Study of Nitrogen Atom Recombination by Optical Emission Spectroscopy

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The reaction kinetics in nitrogen flowing afterglow was studied by optical emission spectroscopy. The DC flowing post-discharge in pure nitrogen was created in a quartz tube at the total gas pressure of 1000 Pa. The optical emission spectra were measured along the flow tube. It was found that N atoms are the most important particles in the late nitrogen afterglow. In order to explain the decrease of N atom concentration, it was also necessary to include the surface recombination of N atoms to the model.

Keywords: optical emission spectroscopy, nitrogen afterglow, surface recombination coefficient

1 INTRODUCTION

In flowing nitrogen afterglows (post-discharges) at low pressure, a large number of nitrogen atoms is created in the discharge or in the short-lived (pink) afterglow during collisions of nitrogen molecules with electrons, vibrationally excited nitrogen molecules and metastable states. The nitrogen atoms are lost by volume and wall recombination [1]. The probability of volume recombination (a three-body collision) tends to be lower than the wall recombination probability γ. The probability γ is the ratio between the number of atoms effectively recombining at the surface over the number of atom-wall collisions [2]. Nitrogen late afterglow is characterized by a visible emission in the yellow part of the spectrum, associated with the recombination of the nitrogen atoms in the gas phase.

Nitrogen post-discharges are widely used for various industrial applications such as nitriding [3], plasma surface modification [4] or plasma sterilization [5]. Besides laboratory and technological plasmas, the nitrogen post-discharge is studied also in connection with the kinetics of the upper Earth atmosphere (corona borealis [6]) and the processes occurring in nitrogen post-discharges are also taken into account in some extraterrestrial systems, for example in the Titan atmosphere [7].

This paper presents a method for obtaining the atomic nitrogen recombination probability (γ). It is based on the measurement of 11-7 transition intensity in first positive nitrogen spectral system (FPS).

2 EXPERIMENTAL SET-UP

The flowing configuration of nitrogen DC discharge was used for the experimental study. This experimental set-up was already used for our previous study with nitrogen [8, 9]. A simplified schematic drawing of the experimental set-up is given in Fig. 1. The active discharge was created in a quartz discharge tube with the inner diameter of 12 mm at the constant total gas pressure of 1000 Pa and the discharge power of 130 W. Hollow molybdenum electrodes were placed in the side arms (at the interelectrode distance of 120 mm) of the main discharge tube to minimize their sputtering and also to minimize the influence of the light emitted in the electrode regions. The nitrogen gas was of 99.9999 % purity and it was further cleaned by Oxiclear and LN_2 traps. The reactor system was pumped continuously by a rotary oil pump separated from the discharge tube by another LN_2 trap. The gas flow of 800 sccm was automatically controlled by the Bronkhorst mass flow controller. The total gas pressure in the discharge tube was measured by a capacitance gauge connected to the end of the discharge tube. The gas temperature was 300 K.

The bulk flow velocity v_g of nitrogen in the tube was calculated from the continuity equation and the state equation for ideal gas. The calculated velocity v_g was 12 ms^{-1}. The flow analysis was performed in the same way as in previous studies using flowing afterglow [10, 11].

