DYNAMICS OF EXCITED NITROGEN MOLECULAR STATES IN GLOW- AND AFTERGLOW PHASES OF DISCHARGE: EXPERIMENT AND MODELING

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Abstract

Population dynamics for a number of levels from $N_2(A\ ^3\Sigma^+_u)$, $N_2(B\ ^3\Pi_g)$ and $N_2(C\ ^3\Pi_u)$ manifolds was studied spectroscopically in a long pulse glow discharge in pure nitrogen and in afterglow at pressure 50 Torr. Overshot in time behaviour of $N_2(A\ ^3\Sigma^+_u)$, $N_2(B\ ^3\Pi_g)$ and $N_2(C\ ^3\Pi_u)$ levels populations was revealed. A rather complete kinetic model is 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. For instance, the high concentration of these species results in increase of the rate of ionization in the bulk of plasma and, also, in decomposition of many pollutants in the exhausted gas energized by a discharge. Spectroscopic study of electronic excited states of N_2 was therefore always of special attention of researchers. Of the latest papers devoted to this topic, the articles [1-3] 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 $N_2(A\ ^3\Sigma^+_u)$, $N_2(B\ ^3\Pi_g)$ and $N_2(C^3\Pi_u)$ 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 photo-multiplier. 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.

2. Experiment

The object of our investigation is the quasi-stationary volume dominated glow discharge in high-purity N_2 (99.999) at pressure 50 Torr. A sketch of experimental set up is shown in Fig. 1. 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 generate 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 equaled to 1.6 kΩ.

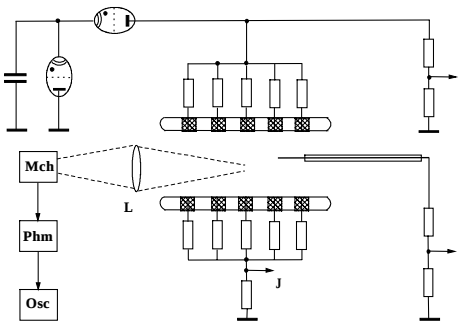


Fig.1. Sketch of experimental set up to generate discharge pulse with controlled duration and to record the discharge light emission in real time. Mch is the monochromator, Phm is the photo-multiplier, Osc is the digital oscilloscope

