [N_2(B)](A_4 + k_Q [N_2(X)]) \\ \frac{\partial [N_2(C)]}{\partial t} = k_{A-A}^C [N_2(A)]^2 - A_1 [N_2(C)] . \end{cases}$$

These equations also depend on the temporal evolution of $[N_2(X^1 \Sigma_g^+, v'=6)]$ [16] and $[N]$ [17] densities. The temporal evolutions of these species are slow, on the order of a few milliseconds. During the observed fluorescence, we can suppose that $[N_2(X^1 \Sigma_g^+, v' \geq 6)]$ and $[N]$ are constant.

The values of density at the beginning of the afterglow presented in Table II have been determined in d.c. discharges for $N_2(A^3 \Sigma_u^+)$ [18], $N_2(B^3 \Pi_g)$ [19] and $N_2(C^3 \Pi_u)$ [20]. The $N_2(X^1 \Sigma_g^+, v' \geq 6)$ density is taken from the results of a numerical simulation [21].

Figure 6 shows calculated $N_2(A^3 \Sigma_u^+)$, $N_2(B^3 \Pi_g)$ and $N_2(C^3 \Pi_u)$ densities in the afterglow for $[N] = 3 \times 10^{14} \text{ cm}^{-3}$ and $P = 0.9 \text{ Torr}$. We obtain monoexponential decays for the three states. The $N_2(B^3 \Pi_g)$ and $N_2(C^3 \Pi_u)$ characteristic decay times are not the same, which is the contrary to the experimental observations (Fig. 5). $N_2(A^3 \Sigma_u^+)$ and $N_2(B^3 \Pi_g)$ present the same decay. This is due to the strong coupling between these two states *via* the reaction R7.

$N_2(X^1 \Sigma_g^+, v' \geq 6)$ density could be overestimated and so, $N_2(B^3 \Pi_g)$ gain due to reaction R7 could be overestimated too. If we neglect reaction R7 in our kinetic scheme, we obtain the $N_2(B^3 \Pi_g)$ and $N_2(C^3 \Pi_u)$ normalized fluorescences (calculations) shown in Figure 5. A good agreement with experimental fluorescences in the far afterglow is obtained. The calculated decay of $N_2(B^3 \Pi_g)$ state presents two slopes. The fastest one is not in good agreement with the experiment which is slower. In our modelling, the fast decay is only due to radiative loss. So there could be a missing fast gain process for $N_2(B^3 \Pi_g)$ in our kinetics. Anyway, this disagreement stops in the far afterglow where calculated and measured fluorescences for the two states becomes parallel. Consequently, as we obtain a good fit of experimental fluorescences in the far afterglow neglecting reaction R7, we will not consider any more this process in our kinetics.

Table II. — *Initial density at the beginning of the afterglow.*

Pressure (Torr)	Initial density (cm ⁻³)				
	[N ₂ (A)] ₀	[N ₂ (B)] ₀	[N ₂ (C)] ₀	[N ₂ (X)]	[N ₂ (X,w=6)]
0.09	6 10 ¹¹	6 10 ¹⁰	6 10 ⁷	3.2 10 ¹³	1.2 10 ¹³
0.2	9 10 ¹¹	8 10 ¹⁰	5 10 ⁷	7.1 10 ¹³	2.8 10 ¹³
0.5	1.5 10 ¹²	10 ¹¹	4 10 ⁷	1.7 10 ¹⁶	6.8 10 ¹³
0.9	1.2 10 ¹²	1.1 10 ¹¹	2 10 ⁷	3.2 10 ¹⁶	1.4 10 ¹⁴
3.85	5 10 ¹¹	2 10 ¹¹	10 ⁷	1.4 10 ¹⁷	5.6 10 ¹⁴

Fig. 6. — Calculated densities of N₂(C³Π_u), N₂(B³Π_g) and N₂(A³Σ_u⁺) for P = 0.9 Torr assuming an atomic density [N] = 3 × 10¹⁴ cm⁻³.

Calculated N₂(C³Π_u) fluorescences are shown in Figure 7 for P = 0.9 Torr with atomic density as input parameter. N₂(C³Π_u) fluorescence becomes shorter as atomic density increases. This is due to the quenching of N₂(A³Σ_u⁺) by atomic nitrogen (reaction R5). N₂(A³Σ_u⁺) losses reduce N₂(C³Π_u) gain by pooling reaction R3.

In Figure 8 the atomic nitrogen density (used as input data) is shown as a function of the calculated N₂(C³Π_u) decay frequency. For low atomic density, the dependence of calculated N₂(C³Π_u) decay frequency on atomic density becomes weak. When the atomic density de-

creases, $N_2(A^3\Sigma_u^+)$ loss by atomic quenching decreases towards the loss by diffusion and then the sensitiveness of $N_2(C^3\Pi_u)$ fluorescence to atomic density becomes low. We can see in Figure 8 that this effect increases as the pressure decreases.

