Direct optical measurements of reactive nitrogen species (RNS) in cold atmospheric-pressure plasma jets

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Abstract: To guarantee the safe and efficient use of atmospheric-pressure plasma jets (APPJs) in plasma medicine applications, it is vital that a thorough understanding of the physics and chemistry of these plasmas is established. Reactive nitrogen species (RNS), e.g. N, NO, play a crucial role in the applications of APPJs. We present the first direct measurements of atomic nitrogen species in an APPJ using a two-photon laser-induced fluorescence diagnostic.

Keywords: atmospheric-pressure plasma jet, TALIF, reactive nitrogen species

1. Introduction

Atmospheric-pressure plasma jets (APPJs) in noble gas, driven with radio-frequency (rf) power can operate in open air, remain at room temperature and still have a selective chemistry. The unique combination of characteristics of these APPJ devices makes them ideal tools for healthcare [1, 2]. Emerging applications in plasma medicine include surgical tools for clean cutting, new sterilization and decontamination techniques for medical instruments and development of techniques to directly treat living cells and human tissue [3–6].

It is vital that a thorough, fundamental understanding of the physics and chemistry in APPJs is established to guarantee the effectiveness and safety of these devices in healthcare applications. Currently, the exact mechanisms through which APPJs affect biological materials like cells, bacteria and DNA are largely unknown. Recent studies [7] in this field suggest the importance of reactive oxygen and nitrogen species (RONS) such as O, N, $O_2*(^1\Delta)$, O_3, OH, NO, H_2O_2, O_2^-, N_2O, HNO_2. New research in cell biology shows that RONS are of key importance in many cellular processes, e.g. cell response, neurotransmission, immune system response and wound healing. For this reason, RONS are actively studied for current and future therapeutics, e.g. antibiotics and redox cancer treatment.

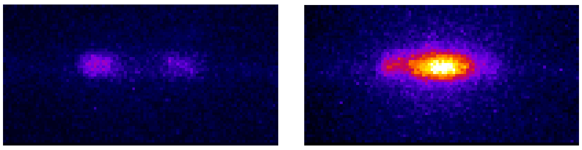
APPJs are expected to produce large quantities of RONS, possibly explaining their biological effects. However, which RONS are created in plasma jets and in which concentrations is largely unknown. The starting point for the creation of many of the different RONS is the production of atomic oxygen and nitrogen. These species are created in large quantities in the APPJ by breaking up oxygen and nitrogen gas molecules. Subsequently these oxygen and nitrogen radicals move downstream in the jet undergoing further reactions with the surrounding air, creating different RONS such as NO, O_3, OH and H_2O_2 which interact with the biological material. In order to fully understand and control the production and effects of different RONS it is important to measure atomic oxygen and nitrogen species in APPJs. Unfortunately, measuring these species is experimentally challenging.

Two-photon absorption laser-induced fluorescence (TALIF) spectroscopy is a powerful technique which has been used to provide information on absolute, ground-state densities of plasma species in low-pressure plasma applications and recently also been applied to an APPJ like ours to measure absolute atomic oxygen densities [8]. However, so far this technique has not been applied to atomic nitrogen, despite the significance of N in the production of RONS. In this paper we present our atomic nitrogen TALIF diagnostic and, to our knowledge, the first direct measurements of these atomic nitrogen species in an APPJ device.

2. Experimental arrangement & diagnostic technique

The plasma jet under study is a radio-frequency (13.56 MHz), micro-scaled APPJ device designed for optimal access for optical diagnostics [9]. It is operated in helium gas with a molecular nitrogen admixture of up to a few percent. This jet has been studied extensively in the past with for instance measurements of gas temperature, helium metastable, ozone, singlet delta oxygen and atomic oxygen densities. In addition, the effects of our APPJ on biological materials, e.g. plasmid DNA, have been investigated.

Our two-photon absorption laser-induced fluorescence (TALIF) diagnostic uses 206.65 nm photons from a tuneable dye laser for excitation of ground-state N atoms. Fluorescence of 3 spectral lines in the range 742-746 nm is observed using an interference filter and an intensified CCD camera. TALIF measurements are performed in an APPJ at a point 1 cm from the output of the plasma channel. More details on both the APPJ and the TALIF technique can be found in [10].



l = 206.6580 nm
0.0075 nm off resonance

l = 206.6505 nm
2-photon excitation

Fig.1 ICCD images of observed fluorescence. Left: laser is 0.0075 nm off the two-photon resonance. Observed emission is scattered laser light, not fluorescence. Right: Fluorescence when laser wavelength is at the two-photon absorption transition.

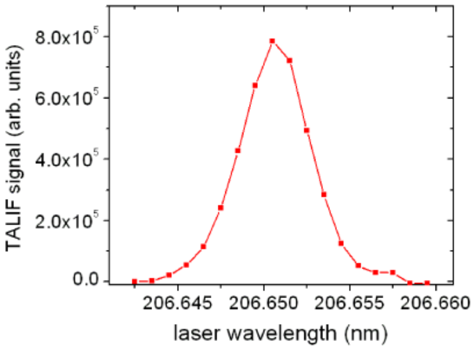


Fig.2 Fluorescence signal as function of laser wavelength when scanned across the two-photon absorption transition.

