Determining Localized Density of H_2O_2 Using Absorption Spectroscopy in Plasma Jets

November, 2023

ABSTRACT

Researchers from Germany have developed and demonstrated a new diagnostic technique for obtaining local distribution of gas phase hydrogen peroxide (H_2O_2) in plasma jets. Continuous-wave cavity ring-down spectroscopy, with a quantum cascade laser at a wavelength of 8.12 µm, is used to determine the effective absorption length of a cold atmospheric pressure plasma jet and to determine the localized density of H_2O_2 in the effluent of the plasma jet. With axial and radial scans and radial distributions, the effective absorption length was calculated to be 1.6 mm close to the nozzle and 5 mm at a distance of 10 mm from the nozzle. The maximum density of H_2O_2 was 2×10^{14} cm^{-3} in the center of the effluent close to the nozzle. This work shows the formation and consumption mechanisms of H_2O_2 and enables other biomedically relevant species in the plasma zone to be studied using this technique.

PLASMA JETS & H_2O_2

Plasma science has been studied and implemented for many decades, and the number of applications have been steadily rising.[1] Cold atmospheric pressure plasma jets (CAPJs) are relatively new in this field with benefits for plasma medicine and industrial applications being discovered in the last few years. CAPJs are used for therapy for chronic wounds, anti-tumor effects, immunotherapy in cancer patients, regenerative applications, dental medicine, and oncology.[2] Outside of the medical field, CAPJs can benefit materials processing of heat sensitive targets as well as plasma agriculture. It is expected for the number of applications to rapidly grow and expand, thus the importance of the adaptability of the reactive species composition in CAPJs will also increase.[1]

CAPJs can generate high reactivity from different gases at lower gas temperatures. Compared to high temperature plasma jets and low pressure jets, CAPJs can be handheld and are suitable for localized treatments with small size (mm) distribution. The problem is that there are many unanswered questions on how reactive species are generated in CAPJs.[1] If a better understanding of reactive species generation is achieved, the composition of reactive species can be customized to the appropriate application. To accomplish this task, absolute and spatially resolved distributions of the densities of reactive species in the effluent of the jet are required. For this work, the local distribution of a common reactive species is studied: gas phase hydrogen peroxide.

Hydrogen peroxide (H_2O_2) has been shown to be beneficial for cell growth and death in biomedical applications. It also is a suitable plasma source at room temperature, operating at atmospheric pressure. No previous work has been documented to detect H_2O_2 in the effluent of a CAPJ directly, and few have studied H_2O_2 in the gas phase with absorption spectroscopy methods. H_2O_2 has two important absorption features suitable for absorption spectroscopy: the ν_6-band between 8.510 and 7.460 µm and the ν_5-band around 2.778 µm. Determining the localized density of H_2O_2 in the effluent of a CAPJ will help provide diagnostic techniques and a better understanding of reactive species generation in CAPJs.

PROBLEMS AND GOALS

While many standard diagnostic techniques have previously been established for low pressure plasmas in large chambers, these techniques have to be heavily modified for CAPJs.[1] Another issue with some of these techniques is the high sensitivity required to detect trace levels of a reactive species. Determining absolute densities of reactive species also requires knowledge of the effective absorption length when using absorption spectroscopy, although this is rarely known.

The largest concern with H_2O_2 as the detected reactive species is the absorption features that overlap with water (H_2O). When absorption is measured in open air, the spectrum is a superposition of absorption features of H_2O_2 and H_2O. It is critical that the spectral region to detect H_2O_2 is chosen carefully to account for the strength of the ν_6- and ν_5-band of H_2O_2 while ignoring the absorption features of H_2O. While some researchers have increased the absorption length of the spectroscopy design and therefore increased the detecting limits, measurements were collected from a large container with the gas of the effluent instead of measuring directly in the effluent of the plasma jet. There is no previous absorption spectroscopy design where H_2O_2 is directly detected in the effluent of a CAPJ.[1]