Using the results of the model shown in Figure 8 we can estimate atomic nitrogen density from the experimental $N_2(C^3\Pi_u)$ decay frequencies shown in Figures 4a and 4b. Some results of these estimations are shown in Figures 9a and 9b. In Figure 9a, it can be seen that

Fig. 7. — Calculated $N_2(C^3\Pi_u)$ fluorescence for several atomic density values. $P = 0.9$ Torr.

Fig. 8. — Calculation results. Atomic nitrogen density (input data) versus the obtained $N_2(C^3\Pi_u)$ decay frequency for several pressure values.

atomic density increases with pulse duration. It seems that a steady state for molecular dissociation is not reached in the case of pulse durations shorter than 700 μs . Figure 9b shows that atomic density increases with the discharge current for any pulse duration value.

Fig. 9. — a) Atomic density estimations *versus* pulse duration from the experimental values of $\text{N}_2(\text{C}^3\Pi_u)$ decay frequency reported in Figure 4a. b) Atomic density estimations *versus* discharge current from the experimental values of $\text{N}_2(\text{C}^3\Pi_u)$ decay frequency reported in Figure 4b.

In our experimental conditions, the atomic nitrogen density ranges from $2 \times 10^{12} \text{ cm}^{-3}$ to $5 \times 10^{14} \text{ cm}^{-3}$

5. Discussion

The results of our calculations can be compared with atomic nitrogen measurements in post discharges. Mainly, flowing afterglows of DC or microwave discharges were studied using several technic : mass spectroscopy, VUV optical absorption [28], NO titration and emission of the first positive system.

VUV absorption was used in low pressure afterglow where nitrogen atoms were produced by ionic dissociative recombination [28]. In these conditions, $[\text{N}]$ was about 10^{13} cm^{-3}

The nitrogen atoms can be measured with NO titration. For instance, in discharges working in a gas flow, NO is injected downstream of the plasma, far enough from the discharge in order to observe the NO chemiluminescence without perturbation from the light emitted by the excitation zone. Thus, NO titration gives $[\text{N}]$ measurements only at about one millisecond after the discharge. In DC discharge flowing afterglows, for $I = 100 \text{ mA}$, the $[\text{N}]$ density increases from $2 \times 10^{14} \text{ cm}^{-3}$ to 10^{15} cm^{-3} with pressure increasing from 0.6 to 2 Torr [29]. In microwaves afterglow at 8 Torr, by NO titration the nitrogen density is about 10^{15} cm^{-3} [30].

Mass spectroscopy was used by Yamashita [17] in nitrogen discharge and post discharge. After an absolute calibration with NO titration, the deduced nitrogen density is of $4 \times 10^{14} \text{ cm}^{-3}$ in a 4 Torr microwave discharge. Mass spectroscopy is usable in discharge and post discharge without any time limitation, but this technic is not easy to develop.

In nitrogen flowing afterglow, atomic recombination

leads to the emission of the first positive system in the Lewis Rayleigh Afterglow (LRA) mainly from the vibrational levels $v' = 10, 11$ and 12 of $\text{N}_2(\text{B}^3\Pi_g)$ state [31]. In pure nitrogen microwave afterglow, after NO calibration, emission of the first positive system gives atomic nitrogen densities of about 10^{15} cm^{-3} for $P = 2 \text{ Torr}$ [32]. Because of the pooling reaction mentioned above, the first positive system emission cannot be used for $[\text{N}]$ measurements at the beginning of the afterglow.

The method presented in this paper, useable at the beginning of the post discharge, gives atomic densities in accordance with other technic.

Some other electronic states could exist in the afterglow. So we must now discuss their possible influence on the presented kinetics.

The molecular metastable singlet state $\text{N}_2(\text{a}^1\Pi_g)$ radiative lifetime is $54 \mu\text{s}$. Moreover its effective lifetime is shorter because of the quenching process [14]. So this state does not have any influence on $\text{N}_2(\text{C}^3\Pi_u)$ fluorescence which is observed during a few hundred microseconds.

