NO and O ground state density dynamics in a pulsed microwave discharge

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Abstract: In this work the ground state of NO and O density dynamics is studied in a pulsed microwave discharge using calibrated laser-induced fluorescence spectroscopy. A noticeable drop in both NO and O atom densities is found during the plasma pulse-on time as a result of gas heating causing gas rarefaction. The corresponding densities start increasing already at the begining of the plasma pulse-off time mainly as a result of gas temperature decrease.

Keywords: Pulsed microwave discharge, laser-induced fluorescence, NO and O densities.

Nowadays, plasma-assisted nitrogen fixation is gaining more and more attention as a green alternative method when considering the utilization of intermittent renewable energy sources [1,2]. Numerous efforts have been made to fix chemically inert N_2 into reactive forms such as NH_3 or NO_x, used as a feedstock for the production of fertilizers. Among several plasma types, low-pressure pulsed microwave (MW) discharges [3-5] are found to suit well for plasma-assisted N-fixation due to the significant molecular vibrational excitation. MW discharges, however, remain barely explored in the field of N-fixation.

The investigation of atomic and molecular density dynamics in the MW discharge is of a great importance for better understanding of the plasma chemistry and related mechanisms. Numerous experimental and kinetic modelling studies on NO and O ground state densities in low-temperature discharges have been made at different discharge conditions over the last three decades. However, only few works have addressed the time evolution of NO and O densities during the plasma pulse, especially in MW plasmas. Besides, the direct measurements of NO and O atoms kinetics, particularly in low-pressure pulsed MW plasmas have been weakly explored. Addressing this point, this work reports NO and O densities dynamics in pulsed MW diacharge in N_2-O_2 gas mixtures.

The temporal evolution of NO and O ground state densities during the plasma pulse have been realized using calibrated laser-induced fluorescence (LIF) and two photons absorption laser-induced fluorescence (TALIF) spectroscopy, respectively. Schematic representation of the MW plasma source, the laser setup arrangement and ICCD detector used in this study is given in Fig. 1. A Spectra Physics INDI Nd:YAG pulsed laser with a repetition rate of 10 Hz and a pulse duration of about 5 ns was used. The laser beam at second harmonic generation (SHG) at 355 nm has been guided to a Sirah Cobra Stretch dye laser using Coumarin 450 dye solution. The measured fluorescence signal (LIF or TALIF) was collected through a bandpass filter (λ = 248 nm for NO and λ = 840 nm for O with FWHM = 10 nm), recorded by an Andor iStar 740 intensified charge coupled device (ICCD) camera.

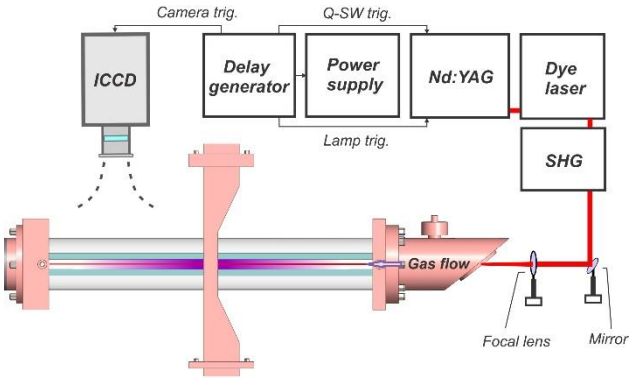

Fig. 1. Laser beam path in the MW plasma. (ICCD - intensified charge coupled device, SHG - second harmonics generator, Nd:YAG - neodymium-doped yttrium aluminium garnet).

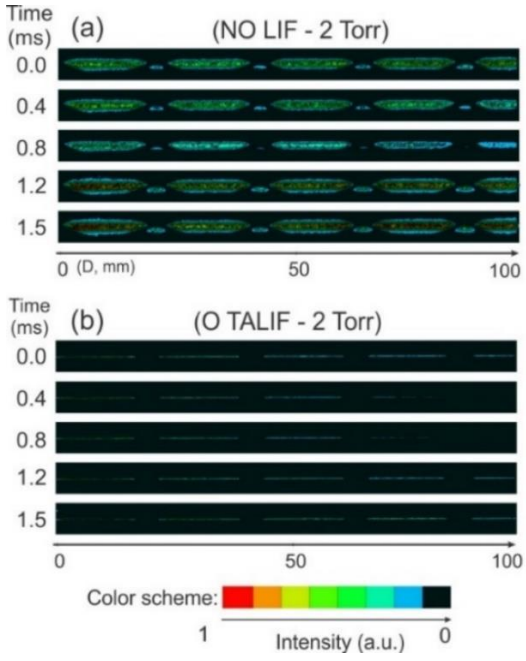

Fig. 2. Time-resolved 2D maps of the NO LIF (a), and O TALIF (b) signals measured downstream (after the waveguide) and at 2 Torr.

