COMPARISON OF MEASURED AND PREDICTED DYNAMICS OF
EXCITED STATES OF NITROGEN UNDER DISCHARGE AND POST
DISCHARGE CONDITIONS

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Abstract

Dynamics of light emission for the \( \text{N}_2(\Lambda \, ^3\Sigma_u^+), \text{N}_2(\Sigma \, ^1\Pi_g) \) and \( \text{N}_2(\Pi \, ^1\Pi_u) \) electronic excited states was studied spectroscopically in a long pulse glow discharge in pure nitrogen and in afterglow at pressure 50 Torr. An appropriate mathematical processing was made to derive population of excited states from these measurements. A rather complete kinetic model was developed for conditions of the experiments. Results of comparison are analyzed.

1. Introduction

It is well known, electronic and vibration excited states of nitrogen play an essential role in the charged species kinetics and in plasma chemical reactions taking place in the non-thermal plasma. Spectroscopic study of electronic excited states of \( \text{N}_2 \) was therefore always of special attention of researchers. Of the latest papers devoted to this topic, the articles [1-2] can be cited. Many issues remain unresolved, and active research into this problem is still being performed.

Experimental results on dynamics of light emission for the \( \text{N}_2(\Lambda \, ^3\Sigma_u^+), \text{N}_2(\Sigma \, ^1\Pi_g) \) and \( \text{N}_2(\Pi \, ^1\Pi_u) \) electronic excited states during discharge and post-discharge periods are presented in this report. An emission of different transitions (the first positive system, the second positive system and the Vegard-Kaplan system) were split by a double-grid monochromator and recorded with a photomultiplier. An appropriate mathematical processing was made to derive population of excited states from these measurements. The kinetic model is also developed for conditions of the experiments and results of calculations are presented.

Preliminary results of our studies were published in [3]. During last months some progress in interpretation of experimental data was achieved and theoretical model was further developed.

2. Experiment

The object of our investigation is the quasi-stationary volume dominated glow discharge in high-purity \( \text{N}_2 \) (99.999) at pressure 50 Torr. The characteristic discharge current density corresponds to several tens of mA/cm\(^2\). The cross-section of discharge is 60 cm\(^2\). The length of inter-electrode gap is 23 mm. To produce the uniform glow discharge under these conditions, we have used the multiple sectioned electrodes both cathode and anode.
The resistance of all ballast resistors is equalled to 1.6 kΩ. A value of initial voltage superposed across inter-electrode gap equals to 4.5 kV. The discharge current goes up to the quasi-stationary value of 2 A for the time about 100 μs (Fig. 1). The reduced electric field strength was evaluated from the measured discharge voltage taking into account a typical cathode voltage drop and existence of a finite-length dark space.

Under such experimental conditions, the maximum specific energy deposition into N2 was not more than 130 J/g. According to earlier interferometer measurements and calculations [4] growth of gas temperature for the time studied is insignificant.

The actual recorded curves have a rather strong noisy component. A smoothing procedure was applied to receive a signal, which was further treated. Populations of the N2(B^3Π_g, v) and N2(C^3Π_u, v) states derived from the smoothed light emission time behavior measured are shown in Figs. 2-3. The populations on N2(B^3Π_g, v) levels are monotonously decreasing from the very beginning of discharge, and exhibit a rapid fall after the discharge switching off. A similar behavior demonstrate populations of N2(C^3Π_u, v) levels for v=0 and v=1, while for v=2, 3 and 4 there appears a maximum at about 80 μs more apparent for higher v values. An additional feature is that decrements of populations of v=3 and 4 at the moment of discharge switch-off are smaller than for v=0, 1 and 2.

Fig. 4 shows emission intensity measured in the wavelength ranges, which correspond to different transitions of Vegard-Kaplan system. The characteristic features of emission are an appearance of maximum within pulse duration and rather smooth diminishing in time without any response to the discharge switching off. Despite the continued discharge, the emission intensity goes over the maximum and diminishes.
3. Theory

Theoretical studies were made by numerical solution of the set of differential equations for the populations of excited vibrational electronic states in combination with equations of vibrational kinetics of the ground state and electron Boltzmann equation for the electron energy distribution function (EEDF). The following processes were taken into account:

