Detection of transient species in an atmospheric pressure plasma jet using cavity-enhanced spectroscopy techniques

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Abstract: Cold non-equilibrium atmospheric pressure plasma jets are increasingly applied in materials processing and plasma medicine. However, their small dimensions make diagnosing the fluxes of generated transient species a challenge. We have overcome these limitations by using cavity-enhanced spectroscopy techniques to achieve effective absorption path lengths of up to 100 meters in mm-sized plasma jets. In this contribution, we report on the detection of HO\textsubscript{2}, N\textsubscript{2}(A'\Sigma\textsubscript{u}^+)\textsuperscript{2}, Ar\textsubscript{2} excimers, and Ar\textsubscript{2}\textsuperscript{+} ions.

Keywords: atmospheric pressure plasma jet, transient species, cavity-enhanced absorption spectroscopy, cavity ring down spectroscopy.

1. Introduction

Over the last decade, non-equilibrium atmospheric pressure plasmas are increasingly applied in materials processing due to their favourable properties. At the same time, cold non-equilibrium atmospheric pressure plasma jets have emerged worldwide and gained strong attention due to their use in the field of plasma medicine [1], where the high reactivity at low gas temperature is crucial for interaction with sensitive biological systems [2]. The same holds for the material processing of temperature sensitive materials. Hence, it is essential to diagnose the fluxes of the species generated by these plasma sources to identify relevant fundamental processes, improve process efficiency and to be able to tailor the produced species for specific applications. Especially, for a comprehensive understanding of the kinetics of the transient species involved high precision measurements of reactive molecular precursors, free radicals and short-lived species are of crucial importance. Due to their small size and high density gradients in space and time, these jets, however, are difficult to diagnose quantitatively. Absorption spectroscopy has become a popular method for characterizing the fluxes of species generated by these plasma sources [3]. To achieve space-resolved densities from the line-of-sight integrated densities, Abel inversion is most commonly used, which leads to a local density as a function of distance from the center [4]. However, the generally small geometry of the effluent of a plasma jet (in \textmu m to cm range) severely limits the sensitivity of absorption spectroscopy, especially for highly reactive transient species.

To overcome the difficulty of small absorption lengths, cavity-enhanced spectroscopy is a promising method for localized measurements of species with low abundances in plasma jets. Since the introduction of cavity ring-down spectroscopy for absorption measurements of gaseous samples in 1988, a wide class of cavity-enhanced spectroscopy techniques has been developed for probing solids, liquids, gases, and plasmas, such as, cavity ring-down spectroscopy (CRDS), off-axis cavity-enhanced, absorption spectroscopy (CEAS), optical feedback cavity-enhanced absorption spectroscopy (OF-CEAS) [5, 6]. All these techniques are based on the principle of coupling light into a high-finesse optical cavity, which in its simplest form consists of two highly reflective mirrors containing the sample under investigation. By measuring the light leaking out of the optical cavity with and without absorbing medium the concentration of absorbing species can be obtained with detectable concentrations at the ppm to the ppt levels. Of these variants, CRDS has been employed for the detection of species in plasmas. An overview of the existing applications of CRDS to characterize various types of atmospheric pressure plasma jets can be found in [7]. In this contribution, we will discuss our latest results concerning the detection of HO\textsubscript{2}, N\textsubscript{2}(A'\Sigma\textsubscript{u}^+)\textsuperscript{2}, Ar\textsubscript{2} excimers, and Ar\textsubscript{2}\textsuperscript{+} ions in plasma jets using CEAS, OF-CEAS as well CRDS.

2. Plasma jet

The non-thermal plasma used to generate the probed species is an argon atmospheric pressure plasma jet operated at a radio frequency around 1 MHz. The so-called \textit{kINPen-Sci} has a pin type powered electrode centered in a dielectric tubing with a circular grounded electrode outside the dielectric [8]. The plasma jet is operated at about 1 W dissipated plasma power.