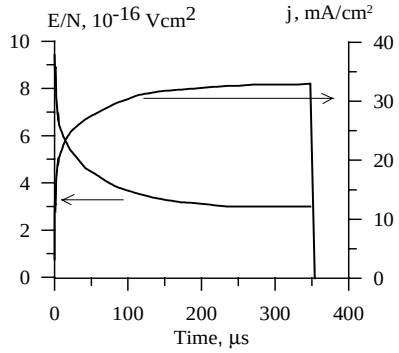
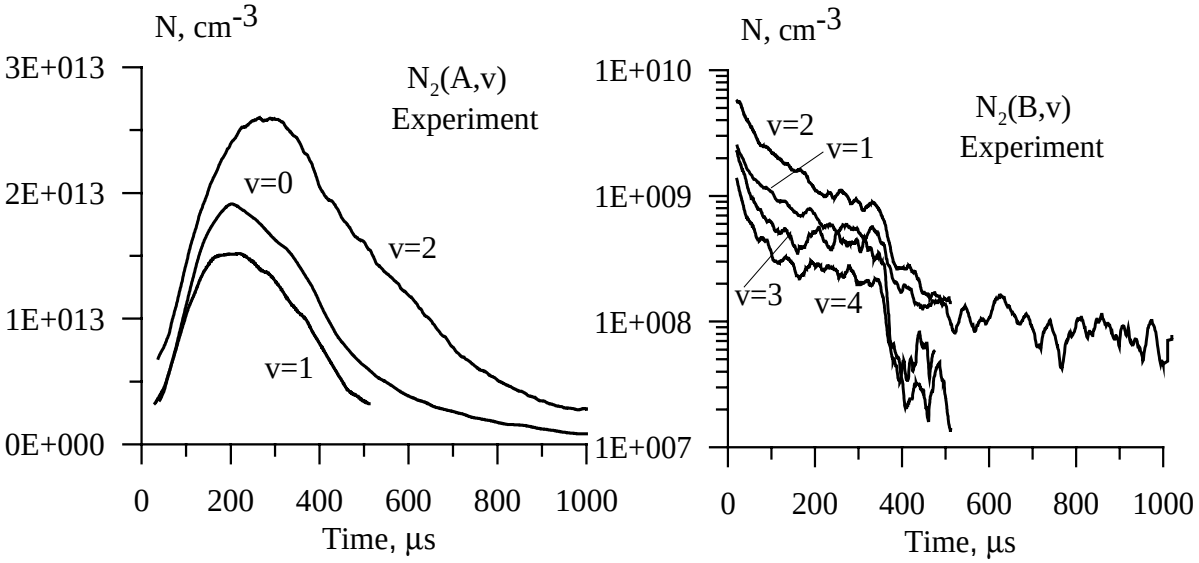
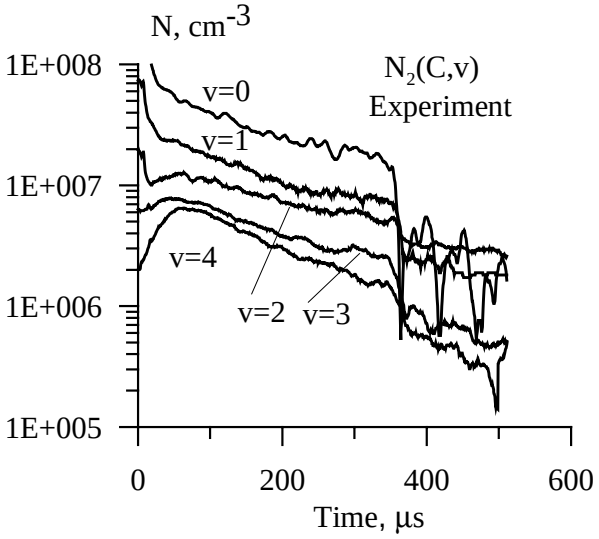


Fig.2. Measured discharge current and the estimated reduced electric field in the bulk of plasma. Pure nitrogen, pressure is 50 Torr. Amplitude of applied voltage is 4.5 kV





Figs. 3-5. Evaluated from measurements populations of excited nitrogen molecular states in glow- and afterglow phases of discharge. Discharge pulse duration 350 μs.

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. 2). 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 N_2 was not more than 130 J/g. According to our interferometer measurements and calculations [4] the variations of gas temperatures under such conditions are small.

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 $N_2(A^3\Sigma^+_u, v)$, $N_2(B^3\Pi_g, v)$ and $N_2(C^3\Pi_u, v)$ states derived from the smoothed light emission time behavior measured are shown in Figs. 3-5.

The characteristic features of measured dynamics of $N_2(A^3\Sigma^+_u,v)$ populations 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 populations go over the maximum and diminish. In contrast, the populations on $N_2(B^3\Pi_g, v)$ 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 $N_2(C^3\Pi_u, v)$ 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.

