FORMATION OF VIBRATIONAL DISTRIBUTION FUNCTION OF ELECTRONICALLY-EXCITED $N_2(A^3\Sigma_u^+)$ MOLECULES IN NITROGEN DISCHARGE PLASMA

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ABSTRACT

A model on formation of the vibrational distribution function of metastable electronically excited $N_2(A^3\Sigma_u^+,v)$ states in nitrogen discharge plasma is presented. It is assumed that the probability of population of $N_2(A^3\Sigma_u^+,v)$ states by collisional deactivation of $N_2(B^3\Pi_g,v')$ molecules is proportional to the Franck-Condon factors of corresponding $N_2(B^3\Pi_g,v') \rightarrow N_2(A^3\Sigma_u^+,v)$ transitions, i.e. that the quenching is essentially vertical. The results of calculations carried out under this assumption are in agreement with measured $N_2(A^3\Sigma_u^+,v)$ vibrational distribution at the end of pulsed high current discharge in nitrogen.

1. INTRODUCTION

Electronically excited $N_2(A^3\Sigma_u^+,v)$ molecules play an important role in gas discharge kinetics in nitrogen and nitrogen-oxygen mixtures [1-4]. In mixtures with a small fraction of oxygen a considerable part of the discharge energy, spent on excitation of electronic degrees of freedom, accumulates in $N_2(A^3\Sigma_u^+)$ state [3]. An important feature of many reactions with $N_2(A^3\Sigma_u^+,v)$ molecules is a dependence of reaction rates and product ratios on a number of the vibrational level.

In a number of recent works, the methods of laser-induced fluorescence (LIF) [2] and intracavity laser absorption spectroscopy at the transitions of the 1^+ system of nitrogen were used for measuring the density of $N_2(A^3\Sigma_u^+)$ molecules [5]. Populations of only a few vibrational levels of $N_2(A^3\Sigma_u^+)$ can be found using these techniques. Thus a model describing the formation and evolution of the vibrational distribution function of electronically excited $N_2(A^3\Sigma_u^+,v)$ molecules in nitrogen discharge plasma is needed for more detailed comparison of experimental results with numerical simulations.

2. MODEL DESCRIPTION

In nitrogen discharge plasma the population of $N_2(A^3\Sigma_u^+,v)$ state occurs mainly due to the radiative-collisional quenching of levels with high energies $N_2(B^3\Pi_g)$, $N_2(B'^3\Sigma_u^-)$, $N_2(W^3\Delta_u)$ and others, the excitation by direct electron impact is not very important [3].

Analysis of experimental results on the population of vibrational levels of electronically excited N_2 states due to recombination of $N(^4S)$ atoms in the afterglow of nitrogen discharge (P = 20 - 760 Torr) is presented in [6]. It is shown that the most part of the excitation flux, passed through the levels $N_2(B^3\Pi_g,v=0\text{-}12)$, also passes through the levels $N_2(A^3\Sigma_u^+,v'=0,1)$. This evidences that in quenching of $N_2(B^3\Pi_g,v)$ molecules the reaction

$$N_2(B^3\Pi_g,v) + N_2(X^1\Sigma_g^+) \rightarrow \qquad (1)$$

$$N_2(A^3\Sigma_u^+,v') + N_2(X^1\Sigma_g^+,v'')$$

is dominant. Similar conclusion based on analysis of experimental data has been made in [7]. This conclusion is really important since in several works the authors assumed the reaction $N_2(B^3\Pi_g,v) + N_2(X) \rightarrow N_2(X,v') + N_2(X,v'')$ as a dominant quenching channel of $N_2(B^3\Pi_g,v)$ state.

