Laser Induced Fluorescence Diagnostics Of Simple Radicals in Atmospheric Pressure Plasma Jets

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In this paper we give a general description of the LIF technique by way of OH absolute measurements in two atmospheric pressure plasma jet systems, namely a plasma gun and a RF plasma jet. We address in detail: the modelling of the LIF measurement, taking into account collisional processes and the spatial non-uniformity of the laser beam; absolute calibration; rotational temperature measurements.

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1. Introduction

The evolution of electrical discharges for technological applications towards non-equilibrium systems at atmospheric pressure (ATP), pushes forward the limits of existing diagnostic techniques. In particular, the requirements of spatio-temporal resolution and selectivity are more stringent, while the interpretation of outcomes in terms of absolute quantities calls for a more detailed knowledge of all elementary phenomena that play a role in the diagnostic process. Non-equilibrium properties of gas discharges include non-Boltzmann distribution functions (of electron energy, vibrational, rotational), dissociation and radicals production well above the thermal one. The measurement of radical concentration and of their time evolution in highly transient discharges is an important issue. Time and space resolution requirements depend on the discharge system. Atmospheric pressure plasma jets (APPJ), in particular, have typical sizes in the mm scale (see figure 1), while species concentrations vary in a sub-mm scale. Time resolution depends on the kind of excitation of APPJs. Plasma Jets have basically three kinds of electrical supply: RF (13.56 MHz) or MW, sinusoidal in the kHz range for Dielectric Barrier Discharge (DBD) types, and pulsed HV with pulse length ranging from tens of ns to μs. The kinetics of short-lived radicals anyway evolves in the μs scale.

Laser Induced Fluorescence is the measurement technique that fits the requirements of sensitivity, selectivity and space/time resolution for the measurement of molecular radicals in APPJs.

2. LIF principles and properties

An ideal LIF process involves two atomic/molecular states coupled by an electric dipole transition excited by interacting with a quasi-resonant laser field - see figure 2. Level 1 is the probed state, while spontaneous emission from level 2 (the fluorescence) is the experimental observable. The absorption rate is given by the spectral energy density of the laser field $\mathscr{E}_L(t)$, multiplied by the absorption coefficient B and the spectral overlap between the laser line and the absorption line Ψ. Preferably, but not necessarily, fluorescence observation is made on a transition different than that used for absorption. The reason for this choice is merely practical, since in this way it is possible to separate spectrally the laser light from the fluorescence light. The LIF process is usually modelled
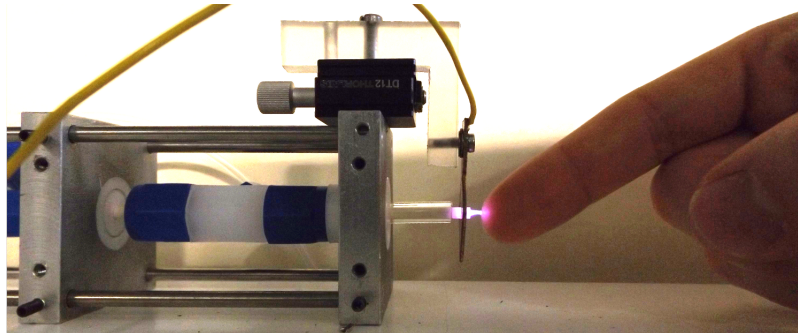

Figure 1: A RF APPJ prototype picture that shows the small size of the plasma region.
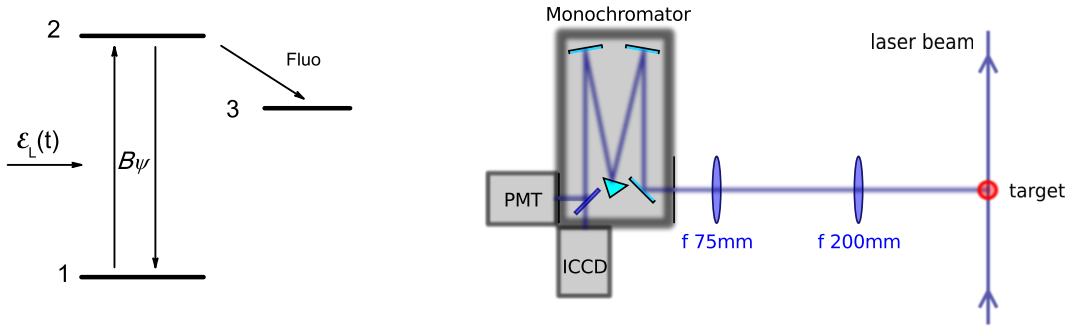
Figure 2: left - LIF two-level scheme and - right - geometry of the experiment with fluorescence detection instrumentation.

