KINETICS OF NEUTRAL AND IONIC SPECIES IN THE SHORT-LIVED AFTERGLOW OF A FLOWING N₂ MICROWAVE DISCHARGE

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Abstract

The optical emissions from N₂(B 3Π_g) and N₂⁺(B 2Σ⁺) states in the short-lived afterglow of a flowing N₂ microwave discharge have been interpreted using a self-consistent kinetic model. Pronounced maxima for the populations of both states are obtained as a final stage of a complex interplay kinetics involving collisions of N₂(X 1Σ_g⁻, v) molecules, in levels as high as v ~ 38–40, with N(1S) atoms, due to the occurrence of a pumping-up effect in the vibrational ladder produced by near resonant V–V energy exchange collisions.

1. Introduction

Flowing microwave discharges in pure nitrogen and in gas mixtures containing nitrogen are of great interest in many applications, such as metallic nitriding [1] and material deposition [2]. With the purpose to fully characterize the kinetics of neutral and ionic species existing in the short-lived afterglow of a flowing microwave discharge in pure N₂, the longitudinal variation of the optical emissions associated with the first positive N₂(B 3Π_g → A 3Σ⁺) and first negative N₂⁺(B 2Σ⁺ → X 2Σ⁺) systems of N₂ have been registered in the ultraviolet-visible range [3]. In this line, also the absolute density and temperature of N₂(A 3Σ⁺) metastables have been determined by intracavity laser absorption spectroscopy [4], while the excitation of N₂(B 3Π, v') levels have been investigated in Ref.[5]. These investigations show, among other aspects, that strong maxima arise in the afterglow for these species, after a dark zone positioned downstream from the discharge, which indicate that they cannot be created in the discharge and carried out to the post-discharge region.

Modelling investigations [6,7] have shown that the observed peaks for the radiative states N₂(B 3Π_g) and N₂⁺(B 2Σ⁺) could be well interpreted by assuming the formation of N₂(A 3Σ⁺) and N₂(A' 1Σ_u) metastables by collisions between N₂(X 1Σ_g⁻, v) molecules, in highly vibrational levels, and N(1S) atoms. During the relaxation of the vibrational distribution of N₂(X 1Σ_g⁻, v), a pumping-up effect for the vibrational quanta occurs producing an enhancement of [N₂(B 3Π_g)] and [N₂⁺(B 2Σ⁺)] concentrations in the afterglow.
However, in Refs. [6,7] some approximations have been made, which avoided that a good agreement with experiment could be obtained. In particular, a sharp decrease in the gas temperature at the end of the discharge has been considered in [7], from $T_g = 1000$ K to 400 K. Furthermore, this latter value has assumed to be constant along the post-discharge. This is indeed an approximation, with large influence on the results, since the $V-V$ and $V-T$ rates are strongly dependent on the gas temperature, as well as the rate coefficients of many other reactions playing a role on the overall kinetics. Here, the kinetic model developed in [6,7] is reformulated by considering the variation of $T_g$ measured along the post-discharge and a comparison is provided with measured relative intensities of $1^+$ and $1^-$ systems of $N_2$ and absolute concentrations of $N_2(A \, ^3 \Sigma_u^+)$ state.

2. Kinetic model

The kinetic model [6,7] used in this paper has a part I, in which the Electron Energy Distribution Function (EEDF), the Vibrational Distribution Function (VDF) of $N_2(X\, ^1 \Sigma_g^+, v)$ molecules, and the concentrations of the various neutral and ionic species are determined in a $N_2$ microwave discharge, and a part II where the relaxation of both the EEDF and the heavy species is analyzed in the afterglow, after the applied microwave field at the end of the discharge has been cut-off. The reader should refer to [6,7] for details concerned with the kinetics of $N_2(X\, ^1 \Sigma_g^+, v)$, $N_2(A\, ^3 \Sigma_u^+)$, $N_2(B\, ^3 \Pi_g)$, $N_2(C\, ^3 \Pi_u)$, $N_2(a'\, ^1 \Sigma_u^+)$, $N_2(a\, ^1 \Pi_u)$, $N_2(w\, ^1 \Delta_u)$, $N(1S)$, $N_2^+(X\, ^1 \Sigma_g^+)$ and $N_2^+(B\, ^3 \Sigma_u^+)$ species in the afterglow. Here, we must just remember that the $N_2(A)$ and $N_2(a')$ metastables are assumed to be created in the post-discharge by collisions of $N_2(X, v)$ molecules, in highly vibrational levels, with $N(1S)$ atoms as follows

$$N_2(X\, ^1 \Sigma_g^+, v \geq 38) + N(1S) \rightarrow N_2(A\, ^3 \Sigma_u^+) + N(1D) \quad (1)$$

$$N_2(X\, ^1 \Sigma_g^+, v \geq 38) + N(1S) \rightarrow N_2(a'\, ^1 \Sigma_u^+) + N(1S) \quad (2)$$

The effects of reaction (2) have been already investigated in [7], while those produced by reaction (1) are evaluated here for the first time.