It is important to underscore that the question about vibrational distribution function of $N_2(A^3\Sigma_u^+,v)$ molecules generated in reaction (**1**) is still open. Calculations of the temporal evolution of $N_2(A^3\Sigma_u^+,v$=0-8) vibrational levels populations in the afterglow of pulsed high current electron beam and RF discharge in nitrogen have been performed in [3]. Comparison of numerical and experimental results allowed improving the rate constants of reaction

$$N_2(A^3\Sigma_u^+,v) + N_2(X^1\Sigma_g^+,v'=0) \rightarrow \qquad (2)$$
$$N_2(A^3\Sigma_u^+,v\text{-}2) + N_2(X^1\Sigma_g^+,v'=1)$$

Data obtained in [3] were used in this study.
Having uniformity of all parameters in the discharge the following expression for the electric field E was used in the present paper:

$$E = \frac{I}{e\mu_e N_e S}, \qquad (3)$$

where I is the discharge current, μ_e is the electron mobility (function of E/N), N_e is the electron density, S is the area of the discharge cross-section.
Dependences of the rates of excitation, ionization and dissociation of molecules by the electron impact on the reduced electric field E/N value are determined from the calculations of the electron energy distribution function (EEDF) using the BOLSIG+ code [8]. Main processes with neutral and charged particles and the rate constants are taken from [9]. Detailed description of the model was given in [3].

3. SIMULATION RESULTS

3.1. Time evolution of population difference between $N_2(A^3\Sigma_u^+,v$=0) and $N_2(B^3\Pi_g$, v=2) states were measured in [4] in a positive column of DC nitrogen pulsed discharge. The discharge was created in a 14 mm inner diameter, 25 cm long pyrex tube. High-voltage pulses of about 2 kV of τ_{imp} = 8 - 20 μs duration and 20 Hz repetition rate were applied to produce bulk discharge in pure nitrogen.

Fig. 1 shows the discharge current [4] and the calculation results of temporal evolution of the reduced electric field E/N under the conditions of [4]. It is clear that the main energy deposition occurs at E/N = 120 - 130 Td. The population difference between $N_2(B^3\Pi_g$, v = 2) and $N_2(A^3\Sigma_u^+,v$=0) states was evaluated from integrated high-resolution laser absorption/gain profiles. Optical gain, due to the population inversion, was present during the first 3 - 6 μs of the discharge pulse.

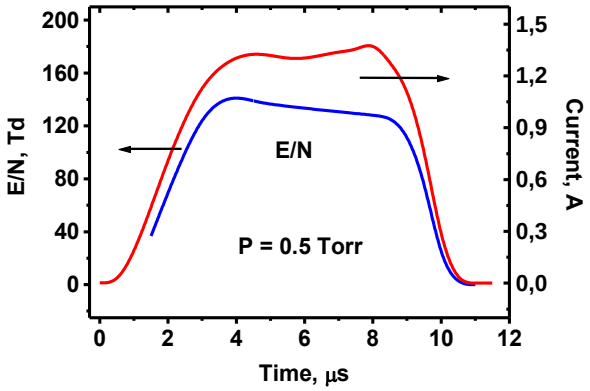

Fig. 1. *Temporal evolution of the reduced electric field E/N and the discharge current under the conditions of [4]: P = 0.5 Torr.*

The population difference was about ΔN_{BA} = $3\cdot10^{11}$ cm^{-3} at the peak current at 6 - 7 μs. In the afterglow the ΔN_{BA} value decreases to ΔN_{BA}^0 = -$1.1\cdot10^{12}$ cm^{-3}. **Fig. 2** shows the experimental data and calculation results of the population difference between $N_2(B^3\Pi_g$, v=2) and $N_2(A^3\Sigma_u^+,v$=0) at P = 0.5 Torr under the conditions of Fig. 1. The main population of the $N_2(B^3\Pi_g$, v=2) state in this case occurs by electron impact from the ground $N_2(X^1\Sigma_g^+)$ state and quenching reaction of electronically excited $N_2(C^3\Pi_u)$ molecules.

