MERCURY TITRATION IN NITROGEN POST-DISCHARGE

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Abstract. This work extends our recent investigation of mercury excitation under post-discharge conditions and presents results obtained during spectroscopic observations of mercury titration in nitrogen DC flowing post-discharges. DC discharge in quartz tube was created at 1 000 Pa and 290 W. The plasma was studied by optical emission spectroscopy in the range of 300–800 nm and 248–260 nm, respectively. Three nitrogen spectral systems and mercury spectral line at 254 nm were identified. The results showed dependence of mercury spectral line maximal intensity on the decay time. The kinetic explanation can be made through a strong depopulation of the level \( N_2 (X \Sigma^+_g, v = 19) \) creating the mercury \( ^3P_1 \) state that is upper state of mercury UV line at 254 nm. The numeric model was used for the comparison of proposed kinetic processes to the experimental data.

1. INTRODUCTION

Post-discharges containing nitrogen are used for various applications such as nitriding (Bockel et al. 1997), remote plasma enhanced chemical vapor deposition of thin nitride films (Meikle et al. 1990) or plasma sterilization (Pintassilgo 2005). Although there is a long interest of nitrogen post-discharge kinetics itself there are still various open problems. Relaxation processes of atomic and various metastable molecular nitrogen states created during an active discharge lead to the common thermodynamic equilibrium at given temperature. Besides collision processes, light emission plays a significant role in the energy loss. Visible light can be observed up to one second after switching off the active discharge depending on the discharge conditions, mainly on pressure. The first period (up to about 3 ms) of the post-discharge in the pure nitrogen is characterized by a strong decrease of the light emission. After that, the strong light emission is observed at decay time of about 5–14 ms after the end of an active discharge. This light emission is known as the pink afterglow or short live afterglow and it can be observed in nitrogen only (Sa et al. 2004, Loureiro et al. 2006). Electron density measurements during the afterglow showed...
the strong increase of the free electron concentration during this post-discharge period. The effect of the nitrogen pink afterglow can be studied only in pure nitrogen and various traces quench it dramatically (Hubenak and Krema 2000, Krema et al. 2007). The present work is focused on the experimental study of the nitrogen post-discharge kinetic changes caused by mercury vapor added directly into the afterglow.

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 Quartz discharge tube with a 120 mm electrode distance and the constant discharge power of 290 W. The total gas pressure was 1000 Pa. Hollow molybdenum electrodes were placed in the side arms of the main discharge tube to minimize their sputtering and also to minimize scattering of the light emitted in the electrode regions. Nitrogen was of 99.9999% purity and it was further cleaned by Oxiclear and LN$_2$ traps. The reactor system was pumped continuously by rotary oil pump separated from the discharge tube by another LN$_2$ trap. The gas flow of 800 Sml min$^{-1}$ was automatically controlled by mass flow controller. Total gas pressure in the discharge tube was measured by a capacitance gauge connected to the end of the discharge tube. The titration capillary tube was made from Pyrex and it was inserted upstream from the discharge into the Quartz tube at its axis. Nitrogen flow rate of 7.5 Sml min$^{-1}$ (99.9999% purity) was enriched by saturated mercury vapor from a vial. Mercury was added into different positions of flowing pure nitrogen post-discharge through this capillary.

Optical spectra were measured by Jobin Yvon monochromator TRIAX 550 with 55 cm focal length. The 300 gr/mm grating was used for overview spectra (300–800 nm), the grating with 3 600 gr/mm was used for the mercury line obser-
vations. The emitted light was led to the entrance slit of the monochromator by the multimode quartz optical fibre movable along the discharge tube. CCD detector was cooled by liquid nitrogen. The 1st positive ($N_2 (B^3\Pi_g) \rightarrow (A^3\Sigma_u^+)$), 2nd positive ($N_2 (C^3\Pi_u) \rightarrow (B^3\Pi_g)$) and 1st negative ($N_2^+ (B^2\Sigma_u^+) \rightarrow (X^2\Sigma_g^+)$) nitrogen spectral systems and mercury line at 254 nm were recorded in all spectra. No other atomic or molecular emissions were observed.

3. RESULTS

An example of the recorded post-discharge overview spectrum with mercury addition is given in Fig. 2.

![Figure 2](image1.png)

**Figure 2:** Overview spectrum of nitrogen post-discharge with mercury titration. The position of the titration capillary tube was 25 cm from active discharge (20 ms of decay time).

![Figure 3](image2.png)

**Figure 3:** Mercury line integral intensity during the post-discharge at mercury titration point at 20 ms.

The titration was arranged in different positions from the active discharge. The mercury line was identified a few ms after the titration point and its intensity reached rapidly maximal value. After that, an exponential decrease of the line intensity was observed as it is demonstrated in Fig. 3. The dependence of maximal measured intensity as a function of decay time corresponded with titration position is shown in Fig. 4-left. It can be seen that mercury line emission is observed at the titration point of about 5 ms that corresponds well with the maximum of pink afterglow emission in pure nitrogen, as it was pointed in Introduction.

The simple kinetic model presented in Kanicky et al. (2007) proposed that mercury line is created under post-discharge conditions by the following reaction

$$N_2 (X^1\Sigma_g^+, \nu = 19) + Hg (1S_0) \rightarrow N_2 (X^1\Sigma_g^+, \nu = 0) + Hg (3P_1)$$

The numeric model describing nitrogen post-discharge kinetics (Sa et al. 2004) shows the enhancement of population at the nitrogen ground state vibrational level 19 at decay time of a few ms as it is demonstrated in Fig. 4-right. Comparing both graphs in Fig. 4 we can conclude a qualitative agreement between experimental
and theoretical data but more detail experiment is needed for the quantitative comparison.

Figure 4: Left – dependence of measured relative intensity on decay time (position of titration capillary tube). Right – dependence of relative population on vibration level \( v = 19 \) calculated from kinetic model.

4. CONCLUSIONS

The optical emission spectroscopy was used to investigate nitrogen post-discharge by mercury titration. The mercury spectral line at 254 nm was recognized in all spectra recorded in time evolution. The dependence of its maximal intensity on position of titration capillary tube was compared to calculated concentration of \( \text{N}_2 (\text{X} \, ^1\Sigma_g^+, \, v = 19) \) state that was proposed as its precursor and good qualitative agreement was observed. The further experiments will be needed to obtain also quantitative correspondence with model.

Acknowledgements

This work was supported by the Czech Science Foundation, project No. 202/08/1106 and project No. 104/09/H080.

References