METHOD

Researchers from the Leibniz Institute for Plasma Science and Technology (INP) in Greifswald, Germany, have developed an efficient way to determine the localized density of gas phase H_2O_2 in the effluent of a cold atmospheric pressure plasma jet by utilizing continuous-wave cavity ring-down spectroscopy (cw-CRDS). The setup in **Figure 1** shows the kINPen-sci plasma jet, quantum cascade laser (QCL), current driver and temperature controller, and the setup for cw-CRDS. The kINPen-sci jet uses a needle-to-grounded-ring-electrode configuration in a dielectric capillary with a diameter of 1.6 mm and operated with 3 slm argon at a frequency of 860 kHz.

The cavity is comprised of two highly reflective mirrors (99.98%) with a length of 54.5 cm. Two metallic tubes are used to protect the cavity from dust particles and are purged with N_2 to reduce dust and water in the beam path. The laser used for the cw-CRDS is a QCL source with a tuning range of 8.170 to 8.106 µm. The current for the QCL was controlled by Wavelength Electronics' QCL1000 low noise driver, and the QCL temperature was controlled with Wavelength Electronics' PTC5K-CH controller. An acousto-optic modulator (AOM) controlled the intensity of the QCL beam while also providing the 0th diffraction order for wavelength analysis. The 1st diffraction order from the AOM was directed into the optical cavity for cw-CRDS. Using a detector after the cavity, the ring-down event can be observed and initiated by turning the AOM off. A total of 3,600 ring-down times were recorded to find the appropriate number of averages. Using Allan-Werle deviation analysis, the signal-to-noise ratio can be improved. Unfortunately, as the measurements are recorded in open air, the noise is almost a factor of 10 higher than when recorded in a contained box. However, as the values for the Allan-Werle deviations were the same for both tests, plasma on and plasma off, the influence of the plasma on the cavity is smaller than the fluctuations introduced by the gas flow.[1] With an absorption coefficient of 2.3×10^{-19} cm^2 for H_2O_2, the detection limit due to cavity stability is determined to be 2.4×10^{11} cm^{-3}.

Although the most prominent absorption features for H_2O_2 can be measured around 1,250 cm^{-1}, broadband absorptions from other species such as nitric acid (HNO_3), nitrous acid (HONO) and dinitrogen pentoxide (N_2O_5) molecules as well as absorptions lines from hydroperoxyl radicals (HO_2), methane (CH_4), and nitrous oxide (N_2O) also overlap with absorption features of H_2O_2 in this region. Because these species are either generated by the kINPen-sci plasma jet or are present in the laboratory, the range between 1,230.5 and 1,232.0 cm^{-1} was selected instead. This range and the absorption features, with low contributions from other species, can be seen in **Figure 2**.