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\begin{align*}
N_2(X,0) + e &\rightarrow N_2(X,v) + e, \quad v=1, \ldots, 8 \\
N_2(X,v) + N_2(X,v') &\rightarrow N_2(X,v+1) + N_2(X,v'+1), \quad v=1, \ldots, 30 \\
N_2(X,0) + e &\rightarrow N_2(A,v) + e, \quad v=0, \ldots, 13 \\
N_2(X,0) + e &\rightarrow N_2(B,v) + e, \quad v=0, \ldots, 17 \\
N_2(X,0) + e &\rightarrow N_2(C,v) + e, \quad v=0, \ldots, 4 \\
N_2(X,0) + e &\rightarrow N + N + e \\
N_2(C,v) &\rightarrow N_2(B,v') + hv, \quad v=0, \ldots, 4; \quad v'=0, \ldots, 9 \\
N_2(B,v) &\rightarrow N_2(A,v') + hv, \quad v=0, \ldots, 12; \quad v'=0, \ldots, 13 \\
N_2(A,v) + N &\rightarrow N_2(X,0) + N, \quad v=0, 1 \\
N_2(A,v) + N_2(X,0) &\rightarrow N_2(A,v-2) + N_2(X,1), \quad v=2, \ldots, 9 \\
N_2(A,v) + N_2(X,0) &\rightarrow N_2(A,v-2) + N_2(X,1), \quad v=10, \ldots, 13 \\
N_2(B,v) + N_2(X,0) &\rightarrow N_2(X,0) + N_2(X,0), \quad v=2, \ldots, 12 \\
N_2(A,v) + N_2(X,0) &\rightarrow N_2(B,v') + N_2(X,0), \quad v=7,10, \ldots, 13 \\
N_2(C,v) + N_2(X,0) &\rightarrow N_2(C,v-1) + N_2(X,0), \quad v=1, \ldots, 4 \\
N_2(C,v) + N_2(X,0) &\rightarrow N_2(B,v') + N_2(X,0), \quad v=0, \ldots, 4 \\
N_2(A,0) + N_2(A,0) &\rightarrow N_2(C,v) + N_2(X,0), \quad v=0, \ldots, 4 \\
N_2(A,0) + N_2(A,1) &\rightarrow N_2(C,v) + N_2(X,0), \quad v=0, \ldots, 4 \\
N_2(A,1) + N_2(A,1) &\rightarrow N_2(C,v) + N_2(X,0), \quad v=0, \ldots, 4 \\
N_2(A,0) + N_2(A,0) &\rightarrow N_2(B,v) + N_2(X,0), \quad v=0, \ldots, 12 \\
N_2(A,0) + N_2(A,1) &\rightarrow N_2(B,v) + N_2(X,0), \quad v=0, \ldots, 12 \\
N_2(A,1) + N_2(A,1) &\rightarrow N_2(B,v) + N_2(X,0), \quad v=0, \ldots, 12 \\
N_2(A,0) + N_2(A,0) &\rightarrow N_2(HIR) + N_2(X,0) \\
N_2(A,0) + N_2(A,1) &\rightarrow N_2(HIR) + N_2(X,0) \\
N_2(A,0) + N_2(X,v) &\rightarrow N_2(B,v') + N_2(X,v''), \quad v=4, \ldots, 10 \\
N_2(A,1) + N_2(X,v) &\rightarrow N_2(B,v') + N_2(X,v''), \quad v=3, \ldots, 9 \\
N_2(A,2) + N_2(X,v) &\rightarrow N_2(B,v') + N_2(X,v''), \quad v=3, \ldots, 9 \\
\end{align*}
\]

It should be noted, that emission from transitions NO(A,v=i) \rightarrow NO(X,v=j) also contributes to measured emission intensity in mentioned wavelength ranges, even if the concentration of NO admixture is relatively small. In particular, transitions 0 \rightarrow 3, 2 \rightarrow 7, 0 \rightarrow 1, 2 \rightarrow 5 and 1 \rightarrow 4 will contribute to measured emission in wavelength ranges of 0 \rightarrow 5, 0 \rightarrow 6, 1 \rightarrow 4, 1 \rightarrow 5 and 2 \rightarrow 6 transitions of Vegard-Kaplan system, respectively. For this reason, populations of the N_2(A \ ^1 \Sigma_u^-, v) states can not be found unambiguously.
N$_2$(HIR) designates the upper level for the Herman infrared system. In the last column, there are references to sources from which values of rate constants were taken. BE denotes the rate constants calculated by solving the electron Boltzmann equation with a given E/N value taken from Fig. 1. Rate constants for the last group of processes were estimated in the same manner as in [14] using the Frank-Condon factor and energy gap scaling law. The set of cross sections for the electron scattering from nitrogen molecules was taken from [15]. To obtain cross sections for the excitation of different vibrational levels of A, B and C states from the ground state, total cross sections for the excitation of these states were split using known values of Frank-Condon factors. Rate constants for all reverse processes were calculated from the detailed balance principle. Rate constant for the dissociation of N$_2$ by electron impact was calculated using effective cross section taking from [16]. Electron concentration as a function of time was estimated using measured value of discharge current and calculated electron drift velocity. Some results of calculations are shown in Figs. 5-7.