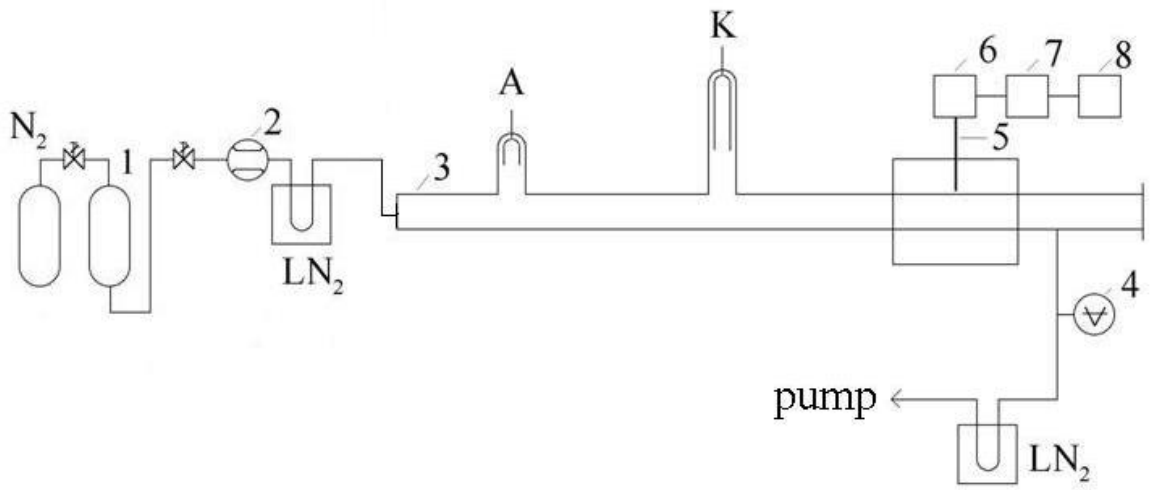

Fig. 1: Scheme of the experimental setup. 1- catalyzer Oxiclear; 2- mass flow controller; 3- quartz discharge tube; 4-capacitance gauge; 5-quartz optical fiber; 6-monochromator Jobin Yvon Triax 550; 7-CCD; 8-PC

The distance d needed to develop a full parabolic velocity profile is given by $d = 0.277\ a\ R$, where a is the flow tube radius (0.6 cm) in cm and R is the Reynolds number. For our experimental conditions, the Reynolds number R is equal to 184, which gives d = 31 cm. Furthermore, our experimental setup introduced perturbations into the flow pattern at the side arms and at the nitrogen inlet. So, the flow will be in transition between plug and parabolic flows and in this case the bulk flow velocity can be used for the calculation of the decay time. This approach was found to be correct in previous studies [8-10]. In present experiment the line intensities (which are proportional to the exited particle concentrations) were measured across the diameter of the flow tube. Bolden et al. [12] have experimentally demonstrated that this is equivalent to monitoring the concentration at the center of the tube for fully developed parabolic flow conditions.

The optical spectra were measured by Jobin Yvon monochromator TRIAX 550 with CCD detector. The 300 gr/mm grating was used for overview spectra in the range from 300 nm to 600 nm. The emitted light was led to the entrance slit of the monochromator by the multimode quartz optical fiber movable along the discharge tube.

3 RESULTS

The optical spectra were measured as a function of position along the flow tube in the distances 30 – 52 cm from the active discharge. An example of the typical recorded post-discharge spectrum is shown in Fig. 2. The nitrogen late afterglow emission is dominated by the

$$N_2(B, v=11) \rightarrow N_2(A, v=7) \qquad (1)$$

band of the first positive system at 580 nm [13], see also Fig. 2. This band is correlated with the three-body recombination process with the rate constant $k_{vol} = 4.4 \times 10^{-33}$ cm^6 s^{-1} taken from [14]

$$N + N + N_2 \rightarrow N_2(B, v=11) + N_2. \qquad (2)$$

As the $N_2(B, v=11)$ state can de-excite either radiatively to the A state with a global frequency ν_{rad} or collisionally by quenching with the nitrogen molecules (k_q), the emitted intensity can be written as

$$I_{11-7} \propto [N_2(B, v=11)] \propto \frac{k_{vol}[N]^2[N_2]}{\nu_{rad} + k_q[N_2]} \qquad (3)$$

where the values $\nu_{rad} = 1.7 \times 10^5$ s^{-1} and $k_q = 5 \times 10^{-11}$ cm^3 s^{-1} were taken from [15]. So it appears that the evolution of the N atom concentration can be followed monitoring I_{11-7}. For pressures higher than 133 Pa is $k_q[N_2] >> \nu_{rad}$ and equation (3) reduces to

$$[\mathrm{N}] \propto \sqrt{I_{11-7}} \quad . \tag{4}$$

The N atom concentration determined from equation (4) is shown in Fig. 3 as a function of decay time. These N atom concentrations were multiplied by a constant so that they can be coincident at t = 0 s (distance 30 cm from active discharge) with absolute N atom concentration determined in previous study by NO titration [16].