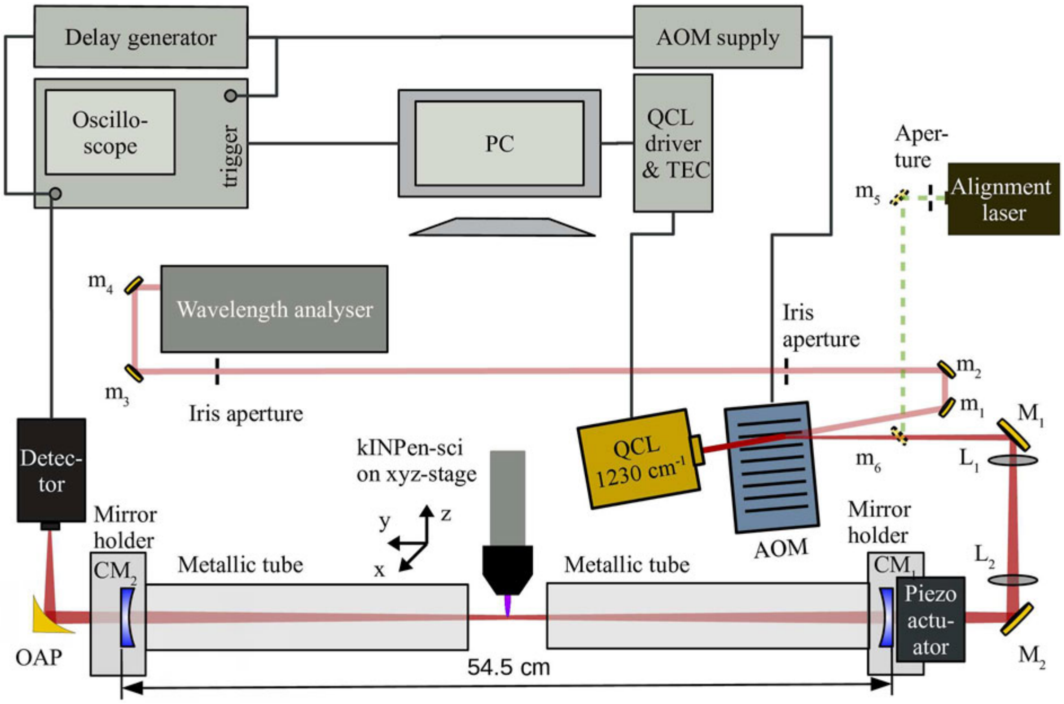

Figure 1. Schematic of the experimental setup to determine H_2O_2 densities in the effluent of the kINPen-sci plasma jet. QCL, quantum cascade laser; TEC, temperature control unit; AOM, acousto-optic modulator; OAP, off-axis parabolic mirror; m_j, gold coated mirrors; M_i, gold coated coupling mirrors to the cavity; L_i, beam-shaping lens with focal length of 75 mm; CM_i, cavity mirrors with 99.98% reflectivity.[1]

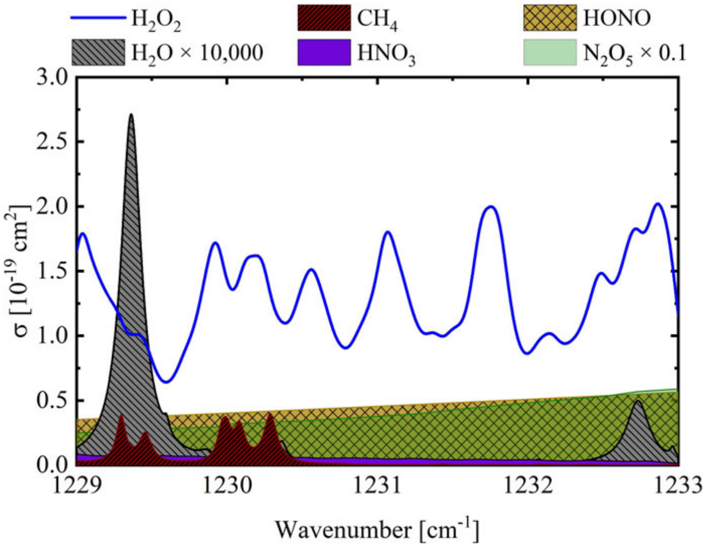

Figure 2. Absorption cross sections for H_2O_2, H_2O, CH_4, N_2O, and HNO_3 at 1,013 hPa, calculated from line positions, line strengths and pressure broadening coefficients taken from the HITRAN database, and absorption cross sections for HONO, and N_2O_2.[1]

From the absorption cross sections, the absorption feature of H_2O_2 between the spectral range of 1,230.8 and 1,231.3 cm^{-1} was selected to determine the localized density. The absorption spectrum of H_2O_2 was obtained by measuring the ring-down times at different spectral positions. Spectra were collected when the plasma jet was switched on and off and are based on the absorption coefficient, cavity length, and diameter of the volume which corresponds to the effective absorption length.[1]

When recording the ring-down events, radial and axial scans, based on an on/off-resonance method, were performed at ν_{ON} = 1,231.07 cm^{-1} for the on-resonance position and ν_{OFF} = 1,230.82 cm^{-1} for the off-resonance position. Axial scans recorded several full spectra at various distances from the nozzle to validate the on/off-resonance method. Absorption spectra were recorded from 3 mm to 10 mm from the nozzle of the plasma jet. Radial scans allowed researchers to determine the effective absorption length using the same on/off-resonance method. Density distributions closer to the nozzle up to 0 mm can be extrapolated from the recorded absorption length data.