by a set of rate equations[1] that describe the time evolution of the populations of levels 1 and 2, while the population of level 3 is irrelevant to the process:

$$\frac{dP_1(t)}{dt} = -B\mathscr{E}_L(t)\psi(P_1(t) - P_2(t))$$

$$\frac{dP_2(t)}{dt} = B\mathscr{E}_L(t)\psi(P_1(t) - P_2(t)) - (Q_2 + A_2)P_2(t) \tag{2.1}$$

Level 2 population is lost by spontaneous emission - with rate A_2 -, collision quenching - with rate Q_2 - and stimulated emission. As long as the absorption rate is low, only a negligible fraction of P_1 is excited to level 2, and the process behaves linearly with respect to the laser radiant energy density. On the contrary, at high laser energy P_1 is no longer constant in time, and stimulated emission also comes significantly into play. In such a case the process enters the saturation regime, in which, at sufficiently high $\mathscr{E}_L(t)$ values, the complete saturation implies $P_1 = P_2 = 1/2P_1(t=0)$. Saturation, although desirable since it implies a simpler data rationalization, is a property of an isolated system together with a spatially uniform laser beam. Both conditions are, unfortunately, not achievable in a real experiment.

Practical implementation of a LIF experiment in gas discharges envisages the use of pulsed tuneable lasers (Dye, OPO, TiSa pumped by a Q-switched Nd:YAG or an excimer laser), with fluorescence observation at 90 degrees with respect to the laser beam, as shown in figure 2b. To-date instrumentation allows easy measurement of both the time-resolved, spectrally integrated fluorescence pulse - $S(t)$, by a photomultiplier (PMT) and a digitizing oscilloscope (DSO), and the spectrally resolved, time integrated fluorescence spectrum - $I(\lambda)$, by an intensified CCD (ICCD):

$$S(t) = CV_sA_{23}P_2(t) \qquad and \qquad I(\lambda) = \int_{t_1}^{t_2} S(\lambda,t)dt \tag{2.2}$$

where C is a constant including all the fluorescence collection, transmission and detection transfer functions, V_s is the sampled volume. The LIF characteristics as a diagnostic technique can be summarized as follows:

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[1]For a discussion on the validity of the rate equations model see [1] and references therein.

Selectivity The ability to select a single specie is close to absolute, since, in addition to the selectivity of laser absorption, a further selection is achieved by fluorescence observation;

Spatial resolution is determined by the sampled volume, that is the intersection of the laser beam with the image on the target of the iris/slit entrance of the detection assembly (see figure 2b). With a focussed laser beam the sampled volume can easily be a cylinder of 0.1 mm diameter and 0.1 mm height. We point out, however, that the LIF signal is proportional to the sampled volume. An increase of the spatial resolution then determines a strong decrease of the signal. For example, downsizing the beam waist from the common 1 mm of the unfocussed case to the 0.1 mm of a focussed one, implies a signal reduction of a factor of 100 . A partial compensation can be obtained by working in a partial saturation regime, provided the rate equation model can adequately reproduce the process. We briefly address this point later.

Time resolution is determined by the laser pulse duration. Common tuneable lasers feature pulse durations of the order of 10 ns. Shorter pulse durations can go down to the fs time scale. Note, however, that for pulse rise times shorter than 1 ns, the rate equations model validity is not ensured [1].

Sensitivity depends on the environment in which the measurement is carried out. Provided the combination of laser pulse energy and absorption probability allows to reach the linearity limit, or to overcome it into partial saturation by focussing the beam, sensititvity is mainly determined by the collision quenching and by the presence of a background radiation. At atmospheric pressure, even in a strongly quenching environment, concentrations as low as about 10^{10} cm^{-3} are measurable [2]

Absolute concentrations of species can be measured by ab initio rationalization of the LIF outcomes provided the constants C and V_s can be determined and the model correctly describes the process by means of known collision rate constants. We examine these two points in the next discussion of the OH case. In practice, ab initio calculations are difficult and introduce large errors, such that a calibration procedure is strongly adviced.

