Atomic oxygen density determination in the effluent of the COST reference source using in situ effective lifetime measurements in the presence of a liquid interface

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Abstract

Spatially resolved, absolute densities of atomic oxygen are measured for several helium-based admixtures in the effluent of the COST Reference Microplasma Jet using two-photon absorption laser induced fluorescence (TALIF). Admixtures investigated include a helium-only admixture, four helium/oxygen admixtures (0.1\%, 0.5\%, 0.6\%, and 1.0\% oxygen), and a helium/water admixture (2500 ppm water), chosen to coincide with previously published characterizations of plasma-treated liquid. The atomic oxygen TALIF signal is calibrated for density using the noble gas xenon, which possesses a very similar two-photon excitation and fluorescence scheme. Measurements are conducted for the jet operating in ambient air with both an open effluent and a liquid surface present, allowing for comparison with liquid phase measurements conducted under similar conditions. The presence of a water surface does not appear to alter the background chemistry in the effluent but reduces O densities close to the liquid interface when compared to a similar distance from the nozzle in an open effluent case. This may be the result of a reduction in flow velocity caused by the liquid obstructing the gas flow. Additionally, measurements near the liquid surface revealed a region of atomic oxygen well outside of where the core of the effluent impinges on the liquid. This is likely relevant for applications as it considerably expands the surface area subject to O absorption. Critically, in situ measurements of the effective lifetimes of the laser-excited $3p^3P_J$ state of atomic oxygen were recorded in the effluent by employing a picosecond (ps) laser and a nanosecond (ns) ICCD. By experimentally determining the contribution from collisional quenching via the in situ effective lifetime measurements, significant improvements in the accuracy of the atomic oxygen density calibration were made, with differences of approximately 30\% from existing methods of

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estimating quenching rates at atmospheric pressure. Finally, spatially resolved atomic oxygen densities allow for an investigation of O formation and extinction pathways in the effluent and a comparison between admixtures.

Keywords: TALIF, atmospheric pressure plasma jet, plasma-liquid interface, atomic oxygen, laser diagnostics

(Some figures may appear in colour only in the online journal)

1. Introduction

Atmospheric pressure plasma jets (APPJs) have shown promise in a variety of applications that require the delivery of reactive oxygen and nitrogen species (RONs) [1–3]. They are of particular interest when a temperature-sensitive substrate is present due to the highly non-equilibrium nature of the discharge [4–6]. This non-equilibrium character results in reactive species production via high-energy electrons in the active plasma followed by their expulsion into an effluent that resides close to room temperature [7]. While this presents an efficient way to deliver a large number of reactive species to a substrate without thermal agitation, the scope of RONS delivered by the plasma can be problematic. Intricate plasma and radical chemistry results in a menagerie of species, many of which have very similar properties [8–10]. For nascent applications involving complex and multi-faceted interactions, identifying the mode of action for a specific response can be particularly challenging [11–13].

One plasma-generated reactive species that has attracted significant attention of late is atomic oxygen. Atomic oxygen was only recently shown to possess the necessary stability to enter plasma-treated liquid from the gas phase [14, 15], but has been increasingly identified as a key player in plasma-liquid chemistry and a number of biomedical applications. This includes the inactivation of THP-1 leukemia cells [16], cleavage of DNA [17], and a source of second-order reactive species production in plasma-treated liquid [14, 18, 19]. However, quantifying plasma-generated atomic oxygen in liquid to understand the extent of its impact has proven exceedingly difficult. Oxygen atoms react with chemical probes in similar ways to other plasma-generated RONS, in particular hydroxyl radicals [8–10]. This lack of selectivity is compounded by an absence of aqueous phase data for O [20, 21]. Furthermore, atomic oxygen efficiently degrades a variety of organic molecules that can be used to detect its presence, including the nitroxides TEMPO [9] and 4-oxo-TEMPO [22], and the chemical probes hydroxy-terephthalic acid (HTA) [9] and phenol [8]. In lieu of a direct measurement technique, comprehensive gas phase measurements of absolute atomic oxygen densities are the best approach to contextualizing existing liquid phase measurements considering their limitations. Taken together, these measurements can provide insights into the influence of atomic oxygen and contribute to a more complete picture of O transport from the gas phase to the liquid.

There are a variety of diagnostic techniques available to quantify atomic oxygen in the gas phase including vacuum UV (VUV) absorption spectroscopy [23], optical emission spectroscopy (OES) [24], molecular beam mass spectrometry (MBMS) [25], and two-photon laser induced fluorescence (TALIF) [26–28]. For APPJs, TALIF is the most commonly used as emission and absorption spectroscopy can be problematic, particularly outside the active plasma. TALIF relies on two photons, with their combined energy tuned to the 2p3P1→3P1 resonance, being absorbed simultaneously by an oxygen atom. The 3P1 state may subsequently de-excite, emitting a photon at 844.9 nm which can be measured by a nearby detector, typically a photo-multiplier tube (PMT) [29] or an intensified charge-coupled device (ICCD) [30]. Conveniently, this technique allows probing of the ground state where the vast majority of oxygen atoms reside outside the active plasma. Additionally, TALIF measurements can be calibrated for absolute density fairly easily using the noble gas xenon, which has a very similar excitation and fluorescence scheme. Along with a readily accessible excitation wavelength, these features make TALIF the preferred diagnostic for recording O densities in the effluent of an APPJ.

Despite its widespread employment, TALIF measurements of atomic oxygen often suffer from numerous shortcomings. Absolute density calibrations require collisional quenching rates for the 3P1 state of atomic oxygen, which are highly dependent on the surrounding gas composition. When a plasma jet—typically ignited in helium or argon—is operated in ambient air, the gas composition across the effluent can vary considerably. This is especially true along the edge of the effluent where the atomic carrier gas mixes with molecular species present in the surrounding air [31]. Here, laser-excited O can have effective lifetimes much shorter than the pulse width of many commercially available lasers, as N2 and O2 collisionally quench O(3P1) very efficiently [31]. This precludes an accurate assessment of collisional quenching rates in this region of the effluent. To circumvent this experimental limitation, TALIF measurements of atomic oxygen are often conducted in a helium atmosphere for APPJs ignited with helium admixtures, allowing for a single collisional quenching rate to be applied to the entire effluent. While allowing for a less error-prone determination of O densities when using ns-lasers, these experimental conditions are not reflective of those found during application or most studies of plasma-liquid chemistry. Additionally, quenching rates of laser-excited O necessary for density calibration are regularly recorded at low pressure and extrapolated to atmosphere assuming a linear relationship. However, this dependence has been shown to be decidedly non-linear at higher pressures in xenon [32] and does not account for variations in impurities or the presence of plasma-generated species, i.e. ozone [25] or hydrogen peroxide [33].