RESULTS

With the on/off-resonance method confirmed with the axial scans, the effective absorption length is determined with the radial scans. With a Gaussian fit for each radial scan for different distances from the nozzle, a slight asymmetry is indicated in the H_2O_2 distribution from the center position of the Gaussian fits. This asymmetrical finding in the plasma zone is a result of the inhomogeneities of the powered needle electrode.[1] The effective absorption length was determined from the radial distributions as a function of the distance from the nozzle. The effective absorption length close to the nozzle at 0 mm was 1.6 mm and increased to approximately 5 mm at a distance of 10 mm from the nozzle.

Using the effective absorption length as a function of distance from the nozzle, line-of-sight integrated densities are determined as a function of distance from the nozzle from full spectra and from an axial scan using the on/off-resonance method. **Figure 3** shows the line-of-sight integrated density using the effective absorption length calculated as a function of distance from the nozzle.

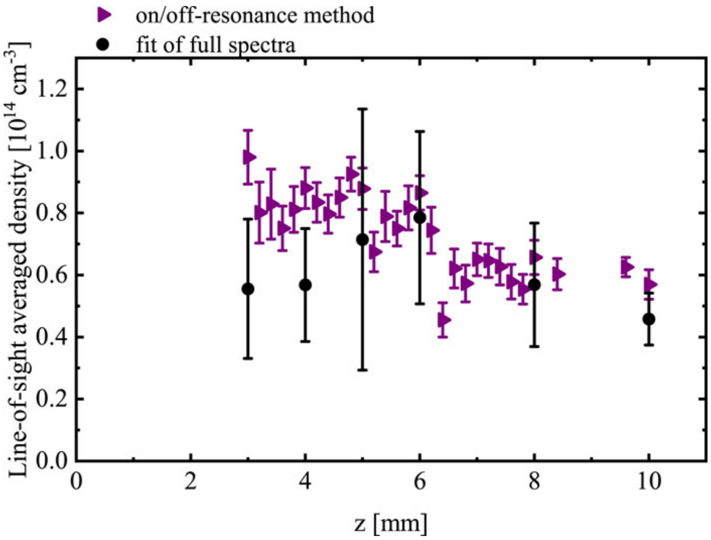

Figure 3. Line-of-sight integrated density of H_2O_2 at x = 0 mm as a function of distance from the nozzle, obtained by the on/off-resonance method and from a fit of full spectra considering an effective absorption length as a function of distance from the nozzle.[1]

The line-of-sight integrated absorption is transformed into a radial density distribution using an Abel inversion. The Abel inversion approximates the kINPen-sci plasma jet by a cylindrical symmetry.[1] **Figure 4** shows the radial density distributions for H_2O_2 for distances from the nozzle ranging from 3 mm to 10 mm. The maximum intensities decrease as the distance increases from the nozzle except for the measurement at z = 4 mm, which is shifted and regarded as an outlier.

Earlier investigations[1] showed an approximately constant distribution of reactive species within the first 3 mm, and the approximation for H_2O_2 follows this trend.

