Non-equilibrium kinetics in N_2 discharges and post-discharges: a full picture by modelling and impact on the applications

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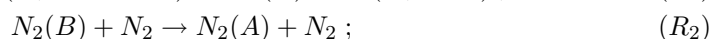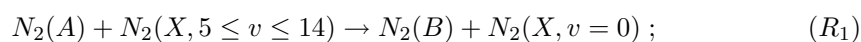[(*)] **jorge.loureiro@ist.utl.pt**

1. Introduction

The study of non-equilibrium kinetics in pure N_2 low-pressure discharges and post-discharges, as well as in mixtures of this gas with Ar, H_2, O_2 and CH_4, is receiving great attention in the past two decades, both experimental and theoretical. Not only due to its large interest in many applications but also for an insight in the understanding of the interplay kinetics of elementary processes. Modelling is an important issue of this research since accurate self-consistent models of the discharge and post-discharge are now available. They have largely improved our understanding of the kinetics of charged and neutral species in these active media [1-6]. The aim of this talk is presenting an overall review of the main aspects dealt with the modelling of such systems and discussing the impact on some applications.
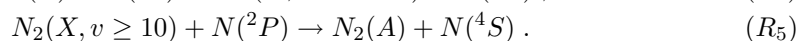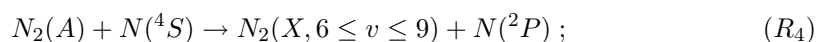
2. Modelling details

This study is based on a detailed numerical kinetic model with two separate modules, one for the discharge and another for the post-discharge, being the solutions obtained in the discharge the initial conditions for the post-discharge. The module for the discharge includes the homogeneous electron Boltzmann equation and a system of stationary rate balance equations for the molecular and atomic species and ions. This coupled system is self-consistently solved either in a dc or a hf field. The maintenance electric field is self-consistently determined. In the case of a discharge in pure N_2, the kinetic model allows to determine the so-called electron energy distribution function (EEDF), the vibrational distribution function (VDF) of $N_2(X,v)$ molecules, the concentrations of the most populated electronic states $N_2(A, B, C, a', a, w)$, $N(^4S, {}^2D, {}^2P)$ atoms, and $N_2^+(X, B)$ and N_4^+ ions. As a gas mixture is considered, such as N_2-O_2 and N_2-CH_4 analyzed in this presentation, other species and ions need also to be included. With respect to the module for the post-discharge, it includes the time-dependent electron Boltzmann equation, with a term describing the transition from ambipolar to free diffusion, and a system of time-dependent rate balance equations for relaxation of the various neutral and ionic species.

3. Dissociation and ionization in N_2

The dominant aspect to be reinforced about the kinetics in N_2 is the strong coupling between the $N_2(A)$ and $N_2(B)$ states via collisional interplay reactions, quenching and radiative decay:

$$N_2(A) + N_2(X, 5 \leq v \leq 14) \rightarrow N_2(B) + N_2(X, v = 0) ; \qquad (R_1)$$

$$N_2(B) + N_2 \rightarrow N_2(A) + N_2 ; \qquad (R_2)$$

$$N_2(B) \rightarrow N_2(A) + h\nu . \qquad (R_3)$$

The $N_2(A)$ metastable is also coupled with the nitrogen atoms $N(^4S, {}^2P)$ through the following reactions:

$$N_2(A) + N(^4S) \rightarrow N_2(X, 6 \leq v \leq 9) + N(^2P) ; \qquad (R_4)$$

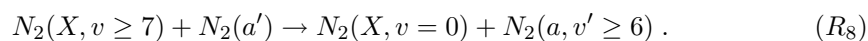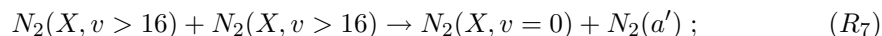$$N_2(X, v \geq 10) + N(^2P) \rightarrow N_2(A) + N(^4S) . \qquad (R_5)$$