In this publication, we present spatially resolved atomic oxygen densities for a series of helium-based admixtures in the
effluent of a reference microscale APPJ, operated in ambient air. These measurements represent a substantial improvement in experimental accuracy compared to similar TALIF measurements of oxygen atoms by recording decay rates of O(3p $^3P_0$) in situ using a ps-laser and a ns-ICCD. To allow for direct comparison to previous liquid-phase measurements, TALIF measurements were also conducted with a liquid surface present for a helium-only, helium/oxygen, and helium/water admixture. Differences with the open effluent case are discussed and recommendations for future measurements made. Atomic oxygen flux at the liquid interface was calculated for the three admixtures and considered alongside existing electron paramagnetic resonance (EPR) spectroscopy measurements using the nitroxides TEMP and TEMPO, designed to account for aqueous O atoms. Finally, an examination of the O production and extinction pathways, informed by the spatially resolved densities for the different admixtures, is conducted.

2. Experimental setup

2.1. Plasma setup

The atmospheric pressure plasma jet used in these experiments was the COST Reference Microplasma Jet [34, 35], a capacitively coupled RF discharge, driven at 13.56 MHz. The COST jet has exhibited excellent reproducibility [36] giving confidence that results from other researchers using the source (or its predecessor) are applicable. The plasma jet operates by flowing feed gas—in this case, helium and helium with small admixtures of oxygen or water—between two stainless steel electrodes, igniting a plasma with an electric field perpendicular to the gas flow. The active plasma region consists of a 1 mm × 1 mm × 30 mm channel, resulting in a 30 mm$^3$ plasma volume. For these experiments, a total gas flow of 1 slm was delivered via stainless steel tubing to reduce the effect of impurities. The helium and oxygen was supplied by Matheson gas and of ultra high purity. For the helium/water/admixtures, dry helium was passed through a bubbler filled with DI water, assumed saturated, and mixed back with dry helium downstream in the appropriate ratio to ensure the correct water concentration in the admixture (0.892 slm dry He, 0.108 slm saturated). During TALIF measurements, absorbed RF power was held constant at 750 ± 10 mW and continuously monitored by integrated current and voltage probes on a Lecroy HDO 6104 oscilloscope. The calibration procedure for the integrated currents and the protocol for measuring dissipated power in the COST jet, a widely-tunable EKSPLA PL2230 laser was used, consisting of a Nd:YAG laser, frequency doubler, ps-OPA, and a variety of non-linear optics. The laser features a pulse width of 30 ps and a repetition rate of 50 Hz. The relatively slow pulse rate combined with the gas flow in the effluent allows for the environment to reset, limiting the buildup of laser-generated particles which may interfere with the density calibration. An F$^2$ dependence for the TALIF signal, necessary for an accurate density calibration and shown in figure 2, was verified for atomic oxygen and xenon at atmospheric pressure. The resulting pulse energies were 10 $\mu$J for O TALIF and 7.5 $\mu$J for Xe, verified with a broadband, high sensitivity pyroelectric detector and in-line with other TALIF measurements at atmospheric pressure using ps-lasers [30]. The beam was collimated using a 50 cm focal length planoconvex lens to modestly focus the laser to a beam waist of 100 $\mu$m across the effluent.

The TALIF signal for the two atomic species was recorded using an Andor ISTAR Gen III red-sensitive ICCD, with quantum efficiencies of 18.0% and 19.5% at the respective fluorescence wavelengths of O (844.9 nm) and Xe (834.9 nm). The ICCD was used in conjunction with an 840 nm filter (Andover Corporation, FWHM 10 nm), which provided transmittance values of 0.567 at 844.9 nm and 0.021 at 834.9 nm. For spatial scans of the effluent, the laser and detector setup were fixed, while the plasma jet and liquid surface were moved on an x-y-z stage (figure 1). With this optical setup, the ICCD gives 27 $\mu$m × 27 $\mu$m pixel resolution in the effluent of the jet. A delay generator allowed the ICCD, with a minimum gate-width of 3 ns, to be gated in varying intervals before, during, or after the laser pulse. This provided a convenient method to temporally scan the TALIF signal with ns resolution. Coupled with the very fast laser pulse, decay rates of over $10^9$ s$^{-1}$ could be accurately measured, corresponding to effective species lifetimes of less than a ns. A gate width of 10 ns was used for all other TALIF measurements of O, while a 3 ns gate was used for Xe measurements.

2.2. Laser and detection setup

To complete TALIF measurements in the effluent of the COST jet, a widely-tunable EKSPLA PL2230 laser was used, consisting of a Nd:YAG laser, frequency doubler, ps-OPA, and a variety of non-linear optics. The laser features a pulse width of 30 ps and a repetition rate of 50 Hz. The relatively slow pulse rate combined with the gas flow in the effluent allows for the environment to reset, limiting the buildup of laser-generated particles which may interfere with the density calibration. An F$^2$ dependence for the TALIF signal, necessary for an accurate density calibration and shown in figure 2, was verified for atomic oxygen and xenon at atmospheric pressure. The resulting pulse energies were 10 $\mu$J for O TALIF and 7.5 $\mu$J for Xe, verified with a broadband, high sensitivity pyroelectric detector and in-line with other TALIF measurements at atmospheric pressure using ps-lasers [30]. The beam was collimated using a 50 cm focal length planoconvex lens to modestly focus the laser to a beam waist of 100 $\mu$m across the effluent.

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2.3. Density calibration using xenon

The absolute density calibration of the atomic oxygen TALIF signal using the noble gas xenon has been described in detail in a number of publications [26, 30, 32]. It is widely used given the convenience of the nearly identical two-photon excitation and fluorescence schemes of the two species (figure 3), with the primary limitation being the error-prone nature of many of the quantities necessary for calibration—the uncertainty of the absolute calibration is often cited as ±50% [26, 32, 37]. The uncertainty for the measurements presented here is lower at 36.9%, owing primarily to the reduced uncertainty in the contribution of collisional quenching of laser-excited O (discussed at length in section 3.2), and the use of an identical detection setup for O and Xe TALIF. The error estimates of individual terms used to calculate the uncertainty of the absolute calibration (equation (1)) are summarized in table 1 and added in quadrature. It should be noted the estimated uncertainty of

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Figure 1. The plasma and laser setup for TALIF measurements in the effluent of the COST jet from the perspective of the ICCD. The vertical orientation of the gas flow in the effluent is annotated by the black arrow above the water surface. Experiments were conducted in an open effluent (sections 3.1–3.4) and with a liquid target present, as depicted in the figure (section 3.5). The plasma source and, when applicable, water cylinder were mounted to a translational stage to allow for spatial scanning of the effluent by the fixed 225 nm laser.