The plasma jet is equipped with a gas curtain device, which allows control of the atmosphere surrounding its active afterglow [9]. Changing the composition of the curtain gas strongly influences the reactive component composition generated by the plasma. For instance, humidity variation controls the output of H\textsubscript{2}O\textsubscript{2} and OH [10]. The feed gas argon has a flow rate of three standard liter per minute (slm) through the plasma jet. It is
humidity in the case of the HO$_2$ measurements by passing a small fraction (4%–10%) through a water bubbler held at room temperature. The feed gas humidity is measured with a chilled mirror dew point hygrometer (EdgeTech DewMaster) according to the procedure described previously [10]. The gas curtain is operated with a mixture of oxygen and nitrogen at a flow rate of 5 slm, which can be varied from pure O$_2$ to pure N$_2$.

3. Detection of HO$_2$

We recently reported on the detection of the hydroperoxyl radical, HO$_2$, in an atmospheric pressure plasma jet [11]. The HO$_2$ radical is considered an intrinsic part of the chemical reaction network in cold non-equilibrium atmospheric pressure plasmas, due to its involvement in the generation pathways of the hydroxyl radical, OH, one of the most studied reactive species in plasma jets [2, 12, 13]. The OH molecule is generated via pathways which include HO$_2$, which itself is quickly quenched by air derived species [13], and therefore HO$_2$ is mostly confined to the localized afterglow of the plasma jet.

For the detection of HO$_2$, we utilized the OF-CEAS technique in which the laser is scanned over the spectral region of interest and locks, through optical feedback, to successive cavity resonances. Consequently, the optical cavity is used to both greatly increase the optical pathlength through the sample and enhance the measured signal intensity, resulting in very low detection limits being achievable [6]. Initially, near-infrared diode lasers were used as sources [14, 15], but recently OF-CEAS instruments based on quantum and interband cascade lasers have also been reported [16–20]. Here, we present measurements of HO$_2$ employing OF-CEAS using a diode laser at 1506.43 nm as the light source to probe HO$_2$ transitions in the first vibrational overtone of the O–H stretch, the 2v$_1$ band (centered at 6649 cm$^{-1}$).

Fig. 1. Schematic of the OF-CEAS setup with the effluent of the atmospheric pressure plasma jet placed in one of the arms of the cavity. LD: laser diode; DL: delay line; HWP: half-wave plate; PBS: polarizing beam splitter; MPZ: mirror on piez-electric transducer; FM: folding cavity mirror; M1, M2: cavity mirrors; VD: Vidicon camera; PD1, PD2: photodiodes; BD: beam dump; PJ: kINPen plasma jet device.

In Fig. 1, a schematic representation of the OF-CEAS spectrometer is depicted. The plasma jet is introduced into the cavity via a side opening. An xy-stage allowed a precise positioning of the effluent of the plasma jet to intersect the laser beam. The laser beam of 1 mm diameter passed through the plasma effluent at 11 mm distance from the plasma jet’s nozzle as this is the typical distance between plasma jet and treated surfaces. From quantitative schlieren diagnostics on the plasma jet an absorption length of 4 mm for the plasma effluent at 11 mm distance from the plasma jet’s nozzle was obtained [4]. The spectrometer has a minimum detectable absorption coefficient $\alpha_{min}$ of 2.25 x 10$^{-6}$ cm$^{-1}$ with a 100 seconds acquisition, equivalent to 5.5 x 10$^{-8}$ cm$^{-1}$ of HO$_2$ if the absorption is confined to a 4 mm region.

![Fig. 2. Absorption spectra for four values of the feed gas humidity. (a) Without plasma. (b) With plasma. The vertical scales are identical.](image)

