Influence of gas pressure on kinetic processes in nitrogen post-discharge

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Abstract: The work presents results obtain during spectroscopic observations of DC flowing post-discharge of pure nitrogen plasma. The total gas pressure was varied from 500 Pa up to 5 000 Pa. The maximum of intensity of pink afterglow phenomenon was observed at decay time 5 ms at 500 Pa and it was moved to the later decay times up to 20 ms with increasing total gas pressure. Relative populations of \( \text{N}_2 (\text{B } ^3\Pi_g) \), \( \text{N}_2 (\text{C } ^3\Pi_u) \) and \( \text{N}_2^+ (\text{B } ^2\Sigma_u^+) \) states were calculated from measured intensities. Simplified kinetic model was proposed.

Keywords: Post-discharge, pink afterglow, intensity, relative populations, optical emission spectroscopy.

1. Introduction

Nitrogen flowing post-discharges have been applied during the last years in different applications as hard films deposition [1] or plasma sterilization [2].

The neutral nitrogen molecule can form many electronic states. All molecular states under 7.4 eV are metastables that conserve the excitation energy up to seconds. The atomic species recombination and the excitation energy transfer during the collisions among the metastables lead to the formation of some radiative states and the visible light emission can be observed up to one second after switching off an active discharge. This first part of light emission of post-discharge is characterized by the strong emission of pink radiation and is called pink afterglow phenomenon. After that the yellow-orange color is characteristic for the post-discharge emission and this part is known as Lewis-Rayleigh afterglow. These effects depend on the experimental conditions, mainly on pressure. Kinetic modeling of pure nitrogen was given for example in [3]. This study extends our recent experimental works of the changes in nitrogen post-discharge kinetics caused by different gas pressure.

2. Experimental set-up

The DC flowing post-discharge was used for the experimental study. A simplified schematic drawing of the experimental setup is given in Fig. 1.

The active discharge was created in a Pyrex discharge tube with a 120 mm electrode distance and the constant discharge power about 290 W. The total gas pressure was in range 500 Pa up to 5 000 Pa. Hollow molybdenum electrodes were placed in the side arms of the main discharge tube to minimize their sputtering and also to minimize scattering the light emitted in the electrode regions. Nitrogen was of 99.99% purity and it was further cleaned by Oxiclear and LN\textsubscript{2} traps. The reactor system was pumped continuously by rotary oil pump separated from discharge tube by another LN\textsubscript{2} trap. The gas flow was automatically controlled by mass flow controller and the total gas pressure in the discharge tube was measured by a capacitance gauge connected to the end of the discharge.

The optical spectra in the range of 300 – 850 nm were measured by Jobin Yvon monochromator TRIAX 550 with the 1200 grooves per mm grating coupled with multichannel detectors. The emitted light was led to the entrance slit of the monochromator by the multimode quartz optical fibre movable along the discharge tube. The reactor wall temperature was 300 K.

The nitrogen 1\textsuperscript{st} positive (\( \text{N}_2 (\text{B } ^3\Pi_g) \rightarrow (\text{A } ^3\Sigma_u^+) \)) and 2\textsuperscript{nd} positive (\( \text{N}_2 (\text{C } ^3\Pi_u) \rightarrow (\text{B } ^3\Pi_g) \)) and nitrogen 1\textsuperscript{st} negative (\( \text{N}_2^+ (\text{B } ^2\Sigma_u^+) \rightarrow (\text{X } ^2\Sigma_g^+) \)) spectral systems were recorded in all spectra. Although the Oxiclear purifier column was used, the bands of NO\textsubscript{β} system (NO (B \( ^2\Pi \)) \rightarrow NO (A \( ^2\Sigma^+ \)) dominantly originating at vibrational level 0 were observed, too, mainly at the higher pressures and later decay times. No other molecular emissions were observed. The relative vibrational populations at the selected nitrogen levels were calculated using all measurable emission band intensities. The transition probabilities and wavelengths of the transitions were taken from Gilmore’s tables [4].
3. Results and discussion

The post discharge is shown in Fig. 2. It is visible, that phenomenon pink afterglow was observed in all cases for different total gas pressures.

![500 Pa](image1)

Fig. 2 Post-discharge in pure nitrogen in Pyrex discharge tube at different total gas pressure.

![1 500 Pa](image2)

![3 000 Pa](image3)

![5 000 Pa](image4)

Fig. 3 Dependencies of intensity on decay time for 1\textsuperscript{st} negative nitrogen spectral systems.

