Investigation of atmospheric pressure nitrogen plasmas by cavity ring down spectroscopy

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Abstract. We have applied Cavity Ring-Down Spectroscopy (CRDS) to investigate Nanosecond Repetitively Pulsed Discharge (NRPD) in nitrogen and air at atmospheric pressure in a pin-to-pin electrode configuration. We have measured the concentration of N\(_2\)(A) by probing absorption transitions in the near Infrared at 770 nm. We report on preliminary results about the measurement of the N\(_2\)(A) concentration and its evolution under different discharge regimes. We present here a comparison for an air plasma between the time evolution of N\(_2\)(A) measured by CRDS and the temporal evolution of atomic oxygen measured by two-photon absorption laser-induced fluorescence (TALIF). This study will allow us to compare our experimental results to those given by a kinetic model and help provide a better understanding of the plasma physicochemical processes.

1. Introduction

Environmental issues are today one of the major societal concerns. As a consequence, new engine development is becoming increasingly subject to strict pollution regulations and to a necessity to reduce fuel consumption. Getting the best compromise between the decrease in toxic emissions and the increase in engine power output without raising production costs, becomes a major challenge. One of the possibilities allowing the reduction of these pollutants consists in using lean premixed combustion systems. However, these systems lead to other problems, such as the occurrence of flame extinction and combustion instabilities, especially destructive to the combustion chamber. To resolve these problems, it was shown [1] that one can enhance lean combustion by a local addition of energy that allows a stabilization of the flame by modifying the thermal and reactive mechanisms. The use of high voltage nanosecond repetitively pulsed discharges (NRPD) represents a promising method in answer to this need. The objective of our study is to determine the mechanism that leads to flame stabilization. Following the results obtained using the kinetic model [2] it was predicted that atomic oxygen, which is a key species in the combustion process, is produced through a two-step mechanism. According to this mechanism, electronically excited molecular nitrogen formed via electron-impact excitation, dissociates molecular oxygen, thus generating atomic oxygen which can oxidize the fuel. To validate the kinetic model, the densities of ground state atomic oxygen [3] as well as the excited electronic state N\(_2\)(A) have been measured using two advanced techniques: Two-Photon Laser Induced Fluorescence (TALIF) at 225 nm for detection of atomic oxygen in the ground state, and pulsed Cavity Ring-Down Spectroscopy (CRDS) for the detection of N\(_2\)(A) species. CRDS is a very
sensitive diagnostic tool for low species concentration measurements. The technique is based on measurement of the decay intensity of a laser beam inside a cavity comprised of two high-reflectivity mirrors. We first measure the decay intensity in an empty cavity and then when the cavity contains the absorbing sample. The difference of these decays gives the coefficient of absorption and if the line strength is known we can calculate the absorbing species concentration. A detailed description of the CRDS technique is given in Ref. [4].

2. Experimental setup
The discharges were generated in a pin-to-pin electrode configuration by high voltage pulses of 5 to 8 kV in amplitude, 10 ns is duration, and applied at a repetition frequency of 10 kHz. The experiments were conducted in atmospheric pressure air and nitrogen flows preheated to 1000 K, with an axial flow rate up to 30 l/min. The plasma discharge was produced by applying nanosecond high-voltage pulses between two metallic electrodes. The distance between these electrodes in pin-to-pin configuration was 3 mm.

The cavity consists of two concave high reflectivity mirrors (R > 99.97%) from Los Gatos Research. The distance between the cavity mirrors is 67 cm. The cavity is fed by a tunable pulsed dye laser (Continuum ND 6000) pumped with a Continuum Precision PL 8010 Nd:YAG laser, with repetition frequency of 10 Hz. The output beam passes first through a mode matching optics system and then enters the CRDS cavity. The light collected after the second cavity mirror is detected with a photomultiplier tube (PMT Hamamatsu H9035-03) and recorded onto the oscilloscope. The collected light is filtered by two bandpass interference filters (CVI) with peak transmittance at 770 nm (CVI-F10-770, FWHM 10 nm). Synchronization of the laser pulse with the discharge pulse is achieved with a Berkeley Nucleonics (BNC) 555 four-channel pulse delay generator, which triggers all devices. The experimental set up is depicted in figure 1.

![Figure 1. CRDS Experimental Set Up](image)
PMT: photomultiplier tube, HV: high voltage pulse generator

3. Results and discussion
Figures 2 and 3 show typical CRDS signal intensities in linear and logarithmic scale, measured in the nitrogen plasma preheated at 1000 K.
The black curves show the variation of the intensity recorded by the PMT when the cavity is subjected to 770.055-nm radiation; which corresponds to an off-resonance wavelength for the N$_2$ B-A transition. The red curves are obtained on an absorption resonance at 769.945 nm. The peak absorption at 769.945 nm is the convolution of Q$_{(22)}$ and Q$_{(16)}$ transitions of the band: $\nu' = 2 \leftrightarrow \nu'' = 0$. In logarithmic scale, we notice several slopes in the absorption plot which means that the absorption is not constant with time (thus the decay is not a single exponential function of time). The time dependent absorption coefficient is given by the equation (1):

$$ k(\nu,t) = \frac{L}{c I_{\text{abs}}} \frac{d}{dt} \left( \ln \frac{I_1}{I_3} \right) $$

where $c$ is the speed of light, $I_{\text{abs}}$ is the absorption length, $L$ is the cavity length, $I_1$ is the ring-down intensity off-resonance, and $I_3$ is the ring-down intensity on-resonance.

Using line strengths obtained with Specair [5] the time evolution of N$_2$(A) concentration could be measured.

Next, we examine how different experimental parameters can influence the N$_2$(A) concentration. We started first by measuring the variation of N$_2$(A) concentration with the applied voltage. Figure 4 shows the results averaged over one microsecond immediately after the discharge pulse. In Figure 4, the N$_2$(A) concentration increases linearly when the voltage increases from 6.2 to 7.7 kV. Over this voltage range, note that the plasma produced by the discharge varies from a diffuse regime to a filamentary regime. Over this voltage range, the number of N$_2$(A) molecules increases from 2x10$^{13}$ to 1.4x10$^{14}$ cm$^{-3}$.

The N$_2$(A) spatial distribution, shown in Figure 5, has a nearly Gaussian profile, of Full Width at Half Maximum equal to 0.9 mm. In the following analysis, we therefore assumed that the N$_2$(A) species are approximately uniform in a cylinder of about 1 mm in diameter.
4. Conclusion

CRDS was successfully applied to measure the concentrations of key species in nanosecond repetitively pulsed discharges in nitrogen and air at atmospheric pressure with high spatial (sub millimeter) and temporal (sub microsecond) resolution. CRDS has proven to be a sensitive technique for N$_2$(A) detection.

In nitrogen, the N$_2$(A) density is found to increase linearly with the applied voltage. In air, the characteristic time of N$_2$(A) concentration decay coincides with characteristic time for atomic oxygen formation about 100 ns after the discharge event, suggesting that atomic oxygen production is the result of a two-step mechanism as predicted by the kinetic model. This is a partial validation of the two-step mechanism. For a complete validation, a calibration of the TALIF signal using xenon as a reference for absolute atomic oxygen densities is in progress.

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