The quenching of $N_2(B)$ via reaction R_2 is the most important mechanism for creating $N_2(A)$. This contribution is by far dominant as compared with those due to radiative decay from $N_2(B)$ and electron impact. On the other hand, the $N_2(A)$ metastables are mainly destroyed by reaction R_1 and in a smaller extent in collisions with $N(^4S)$ atoms via reaction R_4. This latter reaction is nearly exactly balanced by the reverse reaction R_5 for production of $N_2(A)$. The diffusion of $N_2(A)$ to the wall presents always a negligible role excepting in the case of lower pressures $p < 0.5$ torr. In the case of $N_2(B)$ molecules, they are mainly created via reaction R_1. The contributions of direct electron impact on $N_2(X)$ molecules, of $N_2(C)$ pooling reactions, radiative decay from $N_2(C)$, and intersystem crossing from $N_2(a')$ are always much smaller than the populating from $N_2(A)$. In conclusion, the combined effect of reactions R_1 and R_2 does not constitute an effective populating/depopulating mechanism for $N_2(A)$ and $N_2(B)$, since they just redistribute a constant population among the triplet manifold [2]. Another coupling occurs with the nitrogen atoms $N(^4S)$ and $N(^2P)$ through reactions R_4 and R_5, although at the earlier instants of the afterglow this equilibrium breaks down due to a much faster deactivation of $N_2(A)$ as compared with the deactivation of $N_2(X,v\sim10)$ levels [7].

It is known since the seventies that dissociation by electron impact alone cannot explain the relatively high concentrations of dissociated atoms $N(^4S)$ observed in nitrogen discharges at pressures typically larger than $p \sim 1$ torr. Moreover, when the VDF of $N_2(X,v)$ molecules are properly taken into account, with the inclusion of vibrational deactivation by V-T processes in N_2-N collisions and vibrational deactivation on the wall, the population of highly vibrational levels rapidly decreases and the contribution of vibration-dissociation (V-D) is unable to explain the discrepancy between measured and predicted $N(^4S)$ concentrations. Thus, the excitation of the pre-dissociative levels $N_2(B,v'\geq13)$:
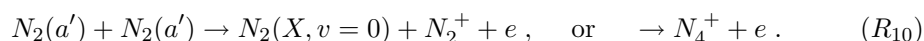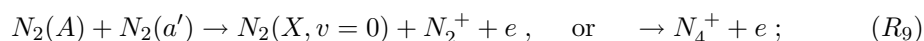
$$N_2(X, 14 \leq v \leq 19) + N_2(A) \rightarrow N_2(X, v = 0) + N_2(B, v' \geq 13) \qquad (R_6)$$
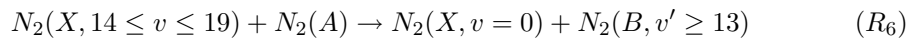
and the two step mechanism involving the excitation of the pre-dissociative levels $N_2(a,v'\geq6)$:

$$N_2(X, v > 16) + N_2(X, v > 16) \rightarrow N_2(X, v = 0) + N_2(a') ; \qquad (R_7)$$

$$N_2(X, v \geq 7) + N_2(a') \rightarrow N_2(X, v = 0) + N_2(a, v' \geq 6) . \qquad (R_8)$$

are the most probable dissociation channels in N_2 since they provide a good interpretation of experimental data [8].

The uncertainties found for the dissociation also exist in ionization. Here, the ionization by electron impact alone cannot also explain the relatively high ionization rates measured in low-pressure discharges, while the VDF at high vibrational levels are not enough populated in order the vibrational-ionization (V-I) may occur. It is now usually assumed that besides ionization by electron impact, either due to collisions on the electronic ground-state $N_2(X)$ or stepwise ionization from $N_2(A)$ and $N_2(a')$ states, the most important ionization paths result from collisions between the electronic states $N_2(A)$ and $N_2(a')$ as follows [9]:

$$N_2(A) + N_2(a') \rightarrow N_2(X, v = 0) + N_2^+ + e , \quad \text{or} \quad \rightarrow N_4^+ + e ; \qquad (R_9)$$

$$N_2(a') + N_2(a') \rightarrow N_2(X, v = 0) + N_2^+ + e , \quad \text{or} \quad \rightarrow N_4^+ + e . \qquad (R_{10})$$

Another possible reaction for associative ionization is that due to collisions between $N(^2P)$ atoms [10]:

$$N(^2P) + N(^2P) \rightarrow N_2^+ + e . \qquad (R_{11})$$

Although R_{11} is not very important in a discharge it may help to explain the anomalously slow decay of the nitrogen discharged plasma at the beginning of the afterglow [7].