$\text{N}_2(\text{E}^3\Sigma_g^+)$ could lead to the creation of $\text{N}_2(\text{C}^3\Pi_u)$ via radiative and collisional transfers [27]. The only $\text{N}_2(\text{E}^3\Sigma_g^+)$ gain process that could maintain this density during the afterglow is atomic recombination :

In order to overestimate $\text{N}_2(\text{E}^3\Sigma_g^+)$ effective lifetime we assume that $\text{N}(^2\text{D})$ density is constant in the afterglow and we only consider loss processes which lead to $\text{N}_2(\text{C}^3\Pi_u)$ creation. Then $\text{N}_2(\text{E}^3\Sigma_g^+)$ density is the solution of the equation :

$$\frac{\partial [N_2(E)]}{\partial t} = -\nu_E [N_2(E)] + G_E$$

where ν_E is the sum of the Einstein spontaneous emission coefficient and of the collisional transfer frequency, G_E is the creation rate by atomic recombination :

$$\nu_E = A_{E-C} + k_{E-C} [N_2] \quad G_E = [N(^4S)][N(^2D)][N_2] k_{N-N}^E.$$

Then $N_2(E^3\Sigma_g^+)$ density is :

$$[N_2(E)](t) = \left([N_2(E)]_0 - \frac{G_E}{\nu_E} \right) \exp(-\nu_E t) + \frac{G_E}{\nu_E}$$

Burns *et al.* [27] have measured the radiative cascade and the collisional transfer from $N_2(E^3\Sigma_g^+)$ to $N_2(C^3\Pi_u)$. The Einstein spontaneous emission coefficient A_{E-C} is equal to 1840 s^{-1} and the collisional transfer coefficient k_{E-C} is estimated equal to $5 \times 10^{-11}\text{ cm}^3\text{ s}^{-1}$. For $P=1\text{ Torr}$, because of quenching efficiency, $N_2(E^3\Sigma_g^+)$ density can be approximated as $[N_2(E)](t) \sim G_E/\nu_E$ after $20\text{ }\mu\text{s}$, if we assume an initial density $[N_2(E)]_0$ lower than 10^{14} cm^{-3} . So we must add a constant $N_2(C^3\Pi_u)$ gain in the form $\nu_E [N_2(E)] \sim G_E$. We can strongly overestimate this gain assuming that $[N(S)] = 10^{15}\text{ cm}^{-3}$ and an atomic metastable density $[N(D)] = 10^{11}\text{ cm}^{-3}$ (which is the maximum value measured in a D.C. discharge [33]) and a recombination coefficient $k_{N-N}^E \sim k_{N-N}^B = 2.4 \times 10^{-33}\text{ cm}^6\text{ s}^{-1}$ [10]. Then, we find $G_E = 7.7 \times 10^9\text{ cm}^{-3}\text{ s}^{-1}$ while the initial gain from the pooling reaction is $2 \times 10^{14}\text{ cm}^{-3}\text{ s}^{-1}$. So it is reasonable to assume that $N_2(E^3\Sigma_g^+)$ has no influence on the $N_2(C^3\Pi_u)$ fluorescence.

Conclusion

The fluorescence of $N_2(C^3\Pi_u)$ is coupled with metastable $N_2(A^3\Sigma_u^+)$ and nitrogen atom concentrations. The experimental decay time of $N_2(C^3\Pi_u)$ can be fitted trying different values of nitrogen atom density in the kinetic model. This method could give a good estimation of nitrogen atom density in electrical discharges.

References

- [1] Hudis M., *J. Appl. Phys.* **44** (1973) 1489, Study of ion-nitriding.
- [2] Wriedt H. A. *et al.*, Binary Alloy phase Diagrams, A.S.M. (October 1986) p. 1081.
- [3] Henrion G., Fabry M., Hugon R., Bougdira J., Spectroscopic investigation of a temporal post-discharge plasma for ion nitriding, *Plasma Sources Sci. Technol.* **1** (1992) 117.
- [4] Ricard A., Oseguera J. E., Falk L., Michel H., Gantois M., Active Species in Microwave Postdischarge For Steel-Surface Nitriding, *IEEE Trans. Plasma Sci.* **18** (1990) 940.
- [5] Capitelli M., Dilonardo M., Non-equilibrium dissociation of nitrogen, *Rev. Phys. Appl.* **13** (1978) 115.
- [6] Loureiro J., Ferreira C. M., Capitelli M., Gorse C., Cacciatore M., Non-equilibrium kinetics in nitrogen discharges : a comparative analysis of two theoretical approaches, *J. Phys. D : Appl. Phys.* **23** (1990) 1371.
- [7] Herron J. M., Franklin J. L., Bradt P., Dibeler V. M., Kinetics of Nitrogen Atom Recombination, *J. Chem. Phys.* **30** (1959) 879.
- [8] Lin C. L., Kaufman F., Reactions of Metastable Nitrogen Atoms, *J. Chem. Phys.* **55** (1971) 3760.