Figure 2. As a two-photon process, an $I^2$ dependence of the TALIF signal on the intensity of the laser pulse, idealized by the dashed lines, ensures that other laser-particle interactions are not interfering with the measurement. For an accurate absolute density calibration, both Xe and O must exhibit this relationship. The pulse energies used for Xe (7.5 µJ) and O TALIF (10 µJ) were well situated in this $I^2$ regime.

The atomic oxygen densities in this work is very close to that quoted in [30], using a similar laser and detection setup.

The equation relating a known quantity of xenon ($n_{Xe}$) to a density of ground-state atomic oxygen ($n_O$) using their respective TALIF signals is given below in equation (1). For Xe measurements, the laser and detection setup remained unchanged from O, and helium with small admixtures of xenon was flowed through the jet without igniting the plasma. This ensured maximum comparability between the TALIF measurements of the two species.

\[
n_O = \frac{T_{Xe} \eta_{Xe}}{T_O \eta_O} \sigma_{\text{Xe}}^2 \left( \frac{h\nu_O}{h\nu_{Xe}} \right)^2 \frac{S_O}{S_{Xe}} \sum_{n_{J}=0,1,2} a_{\text{Xe}} \frac{n_{Xe}}{a_{O} n_{O}}. \tag{1}
\]

The first two terms in equation (1), $T$ and $\eta$, give the relative transmittance and detector quantum efficiencies of the 834.9 nm Xe and 844.9 nm O fluorescence wavelengths for the 840 nm filter and red-sensitive ICCD (detailed in section 2.2). The two-photon excitation cross-sections for the species are denoted by $\sigma_{\text{Xe}}^2$ and $\sigma_{O}^2$ for the transitions of interest. Their ratio, calculated by Niemi et al is approximately $1.9 \pm 20\%$ [26]. Due to the similarities in fluorescence wavelength between the two species, $(h\nu_O / h\nu_{Xe})^2$ approaches 1. The signal intensities of O and Xe, spectrally integrated over excitation and fluorescence wavelength and normalized to the square of the laser intensity, are given by $S_O$ and $S_{Xe}$. Because our measurements probe the $J=2$ state of the triplet ground state of atomic oxygen, a correction factor must be applied to account for the $J=1$ and $J=0$ states. This was accomplished assuming a Boltzmann distribution for the three $J$-states, with the relative population of a $J$-state given by equation (2):

\[
n_J = (2J+1) \cdot \exp \left(-E_J/k_B T_g \right). \tag{2}
\]

Although the gas temperature in the effluent likely varies, from as high as 350 K close to the nozzle [34, 36] to near room temperature at the edges of the effluent, $T_g$ was assumed to be 300 K for the purposes of the correction factor. The calculated
Figure 3. Two-photon excitation and fluorescence scheme of atomic oxygen and xenon. In this work, the $J = 2$ ground state of atomic oxygen is probed with a laser wavelength centered around 225.64 nm.

Table 1. Uncertainty of the terms used for the error estimation of the atomic oxygen density, as given by equation (1). The final uncertainty estimate of 36.9% is lower than many TALIF experiments, largely because of the in situ determination of quenching rates.

|       | $T$  | $\eta$ | $\xi$ | $a$ | $\Sigma n_{J=0,1,2}/n_{J=2}$ | $\sigma_{\Sigma n}/\sigma_{O}$ | $\mu_{O}$ |
|-------|------|--------|-------|-----|---------------------------|-------------------------------|-----------|
| O     | 0.2% | 10%    | 12%   | 7.8%| 3.2%                      | 20%                          | 36.9%     |
| Xe    | 6.6% | 10%    | 10%   | 20% |                          |                              |           |

[a] [32].  
[b] [26].

*Standard deviation of the atomic oxygen signal varied but was generally between 9% and 15%.

value for $(\Sigma n_{J=0,1,2}/n_{J=2})$ is then 1.35. The expected gas temperature range in the effluent (300 K to 350 K) introduces only a 3% variability in the correction factor.

The relative branching ratios of the radiative transitions from the excited states for Xe and O are given by the $a_{O_2}$ and $a_{O_2}$ terms, respectively. The branching ratios convey the probability an excited atom will emit a photon at the wavelength of interest. For Xe and O these correspond to the $6p^3[2]_2 \rightarrow 6s^1[2]_1$ and $3p^3P_{1,2,0} \rightarrow 3s^1S_1$ transitions. Generally, the branching ratio for the transition $i \rightarrow k$ can be described by the following:

$$a_{ik} = \frac{A_{ik}}{A_i + Q_i}.

Here, $A_{ik}$ gives the radiative transition probability from $i \rightarrow k$, while $A_i$ represents the sum of all radiative transition probabilities from the excited state $i$. In a collisionless environment, $a_{ik}$ would simply be the ratio between the two radiative transition probabilities. However, in a collisional environment, a second term, $Q_i$, must be added to the denominator to account for collisional de-excitation of the upper state. At atmospheric pressure, this term can become dominant (depending on the excited state and available quenching partners), and is therefore of considerable importance for calculating the absolute density. A focus of this work is accurately measuring collisional quenching rates of atomic oxygen in situ for a variety of admixtures and treatment conditions, including in the presence of a liquid surface. This is critical for a complete accounting of atomic oxygen production and transport in the conditions most frequently present during applications and liquid chemistry studies.

3. Results and discussion

3.1. Spatially resolved TALIF measurements

The first step in the measurement procedure necessitated resolving the TALIF resonance for atomic oxygen in the effluent of the COST jet. After centering the laser beam under the 1 mm electrode gap of the plasma source, a spectral scan was conducted to probe the $J = 2$ resonance of atomic oxygen using 0.01 nm wavelength steps. The resulting TALIF signal reveals a Gaussian profile centered between 225.64 nm and 225.65 nm. The bandwidth of the laser, cited by the manufacturer as less than 10 cm$^{-1}$, was the dominant broadening mechanism for the resonance with considerably smaller contributions from Doppler and pressure broadening. At a gas temperature of 300 K, their combined effect amounts to less than 1 pm of line broadening [30]. The absolute density calibration requires the integration of the TALIF signal over the resonance for both O and Xe. For the density calibration of atomic oxygen, the Gaussian line profile was integrated from 225.61 nm to 225.69 nm after background subtraction.