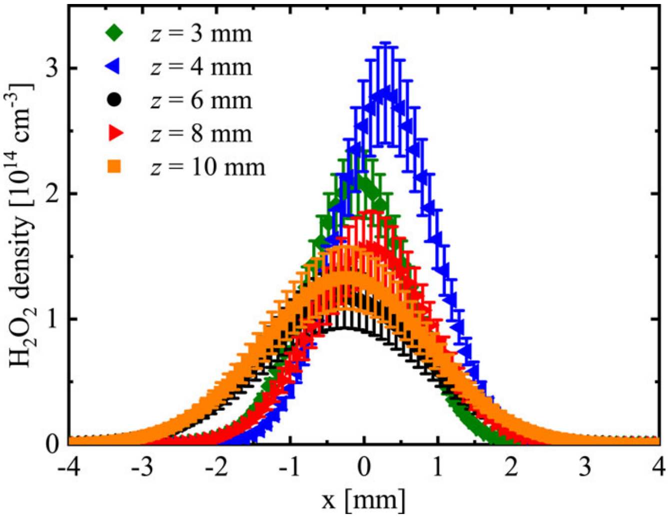

Figure 4. Density of H_2O_2 as a function of x for y = 0 mm at various z-positions, obtained by an Abel inversion of the radial scans.[1]

To obtain a continuous density distribution, radial scans can be interpolated using a polynomial approximation. The resulting localized density distribution of H_2O_2 is illustrated in **Figure 5** as a contour plot. The illustrated plot is in a plane cut along the symmetry axis through the center of the nozzle. This shows the localized distribution of H_2O_2 for the first 10 mm from the nozzle. The densities are distributed within a cone starting at 1.6 mm and ending at 5 mm, the farthest point from the nozzle following the effective absorption length.

The maximum density of H_2O_2 was determined to be 2×10^{14} cm^{-3} in the center of the effluent between z = 0 mm and z = 4 mm. For greater distances from the nozzle, the density decreased to approximately 1×10^{14} cm^{-3} at z = 6 mm and remained constant with larger z values. These findings show that H_2O_2 is significantly generated within the plasma zone of the kINPen-sci plasma jet, and the maximum density is closest to the nozzle. Surrounding gas composition appears to have an impact on the density of H_2O_2 in the middle range of 4 to 6 mm and decreases the distribution.

With these scans, it is clear that H_2O_2 is mainly produced withing the plasma zone of the jet and is partially consumed by the impact of the gas curtain between 4 and 6 mm from the nozzle.[1] Using a cold atmospheric pressure plasma jet, researchers demonstrated the ability and technique to obtain the localized density of H_2O_2 in the effluent of the plasma jet. The absolute and spatially resolved distributions of densities were found using the effective absorption lengths calculated. This work provides better understanding on how reactive species, specifically H_2O_2, are generated and consumed in cold atmospheric pressure plasma jets, and it demonstrates how H_2O_2 can be used for specific purposes and applications.