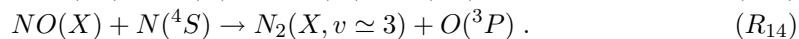## 4. Electron density decay and optical emissions in the afterglow
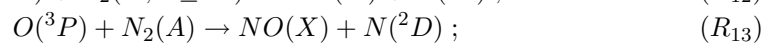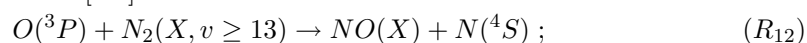
As the applied electric field drops to zero at the end of a discharge, the space-charge field

still remains during a certain period due to the presence of electrons and ions. The loss of electrons by diffusion is then progressively transformed from ambipolar to free diffusion as long as the space-charge field decreases. This leads to an increase of the rate for escape of electrons by diffusion and consequently to a more rapid decay of the electron density. The evolution of the EEDF in the afterglow from the instant $t = 0$ may be studied by solving the time-dependent Boltzmann equation [11]. In general trends, the high-energy tail of the EEDF is rapid depopulated at the earlier instants $t < 10^{-7}$ s, due to electron inelastic collisions, and for $t > 10^{-6}$ s the EEDF attains a quasi-stationary regime, in the range $0.3-3.8$ eV, due to a nearly exact compensation between the inelastic and the superelastic e-V collisions. On the other hand, the electron density remains practically unchanged up to $t \sim 10^{-5}$ s due to the large characteristic time for electron losses by ambipolar diffusion. Only as the electron diffusion changes from ambipolar to free diffusion the electron density starts to decrease significantly [11].

In a flowing N_2 discharge two different afterglow emission zones usually occur. One exists in the far remote zones of the post-discharge, with its origin in the homogeneous three-body recombination of $N(^4S)$ atoms, which leads to a strong emission of the first positive system bands (1^+). The other occurs upstream, at a short distance from the end of the discharge (short lived afterglow), and it is characterized by emission of the first negative systems bands (1^-) associated with transitions between the ionic states $N_2^+(B)$ and $N_2^+(X)$. Due to its pink coloring this emission is usually called pink afterglow. The existence of a dark zone at the end of the discharge just before the enhancement of the spectroscopic emissions of the 1^- bands indicates that the upper emitting ionic-state $N_2^+(B)$ cannot be created in the discharge and carried out to the post-discharge. It needs to be locally produced from $N_2^+(X)$ via a near-resonant vibration-electronic (V-E) exchange reaction, since the rates for $N_2^+(B)$ excitation by electron impact are vanishingly small due to the smallness of the electron cross section for this process together with the depletion of the EEDF at the end of the discharge. Moreover, the $N_2^+(X)$ ions are produced by the Penning ionization reactions R_9 and R_{10} referred above, while the metastables $N_2(A)$ and $N_2(a')$ are created by a V-V pumping-up mechanism involving vibrational molecules in levels as high as v ~ 38 [7]. A maximum on the electron density, $n_e(t)$, arises at the same instant in agreement with the experiment.