Fig. 4 Dependencies of intensity on decay time for 1\textsuperscript{st} positive nitrogen spectral systems.

Fig. 5 Dependencies of intensity on decay time for 2\textsuperscript{nd} positive nitrogen spectral systems.
Graphs in Figs. 3-5 correspond with situation showed at photos in Fig. 2. And they show the dependencies of measured intensity on decay time of post discharge for nitrogen 1st negative, 1st positive, 2nd positive and NOβ spectral system. The highest contribution to the pink afterglow intensity is from the 1st negative system.

At low total gas pressures, the maximum of pink afterglow was observed at decay time about 5 ms and it was very sharp. The pink afterglow effect is shifted to the later decay times with the increase of gas pressure and its maximum is not such sharp as before. The maximum intensity as a function of the pressure is reached at pressure 1 000 Pa-1 500 Pa, as Fig. 7 shows, for nitrogen 1st negative spectral system. Situation is more or less the same also for the other two nitrogen spectral systems.

The slight increase of intensity is visible at decay times of about 60-80 ms at low total gas pressure only. The intensity is pressure independent at high pressure.

The intensities of NOβ system (Fig. 6) are generally very low in comparison with the others and they increase with the increase of pressure. The NOβ emission is nearly constant after the end of pink afterglow.

The relative populations of nitrogen states were calculated from measured intensities and they were normalized to the total population of given electronical states in the active discharge. Vibrational distribution for \( N_2 (B^3 \Pi_g) \) state at decay time 5 ms and 135 ms is shown in Fig. 8. At lower levels up to level 12 the distribution is nearly Boltzmannian. At levels 17-20 the distribution is also nearly Boltzmannian. Significant decrease at levels 13-16 is due to the predissociation. At the later decay times, the levels 10-12 are populated mainly by three body recombination of ground state nitrogen atoms. Absolute values of populations at all levels are decreasing with the increase of decay time.
Fig. 9 Dependencies of relative vibrational distributions for N$_2$ (B $^2\Sigma_u^+$) and N$_2$ (C $^3\Pi_u$) states. Vibrational distributions of N$_2$ (C $^3\Pi_u$) and N$_2$ (B $^2\Sigma_u^+$) states are nearly constant for all decay times. Fig. 9 shows an example of these dependencies at decay time 5ms.

4. Kinetic model

The N$_2$(B $^2\Pi_g$) and N$_2$(C $^3\Pi_u$) states are dominantly created by pooling reactions of lower metastable states, especially by the vibrational excited ground state and by the lowest 8 levels of N$_2$(A $^3\Sigma_u^+$) state that are strongly metastable [4]. The higher ground state vibrational levels populated by v-v process are also precursors for N$_2$(A $^3\Sigma_u^+$) state creation because its concentration at the end of active discharge is not sufficient for the observed results [3, 5]. The contribution of other metastable states, especially metastable singlet states, to the pink afterglow creation is not fully understood yet. Besides pooling reactions, the atomic nitrogen ground states three body recombination significantly contributes to vibrational populations at levels N$_2$(B $^3\Pi_g$, v = 10 – 12). A much more complex description of the mechanisms was described recently in [5].

The kinetics of the molecular ion radiative state can be explained in a two-step scheme. Before the pink afterglow the charged particle concentration is very low due to the fast electron-ion recombination [6], but during the pink afterglow it significantly increases. So the first step is the molecular ion creation. This process is known as a step-wise ionization [7]. In its principle, the highly excited neutral metastable molecules (excited both electronically and vibrationally) can have energy sufficient for the ionization during their mutual collisions. After molecular ion creation, the excitation to the radiative state must be completed. Recent studies have demonstrated that the main process responsible for the population of the radiative N$_2^+$ (B $^2\Sigma_u^+$) state is the collisionally induced energy transfer from the vibrationally excited neutral ground state molecules, namely N$_2$(X $^1\Sigma_g^+$, v ≥ 12) [6].

5. Conclusions

The work presents results obtained during spectroscopic observations of DC flowing post-discharges of pure nitrogen plasma at different total gas pressures. The discharge tube wall temperature was 300 K. Three nitrogen spectral systems and NO$\beta$ bands were identified in the investigated spectral region. The pink afterglow effect was observed at all applied total gas pressures. Maximum of pink afterglow was recognized at about 5 ms and it was very sharp at low total gas pressure. With the increase of total gas pressure, it shifts to the later decay times (up to 20 ms). The relative populations were calculated in the dependence on vibrational quantum number. Based on the experimental results, the simplified kinetic model was proposed.

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References