Both the NO LIF and O TALIF signals measured downstream , i.e. after the waveguide is shown in Fig. 2. After calibrationg these signals, the corresponding absolute number densities were determined. These densities, measured during the plasma pulse-on time and pulse-off time, are presented in Fig. 3(a,b). As we can see, both NO and O number densities decrease during the first 0.6 ms. After that, they show a plateau roughly from 0.6 ms to 1 ms. Finally, at the beginning of the plasma pulse-off time, both densities start increasing, which is finally followed by a saturation.

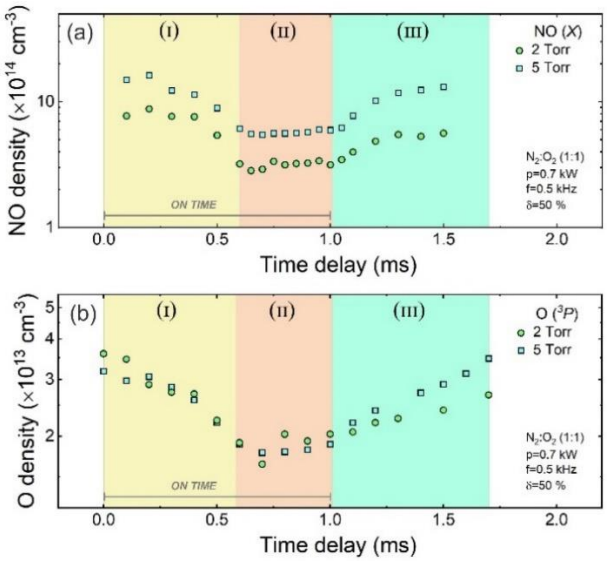

Fig. 3. The time-evolution of the ground state NO density (a), and ground state O atom density (b) measured downstream at 2 and 5 Torr. More information is available in the legend.

The following explanation for these result has been found: at the beginning, when plasma switches ON, the vibrational-vibrational (V-V) energy transfer plays a decisive role in step-wise vibrational excitation as a result of electron impact excitation of first vibrational levels. After several plasma pulses a steady state occurs, which is mainly measured in our case. In this state we may expect certain (accumulated) vibrational excitation during both the plasma-ON and plasma-OFF time. In the case of NO measured number density, for example, the apparent density decrease during the plasma-ON time might be a result of both the gas heating and the vibrational excitation of NO leading to some NO rarefaction.

The gas temperature measurements during the plasma pulse performed at the same discharge condition confirms this hypothesis (see Fig. 4). In the case of O density, the same phenomenon takes place due to gas heating.

Finally, during the plasma-OFF time, collisional vibrational quenching may also leads to additional NO relaxation thus increasing population of the lower vibrational levels. This effect may cause an additional increase in LIF/TALIF signals measured across the plasma cycle, resulting in the overall density restoration to the initial value, measured at the beginning of the plasma-ON time.

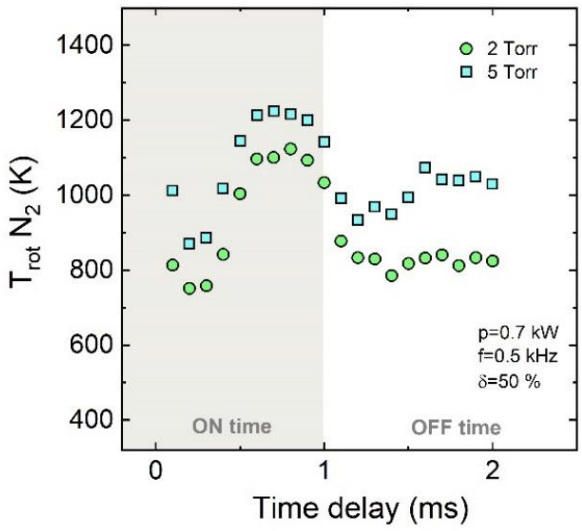

Fig. 4. The evolution of rotational temperature (T_{rot}) of N_2(C, v'=0) state corresponding to the bandheads located at 337 nm determined by rotational spectra fitting (optical emission spectroscopy). The measurements were performed in the N_2-O_2 gas mixture at different pressures.

References

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