3. Simple molecular radicals: the OH case

Diatomic radicals are important reactive intermediates in gas phase in plasma chemistry. OH is a strong oxidant in atmospheric chemistry, combustion kinetics and various applications of atmospheric pressure discharges like pollution control, plasma medicine, film deposition. The most common scheme for LIF detection of OH is shown in figure 3a. With the laser tuned to a ro-vibrational transition of the (1,0) band of the 3064 Å system, fluorescence is observed from the (1,1) band. Further fluorescence can be observed from the (0,0) band if collisional vibrational energy transfer (VET) from level v=1 to v=0 is sufficiently fast, that is often the case at ATP. With the 0.2 cm^{-1} bandwidth of common dye lasers, single rotational transitions can be excited, and the fine structure of the rotational manifold, including spin-orbit and Λ-doubling splitting must be considered (see figure 3b). Note that the $^2\Sigma^+ - {}^2\Pi$ transition type is common to other interesting diatomic radicals, like CH, NO, CN. Two single rotational levels are then interacting with the laser
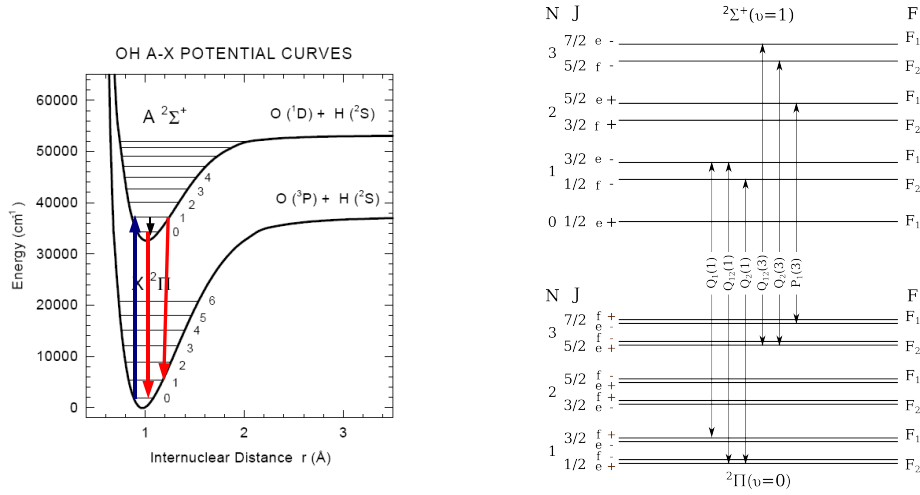
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Figure 3: left - schematization of the OH LIF spectroscopic scheme and - right - detail of the spin-orbit sublevels (F_1 and F_2 and Λ - doubling sublevels (parity + and -) with transition used in the experiment [1].

field. These two levels are however connected to the rest of the respective rotational manifolds by collisional rotational energy transfers (RET), that are very fast (rates of the order of some $10^9 \mathrm{s}^{-1}$ at ATP). The simple two-level model of figure 2a is then insufficient. A more realistic description of the process requires at least a 5-level rate equation model, as shown in figure 4a: the two laser coupled levels, X_N and $A1_N$, two lumped levels, $X1_L$ and $A1_L$, representing the whole rotational manifolds except X_N and $A1_N$, and the v=0 level of A state, A0. The quantitative validity of the model depends on the accurate knowledge of RET, VET and Q rates. VET and Q rates depend on the gas mixture. Even if rate coefficients of individual colliders may be known, the gas mixture composition is often unknown, like in an APPJ expanding towards a liquid target. Collision rates can be anyway measured locally, as we shall see later. RET rates are not very well known, except in few cases and as a general order of magnitude. This is a limit of the model for ab initio calculations of concentrations from LIF outcomes.