Subsequently, spatial scans of the effluent for a variety of helium-based admixtures were performed by moving the plasma source vertically in 0.25 mm steps, starting from the nozzle out to a 10 mm distance. For each scan, the signal was averaged over three $\gamma$-pixels on the ICCD (27 $\mu$m resolution) for each spatial measurement to capture the entirety of the beam radius. The TALIF maps are shown in figure 4 for helium-only, helium with 1% oxygen, and helium with 2500 ppm water. As expected, the spatial maps of the raw TALIF signal revealed large variations in fluorescence intensity for the different admixtures, with the most robust normalized signals.
observed in the helium/oxygen admixtures and the weakest in helium-only. The spatial scans also indicated a tight gradient in signal along the edges of the effluent and differences in the persistence of the fluorescence far from the nozzle. The helium-only plasma appeared to retain proportionally strong fluorescence out to 10 mm, while the admixtures with molecular components preserved a smaller fraction of their highest signal out to this distance. While the raw TALIF signal is helpful as a first-order approximation, drawing more insightful conclusions about O propagation in the effluent required absolute calibration, necessitating measurements of the decay rates of the O(3p 3P_j) excited state under identical operating conditions.

3.2. Experimentally measured quenching rates of laser-excited atomic oxygen

For the absolute density calibration, collisional quenching rates of the O(3p 3P_j) excited state are imperative for accurately capturing the nuances in the spatial distribution of atomic oxygen, but can be difficult to measure. Typically, ns-lasers are not fast enough to determine quenching rates experimentally at atmospheric pressure, particularly when using molecular precursors which tend to quench laser-excited O much more efficiently than noble gases. This frequently leads to researchers measuring quenching rates at low pressure and extrapolating to atmosphere, assuming a linear pressure-quenching relationship. Another issue is the inability to determine the helium-air mixture at different positions in the effluent when operating in ambient air. This is especially problematic along the edge of the effluent where considerable mixing may occur. This has a notable effect on the collisional quenching rates in these regions, where there is already the sharpest gradient in raw signal. To simplify this, TALIF measurements are often conducted with an APPJ operating in a helium atmosphere to allow for one collisional quenching rate to be applied at all positions in the effluent. While such measurements can relate important information about O densities, they may not be reflective of the conditions found during applications or other diagnostic experiments.

To determine the contribution of collisional quenching at different locations in the effluent, spatially resolved decay rates of O(3p 3P_j) were recorded. This was accomplished using a delay generator to offset the time between the laser pulse and ICCD gate to temporally scan the TALIF signal in the effluent. An exponential decay function was fit to the resulting curve for each pixel, giving a spatial map of the decay rates for O(3p 3P_j). The decay rate at the nozzle for the open effluent case. The resulting effective lifetime (τ_{eff}) which can be expressed as:

$$\lambda^{-1} = \tau_{eff} = \frac{1}{A_i + Q_i}$$

(4)

where $A_i$ indicates the radiative decay rate of the excited state. For O(3p 3P_j), $A_i = 2.88 \times 10^7$ s⁻¹, corresponding to a radiative lifetime of 34.7 ns [26]. The quenching term, $Q_i$, is given by the sum of the density of each available quenching partner multiplied by its respective quenching coefficient $k$:

$$Q_i = \sum_j k_j n_j$$

(5)

A temporal map of the TALIF signal at varying distances from the nozzle is shown in figure 5 for a helium-only plasma. The measurements for figure 5 were performed at a slightly higher pulse energy to highlight the time evolution of the laser away from the effluent (centered around 0 ns) and the corresponding instrument response function of the ICCD gate. Close to the nozzle, the atomic oxygen fluorescence persists well past 30 ns after the laser pulse. Here, O largely resides in the core of the helium effluent which has a much smaller collisional quenching coefficient than molecular species in the surrounding air. As the temporal scans are conducted further from the nozzle, the initial fluorescence remains apparent but the signal decays progressively faster, indicating an environment where ambient air readily mixes with the feed gas. The more rapid signal decline is also evident toward the edges of the effluent, prevailing longer near the center, again due to air intrusion.

To spatially map decay rates of laser-excited O for density calibrations, temporal scans were repeated for helium-only, helium/oxygen, and helium/water admixtures at the laser pulse energy (10 μJ) specified in section 2.2. The measurements were performed in 0.5 mm intervals from 0 to 10 mm from the nozzle for the open effluent case. The resulting effective
Figure 5. (a) TALIF signal from laser-excited O as a function of time after the laser pulse in the effluent of a helium-only plasma. The temporal decay is shown at distances of 2, 4, 6, and 8 mm from the nozzle. The longevity of the signal close to the nozzle and in the core of the effluent where little air intrusion occurs is evident. (b) The time decay of O fluorescence for a point near the edge of the effluent, 10 mm from the nozzle, using a He 1% O₂ admixture. The decay rate given by the resulting fit is higher than $10^9$ s⁻¹, translating to an effective lifetime of less than a nanosecond.

Figure 6. Spatially resolved effective lifetimes of laser-excited O(3p $^3P$) in the effluent of the COST jet operated with admixtures of helium-only, helium with 1% oxygen, and helium with 2500 ppm water admixtures.

It should be noted that there is only enough signal to accurately measure effective lifetimes to a certain threshold, beyond which quenching rates should not be considered reliable. This becomes particularly problematic towards the outer edge of the effluent where signal is low and lifetimes approach values of less than a nanosecond. To avoid potentially erroneous effective lifetimes resulting from the inability to properly fit an exponential decay function to the temporally resolved signal, effective lifetimes were only calculated for points with more than 100 counts s⁻¹ of temporally integrated signal after background subtraction. Regions that did not meet this criteria were assigned an effective lifetime of 0 ns. A cross section of the decay constants (the inverse of the effective lifetimes) plotted with a normalized temporally integrated signal after background subtraction (figure 7), indicates the non-physical nature of lifetimes calculated outside the boundary separating the effluent and the ambient atmosphere. Values below the designated threshold for the integrated TALIF signal, and their corresponding decay constants, are annotated by circles in figure 7. Although atomic oxygen may exist in this region, the lack of signal and aggressive quenching environment precludes us from making definitive statements about its presence. Additionally, any O found in this region would react nearly instantaneously with nitrogen or oxygen from the ambient air, forming an array of possible RONS. It is therefore unlikely this O would be of consequence for estimating overall densities.