Figs. 5-7. Calculated populations of excited nitrogen molecular states in glow and afterglow phases of discharge.

The simple estimations show that transitions of Vegard-Kaplan system only can not explain measured emission intensity for predicted N$_2$(A,v) concentrations (see Fig. 3). On the other hand, using calculated N$_2$(A,v) populations and concentration of NO as a parameter, it is possible to estimate the rates of excitation of NO(A,v) states in reactions:

NO(X) + N$_2$(A,v=i) → NO(X,v=j) + N$_2$(X). Rate constants for these reactions (i=0, 1, 2, j=0, 1, 2) can be found in [17, 18]. If to assume that lifetime of NO(A,v) states is controlled by radiative transitions NO(A,v=i) → NO(X,v=j), it is possible to calculate reduced emission intensity for a
given transition. Such a procedure was performed and emission intensities for involved transitions 0→3, 2→7, 0→1, 2→5 and 1→4 were calculated. (All necessary radiative lifetimes and transition probabilities were calculated using data from [19]). As it follows from Fig. 8, NO concentration [NO]=10^{10} \text{cm}^{-3} is enough to provide emission intensity comparable with that measured in the experiment.

4. Discussion

Comparing experimental curves with theoretically predicted, a good qualitative and quantitative agreement in time behavior for populations of N_2(B \ ^3\Pi_g) and N_2(C\ ^3\Pi_u) electronic states is observed. The measured monotonous decrease of N_2(B \ ^3\Pi_g) populations is reproduced by the theory (Figs. 2 and 6). Theory predicts different behavior for populations of ν=3 and 4 levels from that of ν=0 and 1 levels of N_2(C\ ^3\Pi_u) state. This fact is also in agreement with the experiment (compare Figs. 3 and 7). The absolute values of populations predicted by the theory are also in a reasonable agreement with the experimentally measured ones. Even appearance of the maximum in the N_2(C\ ^3\Pi_u) emission for ν=3 and 4 observed experimentally (Fig. 3) is reproduced in numerical simulations. Concerning emission in the frequency range of the Vegard-Kaplan system, the theory predicts non-monotonous behavior as it is observed experimentally. An order of magnitude for the reduced emission intensity from the discharge volume unit is the same in the theory and measurements. There are discrepancies in the sequence of curves in Figs. 4 and 8. The maximum in emission in the spectral range of the transition 2→6 of the Vegard-Kaplan system takes place on a shorter time in the theory in comparison with the experiment.

Problems in interpretation of the observed emission in the range of the Vegard-Kaplan system are associated with overlap of this system with strong A→X transitions of NO. A difference in spontaneous emission rates of 7-8 decimal orders results in comparable inputs from NO and Vegard-Kaplan transitions, even in the high purity nitrogen. On the other hand, neither spontaneous emission nor energy transfer to NO can influence on the dynamics of N_2(A\ ^1\Sigma^+_u, ν) states. This fact makes easier modeling of the system.

Appearance of the maximum in population evolution of N_2(A\ ^1\Sigma^+_u, ν) states is caused by competing between populating of ν=0 and 1 in processes of vibration-vibration exchange (two quanta in A-state exchanged to one quantum in X-state) and pooling reactions. Leveling of N_2(B \ ^3\Pi_g) states population curves in Fig. 2 and 6 to the end of pulse is explained by populating them in collisions of vibrationally excited nitrogen molecules in the ground electronic state and molecules in A \ ^1\Sigma^+_u state (last three lines in the list of processes taken into account in our model). Besides, it was found a remarkable influence of ground-state vibrational excitation on excitation rate by electron impact of N_2(C\ ^3\Pi_u).

Our model can be modified further by inclusion of new processes. In fact, the states B\ ^3\Sigma^-_u and W \ ^1\Delta_u, which are not included in our model because of lack of information about relevant processes, may play some role. To make more tractable data on emission within Vegard-Kaplan system further studies are necessary to identify the input of NO bands.
5. Conclusions

Experimental and theoretical studies on optical emission from $N_2(A\ ^3\Sigma_u^+)$, $N_2(B\ ^3\Pi_g)$ and $N_2(C\ ^3\Pi_u)$ manifolds were performed. Populations of individual vibrational levels were evaluated from spectroscopic measurements in a long pulse glow discharge in pure nitrogen and in afterglow at pressure 50 Torr. Specific features in time behavior of $N_2(B\ ^3\Pi_g)$ and $N_2(C\ ^3\Pi_u)$ levels populations was revealed. A rather complete kinetic model was developed for conditions of the experiments. Results of comparison between the experiment and theory show an agreement in whole, while further detailed studies are necessary to formulate the model capable to do reliable predictions for excited nitrogen states dynamics.

References