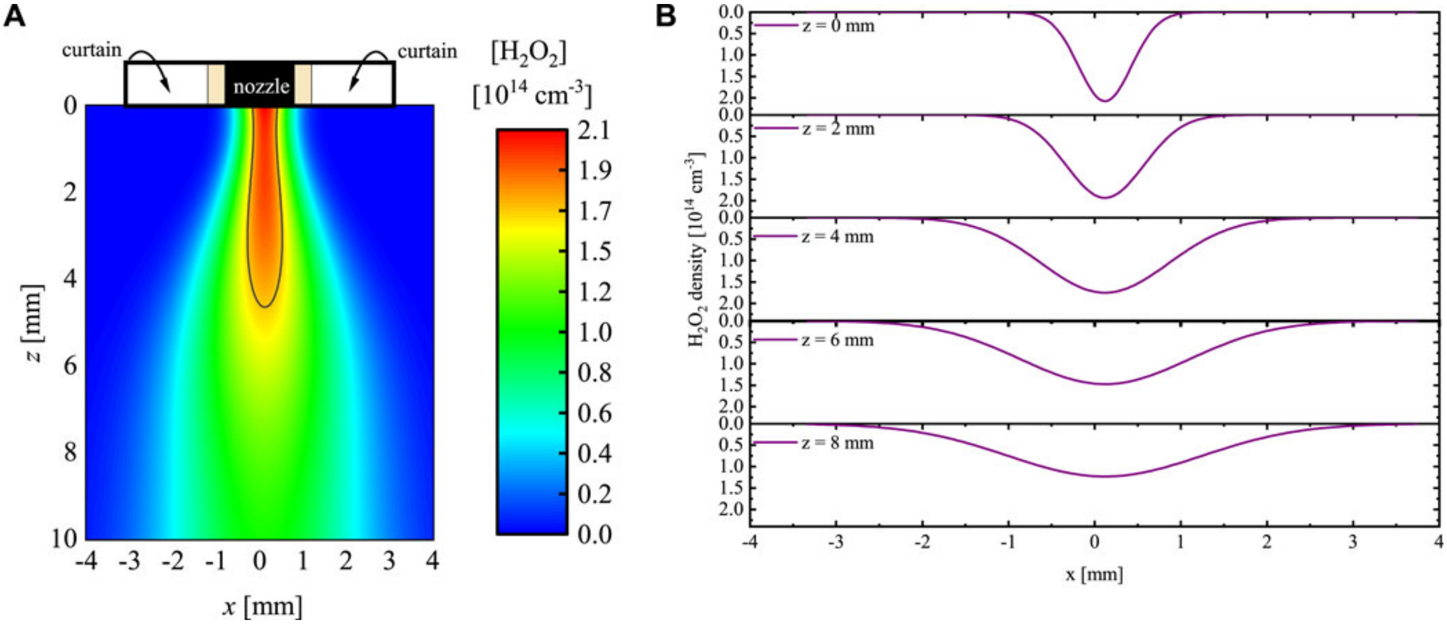

Figure 5. Localized densities of H_2O_2 illustrated as (A) a contour plot in a plane cut along the symmetry axis through the center of the nozzle and as (B) lateral profiles at different z-positions. (A) Contour plot for H_2O_2 (B) Lateral profiles of the contour plot for H_2O_2.[1]

WAVELENGTH'S ROLE

Measuring the localized density of H_2O_2 with high-accuracy requires high precision and stable control of the quantum cascade laser when using continuous-wave cavity ring-down spectroscopy (cw-CRDS). Wavelength Electronics' QCL driver, QCL1000 OEM, enabled precise current control with minimal electronic noise from the QCL. As laser linewidth is a major concern for QCLs, the QCL1000 OEM minimizes noise for open air measurements to as low as 0.7 µA up to 100kHz as well as keeping the average current noise density to as low as 2 nA / √Hz.

The stability of the QCL temperature is also critical for consistent wavelength output from the QCL. Wavelengths' PTC5K-CH temperature controller, can precisely stabilize temperature to as low as 0.0012ºC. The PTC utilizes a PI controller to minimize overshoot and time to reach setpoint temperature. The stability that the QCL driver and PTC controller provided for the QCL made the 3,600 repeatable measurements more reliable. Additional features from the QCL1000 OEM, such as the brown-out, over- and reverse-voltage, soft-clamping current limit, and over- temperature circuits protect the user and the QCL from potential damage and electrical faults.

The QCL1000 OEM QCL driver and PTC5K-CH temperature controller enable localized density detection of H_2O_2 using cw-CRDS. This makes the developed diagnostic method a useful tool for understanding formation and consumption mechanisms of bio-medically relevant species in the plasma zone and the effluent of a cold atmospheric pressure plasma jet.

PRODUCTS USED
QCL1000 OEM, PTC5K-CH

KEYWORDS
Cold atmospheric pressure plasma jet, spatial distribution, cavity ring-down spectroscopy, hydrogen peroxide, localized density, QCL driver, temperature controller, QCL1000, PTC5K-CH

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2. Braný, D., Dvorská, D., Halašová, E., and Škovierová, H., Cold Atmospheric Plasma: A Powerful Tool for Modern Medicine. *Int. J. Mol. Sci.* 2020, **21**, 2932. https://doi.org/10.3390/ijms21082932

USEFUL LINKS

- QCL1000 OEM Product Page
- PTC5K-CH Product Page

PERMISSIONS

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The captions for Figures 2, 3, & 4 were modified. No changes were made to the figures and other captions. They are presented in their original form.

REVISION HISTORY

Document Number: CS-LDTC13

REVISION	DATE	NOTES
A	November 2023	Initial Release