Considering their central role in the density calibration (an inherently error-prone process), it is worthwhile to examine the difference in decay rates between those found experimentally and those calculated using collisional quenching rates measured at low pressure extrapolated to atmosphere. Table 2 shows the measured decay constants for laser-excited atomic oxygen for three admixtures, radially averaged over the center 0.25 mm of the effluent at a distance of 2 mm from the nozzle, where the effects of air mixing can be excluded. For
The helium-only and helium/oxygen admixtures are notably low pressure. The decrease in the decay constants at the boundary of the effluent is a consequence of the lack of signal and not reflective of the collisional environment. For this reason, points with less than 100 counts s⁻¹ of temporally integrated signal were assigned an effective lifetime of 0 ns, denoted by the open circles.

In comparison, the calculated decay constants for each admixture, using values for the collisional quenching coefficients of O(3p ¹P₃) with the individual components of the background gas admixture, are included. The three collisional quenching coefficients used (O(3p ¹P₃) with He, O₂, and H₂O) were determined at low pressure and extrapolated to atmosphere, and are commonly cited in literature in the field of plasma science. More succinctly, these are the literature values that would have been used for the density calibration in this work had the experimental setup precluded in situ determination of the decay rates of laser-excited O. Also shown are the absolutely calibrated atomic oxygen densities averaged over the same spatial region, as well as the O densities had the calculated decay constants from literature been used for the calibration. The only literature values that were not measured at low pressure are those included in the final row of table 2. The values presented here are derived from collisional quenching coefficients measured in situ by Schröter et al using the COST jet and a nearly identical laser [30]. It should then be unsurprising that our values are in good agreement, and the ~20% difference can likely be explained by the considerably different flow rates used (1 slm for this work vs. 0.5 slm) along with the location of the measurement in the effluent (2 mm from the nozzle for this work vs. 1 mm). This provides an additional degree of confidence that in situ measurements of O(3p ¹P₃) decay rates allow for meaningful improvements in the accuracy of the density determination when compared to calculated values derived from collisional quenching measurements at low pressure.

The experimentally measured decay rates in this work for the helium-only and helium/oxygen admixtures are notably higher using the in situ measurements than those calculated using collisional quenching coefficients recorded at low pressure, resulting in higher absolute densities. The reasoning appears to be three-fold. First, a contribution from three-body collisions at higher pressure seems reasonable considering it has been observed in excited states of xenon. For Xe(6p' [3/2]2), collisional quenching increased ∼30% at 1 bar over what would be expected from a linear quenching-pressure relationship [32]. Secondly, in the case of helium in particular, impurities in the gas flow may add appreciably to the quenching. Helium quenches excited atomic oxygen rather slowly, while molecular impurities present in the gas flow do so at a much faster rate, with collisional quenching coefficients of more than two orders of magnitude larger than helium. In aggregate, small impurities of nitrogen, oxygen, and water molecules could have a considerable effect on the observed quenching.

Finally, the production of more complex RONS in the effluent (O₃, HO₂, NO₂−, etc) may increase the quenching rate in a manner that only in situ measurements can capture. This may be of particular importance towards the edge of the effluent where atomic oxygen readily reacts with molecular species. The presence of impurities, ambient air mixing, and plasma-generated RONS precludes the explicit determination of collisional quenching rates for individual species (without extensive assumptions). However, by measuring the decay rates of (O(3p ¹P₃)) experimentally, any variation in the quenching environment can be accounted for. This allows for increased confidence in the veracity of spatially resolved O densities in operating conditions relevant for applications.

3.3. Absolutely calibrated O density distributions

To complete the absolutely calibrated spatial maps, the in situ quenching rate measurements were applied to the spatial maps of the raw TALIF signal. Other quantities for the density calibration (equation (1)), including relative two-photon excitation cross-sections, radiative transition probabilities, and the correction factor for the Boltzmann distribution of the O ground state, were taken from literature and detailed in section 2.2. To ensure maximum comparability to the atomic oxygen measurements, xenon TALIF was conducted at atmospheric pressure by flowing 1 slm of helium with small admixtures of 2 to 4 sccm of xenon through the COST jet and recording the fluorescence using an identical optical setup. As Xe(6p' [3/2]2) is quenched very efficiently by helium, the effective lifetime of the laser-excited xenon state at atmospheric pressure is much less than a nanosecond, and cannot be accurately measured by our experimental setup. While collisional quenching rates can be extrapolated from low pressure measurements, this technique fails to consider two relevant processes: increased collisional quenching of Xe(6p' [3/2]2) at high pressure (reduces αₓe) [32] and intricate collisional resonances that may repopulate Xe(6p' [3/2]2) after collisional de-excitation (increases αₓe) [40]. To account for these competing effects, an approach involving the comparison of the fluorescence signal at high and low pressures in a vacuum chamber to determine the total branching fraction at atmosphere can be used. These measurements were completed for similar helium-xenon admixtures by van Gessel et al to obtain a value for αₓe.
Table 2. Comparison of excited state quenching of laser-excited O between commonly cited literature values in the field and experimentally measured values in this work. Experimental values for this work are taken at a distance of 2 mm from the nozzle and averaged over the inner 0.25 mm of the effluent. The uncertainty denotes the standard deviation of the decay rates in this region.

| Admixture      | This work $\lambda$ (ns$^{-1}$) | This work $n_0$ (cm$^{-3}$) | Literature$^a$ $\lambda$ (ns$^{-1}$) | Literature$^a$ $n_0$ (cm$^{-3}$) | % difference |
|----------------|---------------------------------|-----------------------------|--------------------------------------|----------------------------------|--------------|
| He-only        | 0.094 ± 0.006                   | 5.6 × 10$^{13}$             | 0.064$^b$                            | 3.8 × 10$^{13}$                  | 32.0%        |
| He/O$_2$       | 0.364 ± 0.006                   | 3.9 × 10$^{15}$             | 0.257$^c$                            | 2.7 × 10$^{15}$                  | 29.4%        |
| He/H$_2$O      | 0.125 ± 0.016                   | 1.9 × 10$^{14}$             | 0.316$^b$                            | 4.7 × 10$^{14}$                  | 152%         |
|                |                                 |                             | 0.151$^c$                            | 2.3 × 10$^{14}$                  | 20.1%        |

$^a$[26].
$^b$[39].
$^c$[30].