Once the $N_2(A)$ and $N_2(a')$ states are produced, the ionic ground-state $N_2^+(X)$ is created via the following reactions of Penning ionization:

$$N_2(A\, ^3 \Sigma_u^+) + N_2(a'\, ^1 \Sigma_u^+) \rightarrow N_2(X\, ^1 \Sigma_g^+, v = 0) + N_2^+(X\, ^3 \Sigma_g^+) + e \quad (3)$$

$$N_2(a'\, ^1 \Sigma_u^+) + N_2(a'\, ^1 \Sigma_u^+) \rightarrow N_2(X\, ^1 \Sigma_g^+, v = 0) + N_2^+(X\, ^3 \Sigma_g^+) + e \quad , \quad (4)$$

as well as through other processes involving collisions of $N_2(X, v)$ molecules with $N_2(B)$ and $N_2(a')$ states which are object of discussion in a companion paper [8]. On the other hand, the radiative states $N_2(B)$ and $N_2^+(B)$ are populated through the mechanisms

$$N_2(X\, ^1 \Sigma_g^+, 5 \leq v \leq 14) + N_2(A\, ^3 \Sigma_u^+) \rightarrow N_2(X\, ^1 \Sigma_g^+, v = 0) + N_2(B\, ^3 \Pi_g) \quad (5)$$
\[ N_2(X^1 \Sigma_g^+, v \geq 12) + N_2^*(X^3 \Sigma_g^+) \rightarrow N_2(X^1 \Sigma_g^+, v = 12) + N_2^*(B^2 \Pi_u^+) . \] (6)

The \( N_2(B) \) is also populated in the post-discharge by three body recombination of \( N(4S) \) atoms

\[ N(4S) + N(4S) + N_2 \rightarrow N_2(B^3 \Pi_u) + N_2 . \] (7)

However, the populating rates associated with reaction (7) are negligibly small as compared with those resulting from the conjunction of reactions (1) and (5). Finally, the vibrationally excited molecules \( N_2(X,v) \) at high levels, play a major role in the enhancement of the concentrations of the various neutral and ionic species in the post-discharge, due to an efficient pumping-up effect for the \( v \)-th quanta by near-resonant \( V-V \) energy exchange reactions

\[ N_2(X^1 \Sigma_g^+, v) + N_2(X^1 \Sigma_g^+, v) \rightarrow N_2(X^1 \Sigma_g^+, v - 1) + N_2(X^1 \Sigma_g^+, v + 1) . \] (8)

3. Results and discussion

The kinetic model for the microwave discharge is based on the coupled solutions to the electron Boltzmann equation and a set of rate balance equations for the neutral and ionic species. Further, the sustaining electric field is self-consistently determined. The present working conditions correspond to an \( N_2 \) discharge, in a Pyrex discharge tube of inner radius \( R=1.9 \) cm, at \( \omega/(2\pi)=433 \) MHz and \( p=440 \) Pa. In order to provide a comparison with experimental data [4,9], we have assumed an absorbed microwave power of 300 W, a discharge length of 8 cm, a gas flow rate of 1.5 s l.p.m., and a gas temperature \( T_e=1000 \) K in the discharge. The present calculations determine, among other parameters, the spatially averaged electron density \( \overline{\epsilon}_e=1.9 \times 10^{11} \) cm\(^{-3}\), the concentration \( \overline{N}_2(A^1 \Sigma_u^+) = 1.2 \times 10^{13} \) cm\(^{-3}\), the reduced electric field \( E/N = 6.6 \times 10^{-6} \) V cm\(^{-2}\), and the vibrational temperature of \( N_2(X^1 \Sigma_g^+, v) \) molecules \( T_v=13000 \) K. The relaxation of the concentrations of the species is then analysed in the post-discharge by assuming \( E=0 \) at the beginning of the afterglow.