- [9] Lofthus A., Krupenie P. H., The spectrum of molecular nitrogen, *J. Phys. Chem. Ref. Data* **6** (1977) 113.
- [10] Brunet H., Rocca Serra J., Model for a glow discharge in flowing nitrogen, *J. Appl. Phys.* **57** (1985) 1574.
- [11] de Benedictis S., Dilecce G., Schifano E., Capitelli M., « Decay of excited species in post-discharge regime of He-N₂ RF pulsed discharge », XX ICPIG Conf., Vol. 1 (1991) p. 83.
- [12] Gorbunov N. A., Kolokolov N. B., Kudryavtsev A. A., Development of the electron energy distribution in the plasma of a nitrogen afterglow in the local regime, *Sov. Phys. Tech. Phys.* **36** (1991) 6.
- [13] Gorse C., Capitelli M., Coupled electron and excited-state kinetics in a nitrogen afterglow, *J. Appl. Phys.* **62** (1987) 4072.
- [14] Magne L., Cernogora G., Veis P., Relaxation of metastable N₂(a¹Π_g, v'=0-2) in nitrogen afterglow, *J. Phys. D.: Appl. Phys.* **25** (1992) 472.
- [15] Zipf E. C. Jr, Diffusion coefficient and radiative lifetime of nitrogen molecules in the A³Σ_u⁺ state, *J. Chem. Phys.* **38** (1963) 2034.
- [16] Capitelli M., Gorse C., Ricard A., Time scale consideration on the relaxation of electronic and vibrational energy distributions in a nitrogen afterglow, *J. Phys. Letters* **44** (1983) L251-256.
- [17] Yamashita T., Rate of recombination of nitrogen atoms, *J. Chem. Phys.* **70** (1979) 4248.
- [18] Cernogora G., Ferreira C. M., Hochard L., Touzeau M., Loureiro J., Vibrational populations of N₂(A³Σ_u⁺) in a pure nitrogen glow discharge, *J. Phys. B.: At. Mol. Phys.* **17** (1984) 4429.
- [19] Ferreira C. M., Touzeau M., Hochard L., Cernogora G., Vibrational populations of N₂(B³Π_g) in a pure nitrogen glow discharge, *J. Phys. B.: At. Mol. Phys.* **17** (1984) 4439.
- [20] Ferreira C. M., Hochard L., Touzeau M., Cernogora G., « Vibrational populations of N₂(C³Π_u) in a pure nitrogen glow discharge », XVI ICPIG Conf. **4** (1983) p. 450.
- [21] Loureiro J., Ferreira C. M., Electron excitation rates and transport parameters in direct-current N₂ discharges, *J. Phys. D* **22** (1989) 67.
- [22] Piper L. G., State to state N₂(A³Σ_u⁺) energy-pooling reaction. I. The formation of N₂(C³Π_u) and the Hermann infrared system; *J. Chem. Phys.* **88** (1988) 231.
- [23] Piper L. G., State to state N₂(A³Σ_u⁺) energy-pooling reaction. II. The formation and quenching of N₂(B³Π_g, v'=1-12), *J. Chem. Phys.* **88** (1988) 6911.
- [24] Piper L. G., The excitation of N(²P) by N₂(A³Σ_u⁺, v'=0, 1), *J. Chem. Phys.* **90** (1989) 7087.
- [25] Heidner III R. F., Sutton D. G., Suchard S. N., Kinetic study of N₂(B³Π_g, v) quenching by laser-induced fluorescence, *Chem. Phys. Letters* **37** (1976) 243.
- [26] Piper L. G., The excitation of N₂(B³Π_g, v'=1-12) in the reaction between N₂(A³Σ_u⁺) and N₂(X, v ≥ 5), *J. Chem. Phys.* **91** (1989) 864.
- [27] Burns D. J., Golden D. E., Galliart D. W., Electron excitation of the E³Σ_g⁺ state of N₂ and subsequent collisional deactivation and energy transfer to the C³Π_u state, *J. Chem. Phys.* **65** (1976) 2616.
- [28] Queffelec J. L., Rowe B. R., Morlais M., Gomet J. C., Vallée F., The dissociative recombination of N₂⁺ as a source of metastable atoms in planetary atmosphere, *Planet. Space Sci.* **33** 263-70 (1985).
- [29] Cernogora G., Hochard L., Touzeau M., Ferreira C. M., Population of N₂(A³Σ_u⁺) metastable states in a pure nitrogen glow discharge, *J. Phys. B.: At. Mol. Phys.* **14** (1981) 2977-87.
- [30] Normand Chave C., Etude et modélisation de la post décharge d'une décharge micro-onde d'azote ou d'azote argon en flux. Thesis Université Paris Sud (1991).
- [31] Campbell I. M., Thrush B. A., The recombination of nitrogen atoms and the nitrogen afterglow, *Proc. R. Soc. London Ser. A* **296** (1967) 201-221.
- [32] Ricard A., Oseguera-Pena J. E., Falk L., Michel H., Gantois M., Active species in microwave post-discharge for steel-surface nitriding, *IEEE Trans. Plasma Sci.* **18** (1990) 940-4.
- [33] Cernogora G., Etude des états métastables de l'azote atomique dans une décharge luminescente, Thesis Université Paris Sud (1980).