*Densities are calculated by substituting literature values for collisional quenching coefficients at given admixtures in the absolute calibration.

Figure 8. Spatially resolved ground state atomic oxygen densities in the effluent of the COST jet operated with admixtures of helium-only, helium with 1% oxygen, and helium with 2500 ppm of water. Note the different density scales for the three admixtures used to highlight the nuances of the O spatial distributions.

Figure 9. Atomic oxygen densities along the axis of the effluent in helium-only, helium/oxygen, and helium/water plasmas. The concentration of O atoms in the effluent of helium/oxygen plasmas decays steadily with distance from the active plasma, while helium-only and helium/water plasmas produce more intricate density trends.

... of 0.003 at atmosphere [32], which was applied for our density calibrations.

The resulting absolutely calibrated density plots for helium-only, helium with 1% oxygen, and helium with 2500 ppm water are shown in figure 8. The most pronounced difference between the raw signal and the calibrated density distribution is the outward trend of the O densities for all cases. This stems from the higher quenching rates near the edge of the effluent diminishing the raw signal intensity. Absolute densities were in fair agreement with prior measurements on similar APPIs, including the COST jet predecessor, with the exception of the helium/water admixtures. For these admixtures, our densities were around an order of magnitude higher than previous work. This is of particular interest for our liquid phase measurements and are discussed further in the following section.

Additional helium/oxygen admixtures were measured and calibrated for density. Figure 9 shows O densities as a function of distance from the nozzle for three helium/oxygen admixtures (0.1%, 0.5%, and 1.0%), averaged over the innermost 0.25 mm of the effluent. Atomic oxygen densities compare favorably to those previously measured using the COST jet predecessor with Xe calibrated TALIF and show a similar maximum close to 0.5%. This peak in density has been discussed previously and is a result of modifications to the electron energy distribution function (EEDF) in the active plasma incurred by molecular oxygen in the feed gas. Because atomic oxygen is primarily formed through dissociative collisions between electrons and oxygen molecules in the active plasma in a helium/oxygen admixture, the production process is rather sensitive to the EEDF. With larger O$_3$ densities in the feed gas, the population of high energy electrons capable of dissociation...
is depleted through inelastic collisions with molecules, often leading to rotational and vibrational excitation of \( \text{O}_2 \). Consequently, a smaller fraction of electrons have the requisite energy to dissociate \( \text{O}_2 \). The peak in \( \text{O} \) production observed between around 0.5% is therefore an optimization of the available \( \text{O}_2 \) to dissociate and the ability of electrons in the plasma to do so. While the spatially resolved \( \text{O} \) densities in the open effluent are helpful for general characterization and informative for the understanding of plasma chemistry, they are not representative of operating conditions for applications or other diagnostics, especially those involving liquid. To get a better idea of \( \text{O} \) generation and transport in a more applicable setting, the spatial TALIF and quenching rate measurements were repeated to determine \( \text{O} \) densities in the presence of a liquid environment and are detailed in section 3.5.

### 3.4. Atomic oxygen formation and extinction in the effluent

In addition to density determinations for a variety of admixtures, spatially resolved atomic oxygen densities give substantial insight into \( \text{O} \) formation and destruction processes in the effluent of the COST jet. To investigate, the density profiles along the axis of the effluent for six admixtures, helium-only, helium with three variations of oxygen (0.1%, 0.5%, 0.6%, and 1.0%), and helium with 2500 ppm water, were examined (figure 9). The densities were averaged over the inner 0.25 mm of the effluent. Predictably, there are sizeable differences between the evolution of the \( \text{O} \) density in the effluent for the six admixtures.

In the helium/oxygen effluent, where the production and extinction pathways are the most straightforward, the densities are highest at the nozzle and decline steadily out to 10 mm. In helium/oxygen admixtures, atomic oxygen is formed through dissociative collisions between oxygen molecules and electrons in the active plasma [37], while the primary extinction mechanism is ozone formation through reactions with molecular oxygen [25, 41]. The stable decay rate of atomic oxygen is a product of the (relatively) constant density of molecular oxygen throughout the effluent core. The \( \text{O} \) profiles in admixtures with higher concentrations of oxygen also reveal a faster absolute decay rate, indicative of a higher background \( \text{O}_2 \) density.

For the helium/water plasma, the evolution is somewhat more complicated. With an absence of oxygen molecules to dissociate in the active plasma, atomic oxygen is evidently produced in secondary chemical reactions. The most prominent is hydroxyl radical recombination [30, 42, 43]. The three-body version of this reaction produces hydrogen peroxide, but in the absence of a third partner, \( \text{O} \) and \( \text{H}_2\text{O} \) are produced. Hydroxyl radicals persist well into the effluent, so it should not be surprising that atomic oxygen densities continue to increase out to a few mm. The extinction mechanisms of \( \text{O} \) in the helium/water effluent are also more complex than the helium/oxygen case. Without oxygen in the feed gas, there should be very little \( \text{O}_2 \) available to produce ozone. The \( \text{O} \) decay is also considerably more abrupt than the other gas admixtures, which suggests more efficient processes at work. Atomic oxygen and hydroxyl radicals react quickly to produce \( \text{O}_2 \) and \( \text{H} \), but the importance of this reaction decreases away from the nozzle as OH is chemically short-lived [43]. Rather, long-lived species present well into the effluent seem to govern the sharp decline in \( \text{O} \) density observed in the helium/water admixture. Plasma-chemical kinetics modeling of a COST jet operated with a helium/water admixture has suggested that \( \text{O} \) reacting with \( \text{H}_2\text{O} \) becomes progressively more relevant as \( \text{O} \) traverses the effluent [30]. Reactions with myriad second and third-order species (peroxide in particular) likely play a role as well. The multiple extinction pathways and their reliance on higher-order reactions explains the delay of the prompt decline in \( \text{O} \) density noted in the helium/water effluent.

Atomic oxygen propagation in the helium-only effluent can likely be described by a convolution of the two previously discussed cases. The \( \text{O} \) densities remain relatively stable out to around 4 mm, then begin to slowly decline. This is probably due to the formation mechanisms being impurity dependent, with both direct formation from \( \text{O}_2 \) dissociation in the active plasma and \( \text{OH} \) recombination in the effluent playing a role. \( \text{O} \) extinction in the helium-only effluent is a much slower process than the other two admixtures, illustrated by its rather inconspicuous decay with increasing distance from the nozzle. The slow destruction of atomic oxygen is almost certainly due to the lack of reaction partners compared to the oxygen and water containing admixtures. However, the relevant extinction pathways probably include ozone and hydroperoxyl formation, as well as reactions with peroxide.