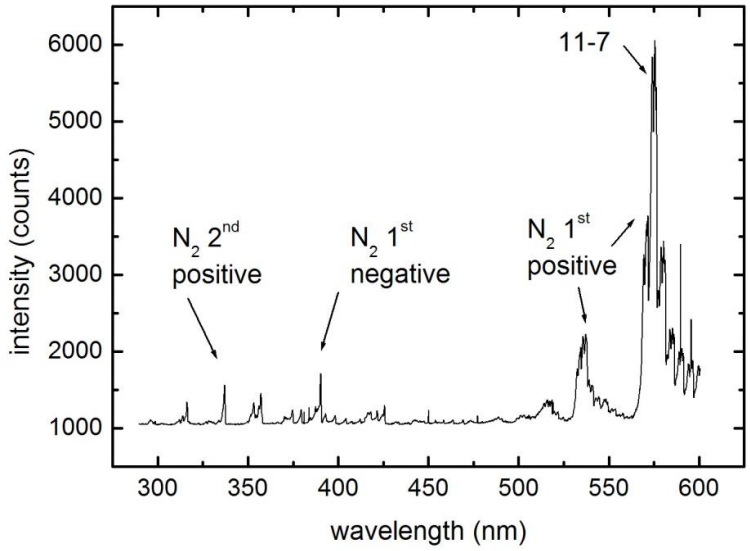

Fig. 2: Overview spectrum of nitrogen post-discharge

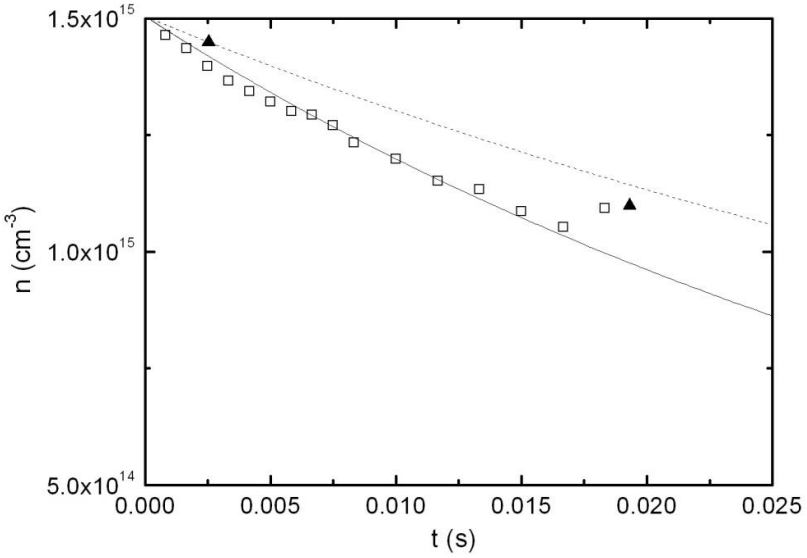

Fig. 3: Time dependence of nitrogen atom concentration. Squares – concentrations determined from Eq. (4); triangles – concentrations determined by NO titration [16]; full line – calculation from the model with $\gamma = 2.16 \times 10^{-6}$; dashed line – calculation from the model with $\gamma = 1.35 \times 10^{-6}$

The kinetic model of nitrogen late afterglow developed previously [9] was used to fit measured data using least square method. The value $\gamma = (2.16 \pm 0.07) \times 10^{-6}$ was obtained

from this method. However, the N atom concentrations determined from measurement of FPS intensity decreases faster than the N atom concentration determined by NO titration and also faster than calculated N atom concentration from the model in previous study [9] with the value $\gamma = 1.35 \times 10^{-6}$. This discrepancy could be caused by incorrect determination of 11-7 transition intensity in FPS due to overlap of this band with neighbouring vibrational bands.

4 CONCLUSION

The recombination of N atoms in nitrogen late afterglow was studied in flowing afterglow experiment at pressure of 1000 Pa. The optical emission spectra were measured at different positions along the quartz flow tube (and hence at different times of afterglow). The spectra were dominated by 11-7 band of the nitrogen first positive system. This band is correlated with three body (volume) recombination of atomic nitrogen and thus it is possible to determine the relative concentration of N atoms from band intensity. Then the wall recombination probability γ for N atoms was calculated from the decrease of N atom concentration along the flow tube and the value $\gamma = (2.16 \pm 0.07) \times 10^{-6}$ was obtained.

Acknowledgements

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