5. Discharges and post-discharges in N_2-O_2 plasmas

The non-equilibrium kinetics of low-pressure plasmas in N_2-O_2 mixtures is nowadays an important field of research in order to improve our understanding of the processes occuring in the atmosphere and the ionosphere, and in a variety of modern plasma technologies. This system has also been studied for plasma sterilization of heat sensitive medical materials and instruments [12]. Since the NO(B) and NO(A) molecules, responsable for the emission of UV NOβ and NOγ bands, and the $O(^3P)$ atoms are known to play a central role in sterilization, a particular interest is attributed to the various reactions describing the kinetics of the nitric oxides NO(X), NO(A) and NO(B). The NO(X) molecules are mainly created by collision of $O(^3P)$ atoms with molecules $N_2(X,v{\geq}13)$ and by collisions of $O(^3P)$ with $N_2(A)$ metastables, while the destruction of NO(X) mainly occurs due to collisions with $N(^4S)$ atoms [2-4]:

$$O(^3P) + N_2(X, v \geq 13) \rightarrow NO(X) + N(^4S) ; \qquad (R_{12})$$

$$O(^3P) + N_2(A) \rightarrow NO(X) + N(^2D) ; \qquad (R_{13})$$

$$NO(X) + N(^4S) \rightarrow N_2(X, v \simeq 3) + O(^3P) . \qquad (R_{14})$$

At pressures typically larger than $p \sim 5$ torr, both $N(^4S)$ and NO(X) species are basically created and destroyed by the same two reactions R_{12} and R_{14}, which present high rate coefficients. The concentrations of these two species are hence strongly correlated with each other. At lower pressures, the sustaining electric field is high and the main populating mechanism occurs via reaction R_{13}. The upper emitting state of NOγ bands is produced

by collisions of $N_2(A)$ metastables with groud-state $NO(X)$ molecules, while the $NO\beta$ bands are produced by three-body recombination of $N(^4S)$ and $O(^3P)$ atoms:

$$N_2(A) + NO(X) \rightarrow N_2(X, v = 0) + NO(A) \; ; \qquad (R_{15})$$

$$N(^4S) + O(^3P) + M \rightarrow NO(B) + M \; , \qquad (R_{16})$$
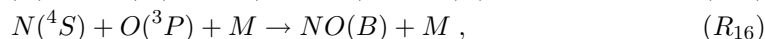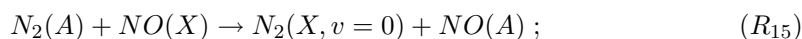
Both NO(A) and NO(B) are lost by radiative decay and quenching [4].

Low-pressure discharges in N_2-O_2 with larger O_2 addition are also extensively used in many applications such as etching of polymers, surface treatments and silicon oxidation. These discharges are known to produce some species with interest for the aplications, such as $O(^3P)$ atoms, $O_2(a)$ metastables, NO, NO_2 and N_2O nitric oxides, and ozone O_3. Here, the kinetics of $O_2(a)$ and $O_2(b)$ states, $O(^3P)$ atoms and negative ions O^- play a central role on the overall kinetics. However, the state of art of the knowledge of the interplay kinetics is significantly less advanced as compared with the case where N_2 is the dominant gas. In particular, collisions between $O_2(a)$ and $N_2(A)$ states leading to an increase of vibrational excitation of $N_2(A,v')$ may explain the observed enhancement of 1^+ emissions when discharged O_2 is added to a N_2 afterglow [13].

6. Conclusions

This presentation gives us a global picture of the dominant processes in discharges and post-discharges with N_2. However, a volume model cannot predict alone some experimental observations since surface reactions, particularly those involving dissociated atoms, may play a crucial role in the overall kinetics. These reactions may largely exceed the simplest recombination of dissociated atoms to ground-state molecules. The charged species and neutral radicals in the volume plasma may create a saturated surface of adsorbed species around it where an important part of the chemistry may take place [14]. The surface reactions may produce molecules in excited states or they may create new molecules in gas-phase. The production of NO from the wall in N_2-O_2 discharges [15], or NH_3 in N_2-H_2 discharges [16], are two examples already considered in the models. Unfortunatelly the lack of data for such processes is tremendous in spite of some recent studies of low temperature plasma-surface interactions [17]. The plasma and surface should thus be regarded as a combined complex system, which must be optimized as a whole. However, we are still way from the time at which the kinetic models present such degree of sophistication.

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