For these admixtures, the spatial distributions of atomic oxygen provide valuable insight into \( \text{O} \) formation mechanisms and pathways in the active plasma and effluent of the COST jet. In addition to their utility for model validation and contextualizing data collected using other diagnostic techniques, these measurements may be helpful for the selective tuning of atomic oxygen delivery with other desirable species for applications [44]. For instance, if one was conducting an application where hydrogen peroxide was desired without the potentially harmful contribution of atomic oxygen (i.e. plasma-driven biocatalysis [6]), a helium/water plasma with a treatment distance of 8 mm would be ideal. On the other hand, if an application benefited from both (i.e. killing cancer cells [16]), a treatment distance of 2–4 mm may be preferable.

### 3.5. Plasma-generated \( \text{O} \) transport in the vicinity of a liquid interface

Absolutely calibrated TALIF measurements with a liquid surface present were conducted using three gas admixtures: helium-only, helium with 0.6% oxygen, and helium with 2500 ppm water, chosen to correspond with previously conducted liquid-phase characterization of \( \text{O} \) using EPR spectroscopy [9]. As in the liquid phase measurements, \( \text{O} \) TALIF was recorded with a 4 mm distance from the nozzle of the jet to the water surface. Although the liquid-phase measurements were performed in a 12-mm well, a well size with a larger surface area was chosen to limit the effect of evaporation and allow optical access to the liquid interface. For our setup, this amounted to a water level drop of approximately 1 mm h\(^{-1}\), compared to the typical measurement time of 10–20 min.
Atomic oxygen densities with the liquid surface present are initially similar to the open effluent case close to the nozzle of the jet, as shown at the 0 mm position in figure 10. However, the amount of atomic oxygen declines considerably faster than the open effluent case for all three admixtures. In the helium/oxygen effluent, the decline is rather consistent from the nozzle to the water interface, whereas the other two gas admixtures exhibit slight increases out to 2 mm followed by a precipitous drop in the last mm above the water. As with the open effluent case, the differing density trends as a function of distance from the nozzle are likely a result of O production occurring exclusively in the active plasma for the helium/oxygen case, while second-order O formation continues well into the effluent for the helium-only and helium/water admixtures.

As a prerequisite to the absolute density determinations, spatially resolved decay rates of laser-excited O were also measured for the three admixtures in the presence of the liquid. Perhaps surprisingly (considering the evaporation induced by the gas flow), decay rates were nearly identical to the open effluent case for the three admixtures, both in magnitude and spatial extent. For reference, figure 11 shows the effective lifetimes of laser-excited O in the effluent of a helium 0.6% oxygen plasma with an open effluent out to 4 mm (left) and a liquid interface at 4 mm (right). The spatial distributions of effective lifetimes are nearly identical with the exception of a small expansion of the less aggressive quenching environment near the water surface. These trends were observed for each admixture and indicate an expansion of the helium flow as it impinges on the surface. Because the decay rates of laser-excited atomic oxygen are primarily mediated by collisional quenching, they are rather sensitive to the surrounding gas composition. The similarities between the spatial distributions of the effective lifetimes (and therefore, decay rates) indicate the background environment remains largely unchanged. It then follows that changes observed in the propagation of O atoms in the plasma effluent in the presence of a liquid interface are not a result of alterations in the effluent chemistry. Instead, a reduction in the flow velocity due to the obstructed gas flow is seemingly at fault. This has previously been documented using a 2D axially symmetric fluid model of the effluent of a COST jet predecessor incident on a solid surface by Hefny et al [45]. For oxygen atoms traversing the helium/oxygen plasma effluent, the diminished flow velocity allows for more time to interact with O\textsubscript{2} in the feed gas, leading to a proportionally faster extinction rate. Conversely, for the other two admixtures, where peak O densities are not realized until 3–4 mm from the nozzle in the open effluent case, a truncated increase in O formation followed by a sharp decline would be anticipated for a slower flow rate. These changes are well reflected in the corresponding O density distributions. It is worth noting that a high surface loss probability, potentially mediated by the composition of the liquid target itself, may considerably reduce the atomic oxygen density in close proximity to the surface [8, 46]. However, given the flow-induced surface deformation (figure 1), the region where this decline in O density is expected to occur (according to fluid model solutions [8]), is not optically accessible with this experimental setup. Further study may provide greater insight into whether changes in O density are exclusively a product of flow modification, as this data suggests.

Although measurements of atomic oxygen in the presence of water reveal an appreciable reduction in density close to the surface, likely as a result of decreased flow velocity, effective lifetime measurements reveal that the helium effluent remains intact down to the liquid interface. This allows for oxygen atoms to continue unabated into the liquid without having to contend with additional reaction partners from the ambient air or evaporation. With this assumption, an assessment of the atomic oxygen flux at the liquid surface can be made by taking the O density multiplied by the flow velocity at 1 slm. Table 3 shows the estimated flux of atomic oxygen for three admixtures (helium-only, helium 0.6% oxygen, and helium 2500 ppm water) to a liquid surface 4 mm from the nozzle compared to previously completed EPR measurements of the nitroxide TEMPO under identical plasma conditions [9]. For measurements of the production rate of TEMPO, the spin-trap TEMP is plasma-treated for one minute and the resulting TEMPO concentration is recorded (formed via the oxidation of TEMP by O or other ROS [47]). Degradation rates are derived from plasma-treating TEMPO, which is nominally stable but can be rendered EPR-silent (degraded) by plasma-generated reactive species. When examining the O flux alongside TEMPO production and degradation, caveats arise from competing processes and the selectivity of the reactions, which are discussed at length in our previous work [9]. To summarize:

(a) Measurements of TEMPO formation are likely an underestimate of the atomic oxygen delivery to the liquid, due to the concurrent degradation of TEMPO by plasma-generated ROS.
The effective lifetimes of laser-excited atomic oxygen in the effluent of a He 0.6% O₂ plasma in an open effluent out to 4 mm (left) and in the presence of a liquid surface at the same distance (right). Effective lifetimes remain nearly unchanged for all three admixtures in the presence of a liquid, with the exception of a small expansion of the helium core, indicated by longer lifetimes, near the water surface.