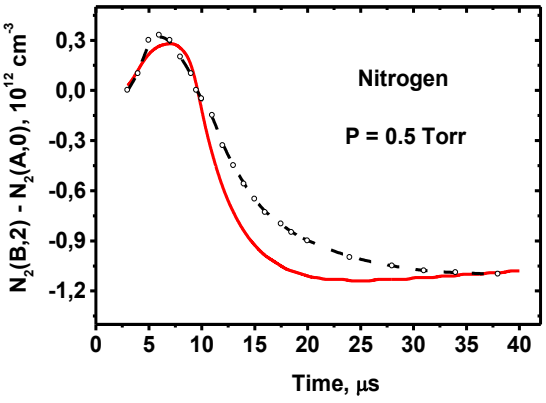

Fig. 2. *Temporal evolution of number density difference: [$N_2(B^3\Pi_g$, v=2)] – [$N_2(A^3\Sigma,v$=0)] under the conditions of [4]. The full curve represents experimental data, the dotted curve – calculation results.*

The production of $N_2(A^3\Sigma_u^+,v=0)$ molecules is associated with radiative - collisional quenching of $N_2(B^3\Pi_g, v)$ state in the reaction (**1**). As can be seen, the calculation results are consistent with the experimental data, which indicates the adequacy of the description of the $N_2(A^3\Sigma_u^+,v=0)$ molecules production under given conditions [4].

3.2. As it was mentioned earlier at present there is no data on the vibrational distribution of $N_2(A^3\Sigma_u^+,v)$ molecules, produced at quenching of $N_2(B^3\Pi_g)$ by nitrogen molecules. In given work it is assumed that the population probability of $N_2(A^3\Sigma_u^+,v)$ in the process of collisional deactivation of $N_2(B^3\Pi_g,v')$ is proportional to the Franck - Condon factors (FCF) of corresponding $N_2(B^3\Pi_g,v') \rightarrow N_2(A^3\Sigma_u^+,v)$ transitions.

For validation of this assumption the calculation results of $N_2(A^3\Sigma_u^+,v)$ vibrational distribution have been compared with the experimental data of [5]. In [5] by means of intracavity laser absorption spectroscopy the vibrational distribution of $N_2(A^3\Sigma_u^+,v=2\text{-}6)$ states have been measured after pulsed (τ_{imp} = 700 ns) high current discharge in nitrogen at P = 230 Torr and T_0 = 300 K.

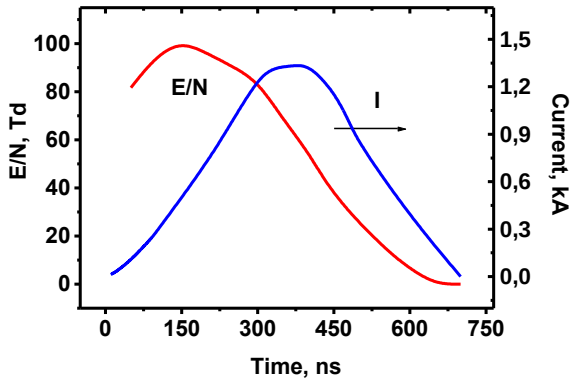

Fig. 3. *Temporal evolution of the reduced electric field E/N and the discharge current in nitrogen under the conditions of [5].*

The area of electrodes was 5×50 cm^2 with the interelectrode distance d = 4 cm. Having uniformity of the discharge parameters the expression (**3**) for the electric field *E* was also used under given conditions. **Fig. 3** shows the current pulse oscillogram [5] and the calculation results of temporal dynamics of the reduced electric field *E/N* under the conditions of [5]. It is clear that the main energy deposition occurs at *E/N* = 50 - 100 Td. Specific energy deposited into the discharge achieved W = $7.5\cdot10^{-3}$ eV/molecule, and that agrees with the experimental estimate ($7.8\cdot10^{-3}$ eV/molecule).

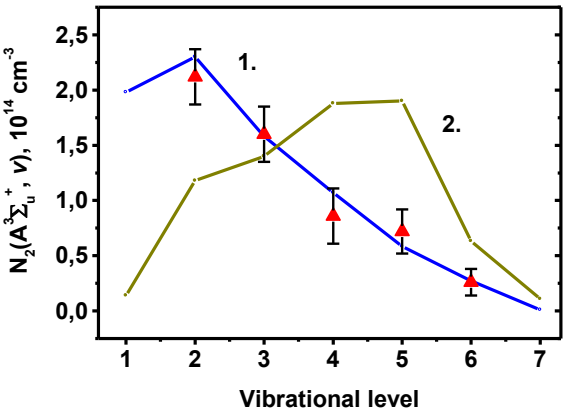

Fig. 4. *Comparison between experimental [5] and predicted $N_2(A^3\Sigma,v=1\div7)$ vibrational level populations at the end of discharge at t = 0.7 μs. The dots are experimental data from [5], curves (1, 2) – are calculation results (see text).*