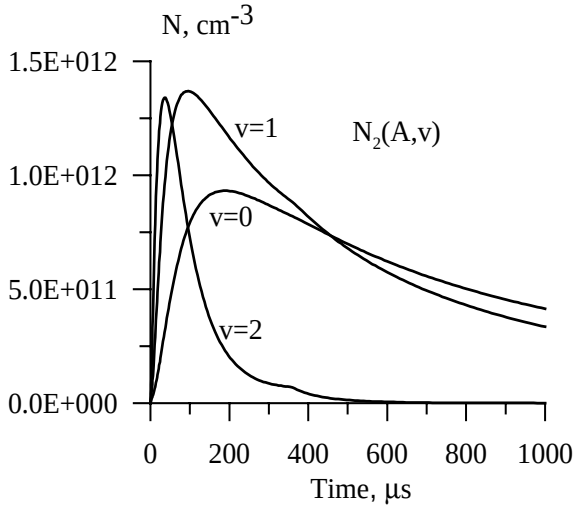
3. Theory

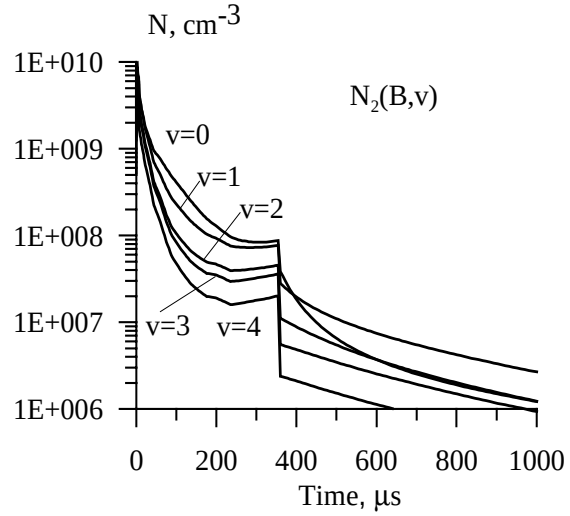
Theoretical studies were made by numerical solution of the set of differential equations for the populations of excited electronic states in combination with equations of vibrational kinetics of the ground state and electron Boltzmann equation for the electron energy distribution function (EEDF). The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

$N_2(X,0) + e \rightarrow N_2(X,v) + e$, v=1, …, 8	BE
$N_2(X,v) + N_2(X,v') \rightarrow N_2(X,v-1) + N_2(X,v'+1)$, v=1, …, 30	[5]
$N_2(X,0) + e \rightarrow N_2(A,v) + e$, v=0, …, 13	BE

$N_2(X,0) + e \rightarrow N_2(B,v) + e$, v=0, …, 17	BE
$N_2(X,0) + e \rightarrow N_2(C,v) + e$, v=0, …, 4	BE
$N_2(C,v) \rightarrow N_2(B,v') + h\nu$, v=0, ..., 4; v'=0, ..., 9	[6]
$N_2(B,v) \rightarrow N_2(A,v') + h\nu$, v=0, ..., 12; v'=0, ..., 13	[6]
$N_2(A,v) + N_2(X,0) \rightarrow N_2(A,v-2) + N_2(X,1)$, v=2, ..., 9	[7]
$N_2(B,v) + N_2(X,0) \rightarrow N_2(X,0) + N_2(X,0)$, v=2, ..., 12	[8]
$N_2(A,v) + N_2(X,0) \rightarrow N_2(B,v') + N_2(X,0)$, v=7,10, ..., 13	[8, 9]
$N_2(A,0) + N_2(A,0) \rightarrow N_2(C,v) + N_2(X,0)$, v=0, ..., 4	[10]
$N_2(A,0) + N_2(A,1) \rightarrow N_2(C,v) + N_2(X,0)$, v=0, ..., 4	[10]
$N_2(A,1) + N_2(A,1) \rightarrow N_2(C,v) + N_2(X,0)$, v=0, ..., 4	[10]
$N_2(A,0) + N_2(A,0) \rightarrow N_2(B,v) + N_2(X,0)$, v=0, ..., 12	[11]
$N_2(A,0) + N_2(A,1) \rightarrow N_2(B,v) + N_2(X,0)$, v=0, ..., 12	[11]
$N_2(A,1) + N_2(A,1) \rightarrow N_2(B,v) + N_2(X,0)$, v=0, ..., 12	[11]
$N_2(A,0) + N_2(A,0) \rightarrow N_2(HIR) + N_2(X,0)$	[10]
$N_2(A,0) + N_2(A,1) \rightarrow N_2(HIR) + N_2(X,0)$	[10]
$N_2(A,0) + N_2(X,v) \rightarrow N_2(B,v') + N_2(X,v'')$, v=4, ..., 10	Our estimation
$N_2(A,1) + N_2(X,v) \rightarrow N_2(B,v') + N_2(X,v'')$, v=3, ..., 9	Our estimation
$N_2(A,2) + N_2(X,v) \rightarrow N_2(B,v') + N_2(X,v'')$, v=3, ..., 9	Our estimation