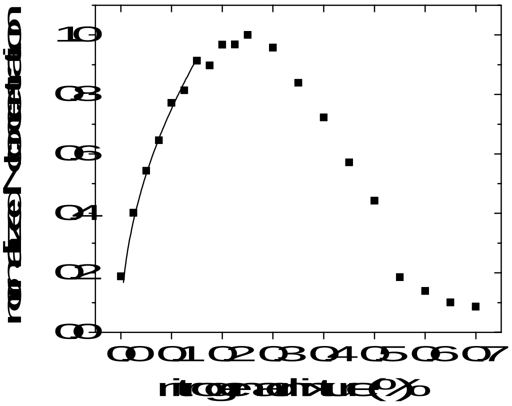


Fig. 3 Measured relative atomic nitrogen concentration as a function of nitrogen admixture in the feed gas for the APPJ.

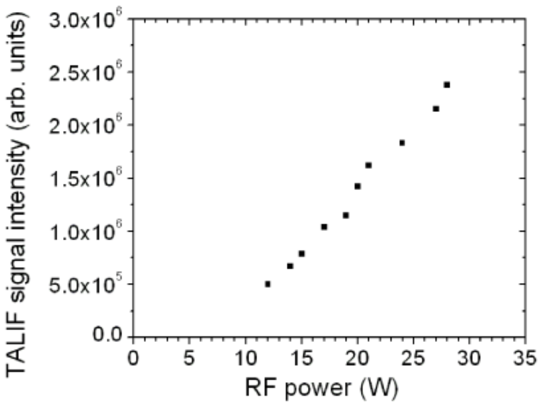


Fig. 4 Measured relative atomic nitrogen concentration as a function of applied rf power. The nitrogen admixture is kept constant at 0.25%.

3. Results and discussion

Fig. 1 shows the observed fluorescence signal when the laser is 0.0075 nm off the two-photon resonance (left image) and when it is exactly on the resonance (right image). The light intensity observed in the off-resonance image (left) is not fluorescence light but laser light scattered off the APPJ windows, leaking through the interference filter. Fig. 2 shows the integrated fluorescence intensity as a function of the laser wavelength. The laser beam was focused to a spot of about 600 μm diameter with an energy of 0.15 mJ per pulse and was sent through the plasma jet at an angle of 45° at a point 10 mm from the output of the plasma channel. The ICCD camera, observing the fluorescence radiation perpendicular to the laser beam, was cooled to −20 °C, the intensifier gate width was 25 ns and the exposure was synchronized with the laser. For every measurement, signals from 500 laser shots were accumulated on the ICCD.

Next, the laser was tuned to the resonance and the APPJ was operated with different admixtures of molecular nitrogen ranging from 0 to 0.7 vol% while the applied rf power was kept constant. The results of the TALIF measurements for different admixtures of molecular nitrogen are presented in Fig. 3. In these measurements, the observed fluorescence is spatially integrated over the entire laser spot and corrected for collisional quenching. The resulting, relative atomic nitrogen concentration increases from 0% N_2 by a factor of 5 to a maximum at 0.25% N_2. For higher nitrogen admixtures, up to 0.7%, the N concentration decreases again to low values similar to the case with 0% admixture. A further increase in nitrogen admixture causes the discharge to extinguish. The origin of the atomic nitrogen measured in the 0% admixture case is not quite clear, but likely to be related to residual nitrogen on discharge electrode and window surfaces, residual nitrogen in the helium feed gas, or mixing of surrounding, ambient air.

Fig. 4 shows the observed relative TALIF signal intensity when the applied rf power is varied while keeping the nitrogen admixture constant at 0.25%. A continuous increase in signal and therefore N density can be observed with increasing RF power. It should be noted that this APPJ is not optimized for power efficiency and hence there are significant losses in the cables and electrodes. It is estimated that the actual power dissipated in the plasma is only 1-2 W.

It is interesting to note that the observed dependence of atomic nitrogen concentration on molecular admixture is similar to what has been observed for atomic oxygen in an APPJ of the same design operated in helium with O_2 admixtures. Here, the maximum density was found at 0.6 vol%, considerably higher than what we find for nitrogen, i.e. 0.25 vol%. Nevertheless, the trend is similar, despite the fact that the He/O_2 chemistry is much more complicated than the He/N_2 case.

Detailed modelling is needed to fully understand the dynamics of these APPJ devices, including the production of reactive species like atomic nitrogen and oxygen. For such a model, many different species and reactions need to be taken into account to capture the complex chemistry of APPJs in helium with nitrogen and/or oxygen admixtures.

Future experiments are planned to measure absolute values for N densities with TALIF by using a calibration method based on a comparative TALIF measurement at a spectrally close two-photon resonance in krypton gas.

In conclusion, we present a TALIF diagnostic technique which allowed us to perform the first direct measurements of atomic nitrogen in an APPJ. A maximum in the N density was observed for a 0.25 vol% nitrogen admixture to the helium feed gas. These measurements will contribute to developing a better understanding, and ultimately better control, of the plasma operation of these APPJ devices in new plasma medicine applications.

Acknowledgments

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