The calculation results of vibrational distribution of $N_2(A^3\Sigma_u^+,v)$ and the experimental data of [5] are shown in **fig. 4**. In this case the main excitation of $N_2(A^3\Sigma_u^+,v)$ molecules is due to the quenching of $N_2(B^3\Pi_g)$ state. The calculation results and experimental data of [5] are taken for t = 0.7 μs, correspondent to the end of the current pulse. The calculations made on the assumption, that the population probability of $N_2(A^3\Sigma_u^+,v)$ in the process of collisional quenching of $N_2(B^3\Pi_g)$ was proportional to the Franck-Condon factors of the correspondent $N_2(B^3\Pi_g,v') \rightarrow N_2(A^3\Sigma_u^+,v)$ transitions, are shown with **curve 1**. A good agreement with measurements of [5] is evident.
In conditions under consideration the characteristic times of reaction (**2**) for vibrational levels v = 5, 4, 3 amount to 0.44, 0.94 and 2.9 μs, respectively. Therefore at time scales t ≤ 1 μs an intensive quenching of $N_2(A^3\Sigma_u^+, v \geq 4)$ vibrational levels and hence populating of levels v = 2 and 3 take place. And this is the main reason for relative overpopulation of the level v = 2 at t = 0.7 μs observed in **fig. 4** (**curve 1**).

It should be noted that in a few works it is assumed that in a quenching process of $N_2(B^3\Pi_g)$ state the high vibrational levels of $N_2(A^3\Sigma_u^+,v)$ are mainly populated:

$$N_2(B^3\Pi_g) + N_2(X^1\Sigma_g^+) \rightarrow \quad (4)$$
$$N_2(A^3\Sigma_u^+, v=6,7) + N_2(X^1\Sigma_g^+)$$

For validation of this assumption the calculations with an allowance for the quenching of $N_2(B^3\Pi_g)$ state in accordance with (**4**) have been carried out. **Fig. 4** (**curve 2**) illustrates the results of calculations under the conditions of experiment [5]. Obtained results obviously differ from the experimental data [5]. Thus the assumption about the dominant populating of high vibrational levels of $N_2(A^3\Sigma_u^+, v \geq 6)$ owing to the collisional quenching of $N_2(B^3\Pi_g)$ state seems to be invalid.

4. CONCLUSIONS

A model on formation of vibrational distribution function of metastable electronically excited $N_2(A^3\Sigma_u^+, v)$ states in gas discharge plasma is presented. In nitrogen discharge plasma the excitation of $N_2(A^3\Sigma_u^+)$ molecules takes place mainly by deactivation of electronic states with high energies. In the paper it was assumed that the population probability of $N_2(A^3\Sigma_u^+, v)$ in the process of collisional quenching of $N_2(B^3\Pi_g)$ state is proportional to the Franck-Condon factors of correspondent transitions $N_2(B^3\Pi_g, v') \rightarrow N_2(A^3\Sigma_u^+, v)$, i.e. that the quenching is essentially vertical. The results of calculations carried out under this assumption are in agreement with measured data of $N_2(A^3\Sigma_u^+, v)$ vibrational distribution at the end of pulsed high current discharge in nitrogen at P = 230 Torr [5].

It is also shown that the assumption about preferred population of high vibrational levels $N_2(A^3\Sigma_u^+, v \geq 6)$ in the process of collisional quenching of $N_2(B^3\Pi_g)$ is not valid since in this case the modeling results are inconsistent with the experimental data of [5].

Time evolution of population difference between $N_2(A^3\Sigma_u^+, v=0)$ and $N_2(B^3\Pi_g, v=2)$ states in a positive column of nitrogen glow discharge was calculated under the conditions of experiments [4]. The calculation results are consistent with the experimental data, which indicates the adequacy of the description of the $N_2(A^3\Sigma_u^+, v=0)$ molecules production under given conditions.

ACNOWLEDGMENTS

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