$N_2(HIR)$ 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. 2. Rate constants for the last group of processes were estimated in the same manner as in [12] 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 [13]. To obtain





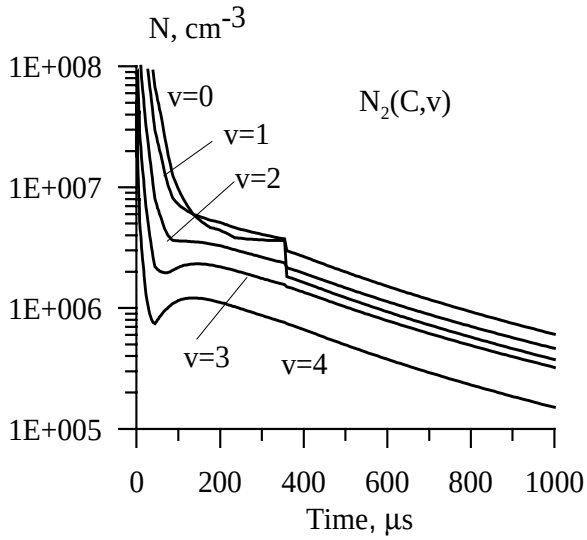


Fig.6-8 Calculated populations of excited nitrogen molecular states in glow- and afterglow phases of discharge.

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. Electron concentration as a function of time was estimated using measured value of discharge current and calculated electron drift velocity. Some results calculated for pulse duration 350 μs are shown in Figs. 6-8.

4. Discussion

Comparing experimental curves with theoretically predicted, a good qualitative agreement in time behavior for populations of all electronic states should be noted. Both, the experiment and the theory show non-monotonous behavior of $N_2(A^3\Sigma^+_u, v)$ states populations. The measured monotonous decrease of $N_2(B\ ^3\Pi_g)$ populations is also reproduced by the theory (Figs. 4 and 7). Theory predicts different behavior for populations of v=3 and 4 levels from that of v=0 and 1 levels of $N_2(C^3\Pi_u)$ state. This fact is also in agreement with the experiment (see Figs. 5 and 8). Concerning the absolute values of populations, the experimentally evaluated magnitudes are as a rule higher than predicted by the theory. In particular, great discrepancy in absolute populations is for $N_2(A^3\Sigma^+_u, v)$ states. Additionally, the theory predicts that the population of v=2 level achieved the maximum at the moment 60 μs, earlier than populations of levels with v=0 and 1, while the experiment shows an opposite trend, and the maximum for population of v=2 level is achieved at the moment about 300 μs.

Numerical simulations demonstrate that appearance of maximum in populations of $N_2(A^3\Sigma^+_u, v)$ states is caused mostly by collisional quenching of these states by vibrationally excited nitrogen molecules in the ground electronic state. Despite the low excitation degree of ground electronic state vibrational excited levels its influence on the rate constants for excitation of $N_2(C^3\Pi_u)$ state is rather remarkable.

Generally, results of numerical simulations are quite sensitive to an exact value of the reduced electric field, which is estimated from the experiment. Let us remind that our model is not self-consistent, because the electric field and electron number density are taken from the experiment. An error associated with a limited accuracy of these evaluated quantities may explain some discrepancies between the experiment and theory.

The other plausible source of discrepancies is not a complete knowledge about processes involving electronic excited states. In particular, some role may play the states $B'^3\Sigma^-_u$ and $W\ ^3\Delta_u$, which are not included in our model because of lack of information about relevant processes. There is no reliable information about energy exchange in collisions of molecules in the state $N_2(A^3\Sigma^+_u, v)$ with ground state vibrationally excited molecules resulting in formation of $N_2(B\ ^3\Pi_g)$ states.

5. Conclusions

Experimental and theoretical studies on population dynamics for a number of levels 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 $N_2(A\ ^3\Sigma^+_u)$, $N_2(B\ ^3\Pi_g)$ 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 a good qualitative agreement, while further detailed studies are necessary to achieve a numerical coincidence of predicted and measured quantities.

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