Table 3. Comparison of atomic oxygen flux calculated via TALIF and from EPR measurements of the production and degradation of the nitroxide TEMPO under identical operating conditions (4 mm treatment distance, 750 mW absorbed RF power). Production and degradation experiments were performed using 50 mM of TEMP and 1 mM TEMPO, respectively. TEMPO production is likely a direct result of O, while oxygen atoms contribute to its degradation [9].

| Gas admixture  | O flux (s⁻¹) | TEMPO pro (s⁻¹) | TEMPO deg (s⁻¹) |
|----------------|--------------|-----------------|-----------------|
| He-only        | 2.4 × 10¹⁴   | -6.7 × 10¹⁴     | 1.5 × 10¹⁴       |
| He/O₂          | 6.1 × 10¹⁵   | -6.3 × 10¹⁵     | 4.0 × 10¹⁵       |
| He/H₂O         | 4.9 × 10¹⁴   | -9.4 × 10¹⁴     | 2.5 × 10¹⁴       |

(b) In addition to atomic oxygen, TEMPO can also be produced by ozone and singlet oxygen, species present in the helium/oxygen plasma effluent. However, this contributes to no more than 25% of the measured TEMPO [9, 19].

(c) Other short-lived ROS can effectively degrade TEMPO (OH in particular) [48].

Given the degradation and selectivity considerations, very good agreement is observed between the calculated O flux and the rate of TEMPO formation for all three admixtures. This further supports previous findings that ozone and singlet oxygen do not play an important role in TEMPO formation as the ratio between the TEMPO production and atomic oxygen flux is similar for all three cases. For the rate of TEMPO degradation, the consensus with the O flux varies between admixtures as a result of the ROS present. In the helium/oxygen admixture, where atomic oxygen is the preeminent short-lived ROS, the rate of TEMPO degradation is an excellent measure of the O delivered to the liquid. For the helium-only and helium/water admixtures, substantial contributions from OH and other ROS give degradation rates two to three times higher than the calculated O flux. When applicable, this comparison validates that liquid phase measurements can provide an accurate indication of O delivery to a liquid target and supports previous assertions about the behavior of atomic oxygen and the nitroxides TEMP and TEMPO.

The final measurements of interest for the plasma-water setup involved scanning the liquid surface with the laser away from the effluent of the jet (in the y-direction in figure 1). The signal recorded using a helium 0.6% oxygen admixture is shown in figure 12. For these measurements, the water surface was moved as close to the beam as possible (without skimming), then moved laterally away from the ICCD, imaging the closest 100 µm to the water surface. Intriguingly, a region of signal was observed well away from the area where the effluent was impinging on the liquid. This signal retained the resonance structure of the two-photon excitation for O and persisted temporally after the laser pulse, confirming it to be atomic oxygen. However, gating the ICCD a further ns after the laser pulse resulted in the disappearance of the signal, indicating an aggressive quenching environment. The very fast collisional quenching precludes an estimation of the O density, but the location of this atomic oxygen would greatly increase the surface area of the water subject to O absorption, similar to what has been found on solid surfaces [45]. This may be of significant potential importance for applications. The source of this atomic oxygen is likely the redirection of the helium flow by the water surface. Because the liquid is deformed by the impingement of the effluent, it is probable the helium flow, along with the interspersed atomic oxygen, is redirected upward and outward along the axis of the v-shaped deformation of the water surface (figure 1). The result would be a circular region of O density like the one present in figure 12. This flow behavior is well-documented at a 4 mm gap distance by a 2D axially symmetric model for the COST predecessor [8].
Figure 12. A circular region of O density was observed well outside the area where the effluent of the He 0.6% O₂ plasma was impinging on the water surface (centered at (0,0)). The region was more pronounced and located further from the center of the effluent when treating the liquid with a 4 mm gap distance (top) than an 8 mm gap distance (bottom), suggesting it is likely a consequence of the gas flow redirecting off the surface.

and is in excellent agreement with our observations. The measurement was repeated at an 8 mm treatment distance where the deformation on the water surface is less pronounced. As expected, the region of O density contracted around the effluent (figure 12, bottom) reaffirming its association with the gas flow. Still, this area of atomic oxygen may be able to provide important insights into the interactions between O and liquid surfaces and is of interest for future work.

4. Conclusion

Spatially resolved atomic oxygen densities have been determined in the effluent of the COST reference jet (a reference μ-APPJ) for a variety of experimental conditions with the aim of addressing shortcomings in the existing literature, particularly as it pertains to potential applications. Absolute density calibrations were completed with TALIF measurements of the noble gas xenon using an identical experimental setup to minimize uncertainty.

Employing a ps-laser and a ns-ICCD, spatially resolved oxygen densities, out to 10 mm from the nozzle, were recorded for a variety of admixtures in the effluent of a μ-APPJ operating in ambient air. Decay rates of laser-excited atomic oxygen, necessary for establishing the extent of collisional quenching at different locations in the effluent, were measured in situ for all conditions, again out to 10 mm from the nozzle. An integral part of the absolute density calibration, this provided a notable improvement in the accuracy of the absolute O densities, with differences of around 30% when compared to calibrating the TALIF signal using extrapolated quenching rates measured at low pressure. Absolutely calibrating TALIF measurements using decay rates recorded for a plasma jet operating in ambient air ensures applicability to experimental conditions commonly found during applications.

Finally, TALIF measurements were completed with a liquid interface 4 mm from the nozzle of the jet. While the spatial distribution of the gas composition in the effluent did not change appreciably, as indicated by the effective lifetimes of laser-excited O, the densities were substantially reduced near the water surface when compared to a 4 mm distance in the open effluent case for all three admixtures. This is likely a result of the reduced flow rates in the vicinity of the liquid surface. Furthermore, calculated O fluxes at the water surface were in very good agreement to liquid phase EPR measurements using the spin trap TEMP. The production rates of TEMPO closely mirrored the estimated O delivery from the TALIF measurements at the liquid interface. In addition, a region of O density well outside the area where the core of the effluent impinges on the water surface was identified. The location of this atomic oxygen coincides well with previously modeled O transport in the presence of a liquid [8] and confirms that not all oxygen atoms present in the effluent enter the water where the gas flow is incident on the surface. Additionally, these measurements suggest that the area subject to O absorption is several mm², an important parameter for applications and similar to what has been documented on solid surfaces [45].

The results included in this work represent considerable progress in the understanding of the evolution and transport of plasma-generated atomic oxygen under conditions relevant for applications. They will be helpful for estimating the spatial distribution of O densities for a variety of admixtures for other researchers working with the COST jet and similar discharges and, more generally, provide insights into O behavior in the presence of liquids—both critical facets for optimizing O delivery for potential applications.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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