The spatial inhomogeneity of the laser beam must also be taken into account, especially when the demand for high spatial resolution pushes to a partial saturation regime choice. The possibility to handle mathematically the spatial distribution requires a clean beam in the experiment. Provided a top-hat beam section is utopia, it is advisable to use a spatial filter that removes high-order diffraction patterns and multiple beam reflections from the beam manipulation optics. A 2D gaussian beam section is then reasonably achieved. The model can then be treated numerically by dividing the beam section into thin annula (see figure 4b), and solving the rate equations for each annulus with the proper radiant energy density and sampled volume. The results for all annula are then summed up. There is no room in the present paper for more details on the model and constants used, that can be found in [1]. We point out that reasonable values of RET rates and of the laser beam waist can be found by fitting model results to the LIF saturation curves, and comparing the parameters to literature data and to rough measurements of the laser beam size. Nevertheless a large uncertainty remains in both RET and beam size, while the sampled volume remains somewhat undefined. Again we underline that a calibration procedure is advisable. Measuring by LIF a
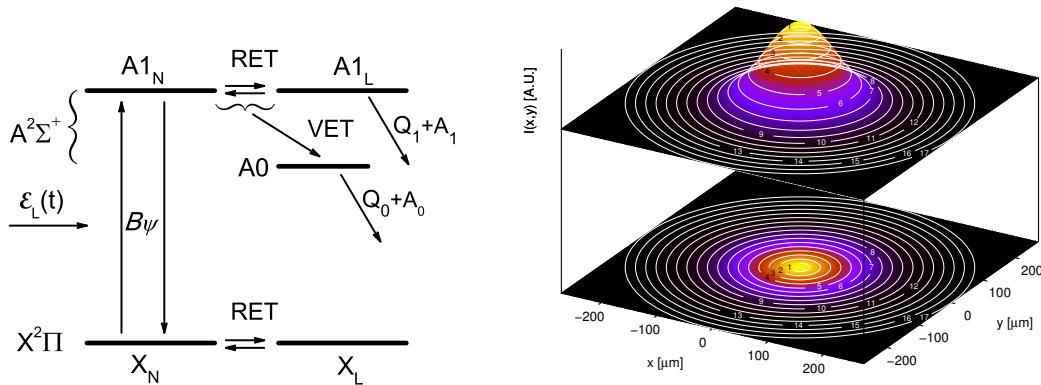
Figure 4: left - 5-level model scheme for LIF on OH and - right - discretization of the gaussian beam section.

known OH concentration allows to determine empirically the product CV_s, in which now V_s has the meaning of an effective volume, while the model with reasonable RET and waist values allows to take into account variations of experimental parameters such as Q and VET rates and laser energy.

4. Collision parameters

Electronic quenching of OH(A) state is quite well known for a good deal of collision partners. Such a knowledge comes from intense efforts done in combustion (see, for ex. [3]) and in atmospheric chemistry research. VET rate coefficients for the main constituents of humid air are also quite well known (for a summary of these data see [4, 5, 1] and references therein). Although many rate coefficients are known, an apriori calculation of Q and VET rates is impossible in a system in which the gas mixture composition is not known and varies in a small spatial scale, as it is the case for a plasma jet hitting a liquid target. Before the availability of extensive knowledge of collision rate coefficients, unknown Q and VET rates were a true problem for application of LIF to combustion research in the early '80s. In addition, at that time the measurement of the fluorescence outcome was made by gated integrators that were unable to recover the time resolved LIF pulse and then measure Q from the pulse decay after the laser pulse. Alternative strategies were attempted to find conditions that could be reasonably independent of the quenching rate. The saturated LIF was proposed to be such a condition in which, at sufficiently high laser power, saturation is achieved and the LIF outcome is insensitive to Q variations. Briefly, due to spatial non uniformity of the laser beam, a true saturation is hardly obtained, and all the efforts to isolate a truly saturated condition ended in a drastic reduction of the detected signal. For a detailed summary on this issue see [6].