Figs. 1 and 2 show the relative concentrations \( [N_2(B)]/[N_2] \) and \( [N_2^*(B)]/[N_2] \) in the post-discharge, as the following rate coefficients for reaction (1) are assumed in the model: (A) \( k_1=10^{-11} \) cm\(^3\)s\(^{-1}\); (B) \( 5 \times 10^{-12} \) cm\(^3\)s\(^{-1}\); (C) \( 10^{-12} \) cm\(^3\)s\(^{-1}\). The rate coefficient of reaction (2) is assumed \( k_2=10^{-12} \) cm\(^3\)s\(^{-1}\). The intensity profiles, in arbitrary units, of the \( N_2(B,2 \rightarrow A,0) \) and \( N_2^*(B,0 \rightarrow X,0) \) bands are also plotted for comparison. While the emission intensity of the band of \( 1^+ \) transition (fig.1) has been measured in [9] for the conditions described above, the band of \( 1^+ \) transition (fig.2) has been recorded in the afterglow of a discharge with \( p=340 \) Pa [3]. The global agreement between theory and experiment may be considered good, in spite of the predicted afterglow time for which the maxima occur are larger in the theory by a factor of two.
Our investigations show that the climbing of vibrational quanta, that gives place to the grow-up of the concentrations in the afterglow, strongly depends on the V–V rates and, in particular, on $T_v/T_p$ ratio. As firstly pointed out in [10], the vibrational relaxation of anharmonic oscillators presents a marked inversion of population for $T_v/T_p >> 1$. Here the values of $T_v$ used in the model are those measured in [9] for the rotational temperature of $N_2(A_v=0)$ molecules. They smoothly decrease from 1000 K in the discharge to 987,
851, 535 and 326 K, at $t=10^{-4}$, $10^{-3}$, $10^{-2}$ and $10^{-1}$ s, respectively. In order to analyse the effects of $T_e/T_g$, we report in figs. 3 and 4 a comparison between the relative concentrations of $N_2(B)$ and $N_2^+(B)$ states calculated using our reference model (full curves), in which $T_g$ smoothly decreases, and those calculated as a sharp decrease is assumed for $T_e$ at the beginning of the afterglow from 1000 to 400 K (broken curves). The full curves (A,B,C) are for the same rate coefficients $k_1$ and $k_2$ as in figs. 1 and 2, while curve D is for $k_1=k_2=0$. The broken curve is for $k_1=10^{-13}$ cm$^3$s$^{-1}$ and $k_2=10^{-14}$ cm$^3$s$^{-1}$. When $T_e$ falls off abruptly, a larger $T_e/T_g$ ratio exists during a relatively extended time-interval, which gives place to a reduction of the instant of the maxima occurrence, as well as to a pronounced increase of the magnitude of the peaks, since the pumping up effect becomes largely more efficient.

This study also shows that only reactions of type (1) and (2), involving collisions of $N_2(X,v)$ molecules at high $v-$th levels, can be responsible for the appearance of the optical emissions in the afterglow. The Lewis-Rayleigh emission resulting from $N_2(1S)$ recombination through reaction (7) can be evaluated by inspection of curve D in fig 3, since $k_1-k_2=0$ in this case. The slight increase of $[N_2(B)]/[N_2]$ in the time interval $10^{-2}$ to $5 \times 10^{-3}$ is a consequence of the enhancement of the rate coefficient $k_1$, as $T_e$ decreases along the post-discharge. However, the increase of $N_2(B)$ population due to atomic recombination is too weak to justify the measured $1^+$ intensities. It is worth noting here that other processes involving collisions of $N_2(X,v)$ molecules in lower levels, as it is the case of reaction

$$N_2(X \Sigma_g^+, v \geq 12) + N_2(X \Sigma_g^+, v \geq 12) \rightarrow N_2(A \Pi_u^-, v=0) + N_2(A \Pi_u^-, v=1),$$

cannot explain the recorded spectra as well, since in this situation a continuous increase of $[N_2(B)]$ and $[N_2^+(B)]$ would be observed and no dark zone appear at the end of the discharge. The different behaviour of reaction (9), with respect to reactions (1) and (2), can be well understood by inspection of fig.5 where the VDF of $N_2(X,v)$ molecules (calculated for the same conditions as curves A in figs. 1–4) is shown for the following instants in the afterglow: (A) $t=0$; (B) $10^{-4}$; (C) $10^{-3}$; (D) $10^{-2}$; (E) $10^{-1}$; (F) 0.2 s. whereas the VDF at levels $v=12$ shows a depletion, the tail of the VDF (v>12) pass through a pronounced maximum at $t=10^{-1}$ s due to the action of $N-V$ processes.

Finally, fig.6 shows the measured $N_2(A)$ and predicted $N_2(A)$ and $N_2^+(A)$ concentrations in the afterglow. The full and broken curves are for $N_2(A)$ and $N_2^+(A)$ states, respectively, for $k_1=10^{-11}$ cm$^3$s$^{-1}$ and $k_2=10^{-12}$ cm$^3$s$^{-1}$ (curves A) and $k_1=k_2=0$ (curves B). The predicted $N_2(A)$ concentrations are larger than the measured ones what may be explained, in part, by the assumption of an axially constant electron density in the model for the discharge. This approximation leads to an overestimation of $n_e$ at the end of the discharge, whose magnitude cannot be evaluated here.
Fig. 5. VDF of $N_2(X,v)$ molecules at $t=0$ (A), $10^{-2}$ (B), $10^{-3}$ (C), $10^{-2}$ (D), $10^{-1}$ (E), and $0.2 \times (F)$.

Fig. 6. $[N_2(A)]/[N_2]$ (full curves) and $[N_2(a')]/[N_2]$ (broken curves) for $k_1=10^{-11}$ cm$^3$ s$^{-1}$ (A) and $k_1-k_2=0$ (B). Experimental data: absolute measurements [9].

4. Conclusions

The optical emissions observed in the short-lived afterglow of a flowing $N_2$ discharge are shown to be well explained by assuming the local formation of $N_2(A)$ and $N_2(a')$ states by collisions between $N_2(X,v)$ molecules, in levels $v \geq 38$, and $N(^4S)$ atoms. Pronounced maxima for the populations of metastable and radiative states are produced in the afterglow in qualitative agreement with previous measurements. The work is in progress to remove partial quantitative disagreements for $N_2(A)$ and $N(^4S)$.

References