In Fig. 2, as an example, the measured spectra for four different feed gas humidities without and with the plasma switched on are shown. The water concentration was determined by a dew point measurement and is rounded to 10 s of ppm. We did not deduce the water concentration from the measured absorptions since these are due not only to the water in the plasma jet, but also to water absorbing along the full length (1.7 m) of the cavity (the optical cavity is open to laboratory air). HO$_2$, on the other hand, being quickly quenched by air derived species, does not diffuse within the cell but is localized in the jet region. With the plasma switched off, the measured absorption spectrum is due to three water transitions at 6637.850 cm$^{-1}$, 6637.995 cm$^{-1}$, and 6638.573 cm$^{-1}$; these are centered at relative frequencies of -0.355 cm$^{-1}$, -0.210 cm$^{-1}$, and 0.368 cm$^{-1}$, respectively. With the plasma switched on, the HO$_2$ absorption feature at 6638.2 cm$^{-1}$, centered at 0 cm$^{-1}$ relative frequency, appears. As can be seen, the ‘plasma on’ spectrum is much noisier due to the plasma disturbing the stability of the cavity. The HO$_2$ concentrations as the feed gas humidity was changed from 1000 to 4000 ppm were in the range of $(3.1 \pm 0.3) \times 7.8 \pm 1.0) \times 10^{13}$ cm$^{-3}$. The main uncertainty in the determination of these concentrations is the absorption path length of 4 mm for the plasma effluent at 11 mm distance from the plasma jet’s nozzle. The number densities are in broad agreement with predictions from modelling of these plasmas [13]. We note, however, that such cavity-based measurements provide a new way of testing and improving our modelling of these complex environments.

4. Detection of N$_2$(A$^3\Sigma_u^+$)

Another interesting species generated in these atmospheric pressure plasma jets in metastable molecular
nitrogen, N$_2$(A$^3$Σ$^+_u$). A relatively novel laser source, a super-continuum source, was employed to produce high resolution spectra of the B$^3Π_g$ ← A$^3$Σ$^+_u$ transition over the 600 – 800 nm spectral range. To achieve the required detection limits, a CEAS experiment using a 4 cm long optical cavity was built with the supercontinuum source as the light source. A 50 nm section of these spectra (750 – 800 nm), corresponding to the 3→1 and 2→0 transitions, was analyzed in-depth to obtain the number density of the v = 0 and v = 1 levels of the A state and the corresponding vibrational temperature.

5. Detection of Ar$_2$ excimers and Ar$_2^*$

It is generally assumed that in argon atmospheric pressure plasma jets the argon molecular ions, Ar$_2^*$, and argon excimers, Ar$_2^*$(^3Σ_u$^+$), are responsible for initiating the main chemistry. We are currently building a CRDS setup using a Nd:YAG pumped dye laser as a light source to investigate the concentrations of the transient argon species Ar$_2^*$(^3Σ_u$^+$), Ar$_2^*$, and Ar$_5^*$. Ar$_2^*$ can be detected at 290 and 340 nm, while Ar$_5^*$ and multiple vibrational states of Ar$_5^*$(^3Σ_u$^+$) can be detected in the spectral range 500 to 525 nm [21]. We will present results on these concentration measurements as a function of the distance from the plasma jet’s nozzle.

6. Conclusions

In summary, we have presented an OF-CEAS experiment and demonstrated its first application to the detection of HO$_2$ in the effluent of a plasma jet. We demonstrated a sensitivity of 2.25 x 10$^{-10}$ cm$^{-1}$ with a 100 seconds acquisition time under ideal conditions, which translates into a sensitivity of 5.5 x 10$^{12}$ cm$^{-3}$ of HO$_2$ assuming an absorption length of 4 mm. In the plasma jet, HO$_2$ concentrations in the range of (3.1–7.8) x 10$^{13}$ cm$^{-3}$ were detected. The HO$_2$ concentration for different feed gas humidity as well as for different gas curtain mixtures of oxygen and nitrogen was investigated. For the detection of N$_2$(A$^3$Σ$^+_u$) CEAS with a supercontinuum source was employed. With this broadband light source, the populations in the vibrational bands of N$_2$(A$^3$Σ$^+_u$) can be detected in a wide spectral range simultaneously. Finally, the detection of the transient argon species Ar$_2^*$(^3Σ_u$^+$), Ar$_2^*$, and Ar$_5^*$ will be presented.

The achieved detection levels indicate that CEAS and CRDS based spectrometers will provide a new way of testing and improving our modelling of these complex plasma environments and will find broad application in future studies of the chemical network in the effluents of plasma jets.

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8. References