A further possibility is to excite a pre-dissociative level. In the OH case, level v=3 of A state. Pre-dissociation rates are so fast as to dominate over electronic quenching, such that variations of the collisional environment produce minor changes in the LIF outcome. The drawback is signal reduction that can be partially compensated by an increase of laser energy. In [7] a KrF laser at 248 nm was used to this end. Another drawback of this approach is that it opens the way to interference from OH produced by photo-dissociation phenomena. At these wavelengths and laser energies both O_3 and H_2O_2 are photo-dissociated into $O_2 + O$ and $OH + OH$ respectively. O then
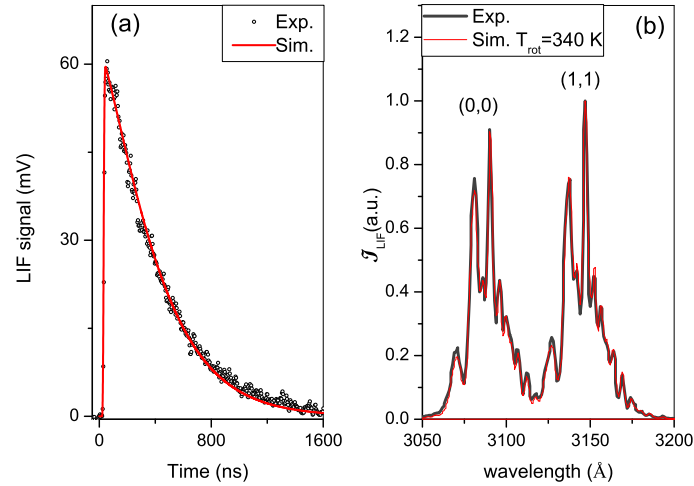
Figure 5: a): LIF outcomes in a He + small H_2O content discharge (by 'small' we mean residual water in the gas line and discharge vessel, without water carrying flux): a) time resolved LIF pulse (measured by PMT + DSO); b) LIF spectrum (measured by ICCD + monochromator). The small water content gives a small contribution to electronic quenching and a large one to VET, as shown by the strong (0,0) band emission.

quickly reacts with H_2O to give 2OH. In discharges containing air and water such an interference can be significant [7]. In other environments this can be a proper scheme for two-dimensional LIF. Nowadays, in addition to the increased knowledge on collision rate coefficients, modern technologies allow, as we have seen, the simultaneous measurement of the time resolved LIF pulse - $S(t)$ and of the LIF spectrum - $I(\lambda)$, from which both Q and VET rates can be deduced. Examples of such measurements, taken by the apparatus of figure 2b, are shown in figure 5. If the gas mixture composition is unknown, two routes are now possible:

If the collision rate coefficients of individual gas components are known, there is a chance to deduce the mixture composition from the measured Q and VET rates. This was done in [8] in a plasma gun after having demonstrated in [5] that in a He/Ar + humid air a given couple of Q and VET rates is uniquely correlated to a couple of air + water concentrations.

If collision rate coefficients are not known (or only partially known), Q and VET rates can be empirically and locally measured such that their correct values can be used in the rate equation model. Detailed knowledge of the mixture composition is not achieved but, strictly, it is not necessary for the rationalization of the LIF outcomes. A drawback of such procedure comes out when electronic quenching is so fast that the LIF pulse time evolution does not differ much from the laser pulse one. The correct recovery of the quenching rate by model fitting then requires the accurate knowledge of the laser pulse time shape. Nevertheless, the degree of collisional VET excitation of level v=0 depends on the ratio of the VET over quenching rates K_{VET}/K_Q, since it is the result of the number of VET events within the lifetime of the states. Model fitting of both $S(t)$ and $I(\lambda)$ then allows a cross check of the K_Q value.

5. LIF thermometry

Since a single ro-vibrational transition interacts with the laser field, the gas temperature must
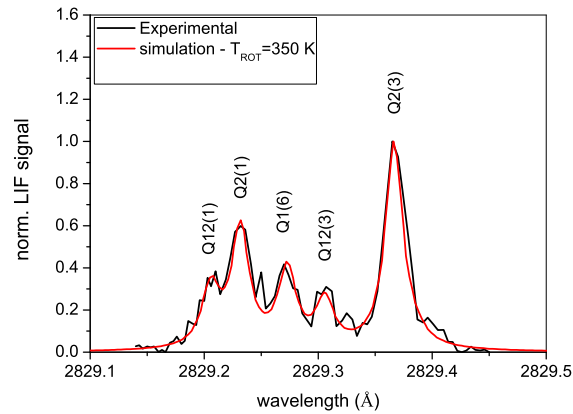
Figure 6: The LIF excitation spectrum in a 0.4 Å wavelength range including rotational levels from N=1 to 6, used in [1] for gas temperature measurements.

be known in order to calculate the population of that level with respect to the total OH ground state population. In addition the gas temperature is anyway an important parameter to be measured. Two LIF methods are available. The simpler one is to fit the fluorescence spectrum by a spectral simulation at a given rotational temperature. Due to fast RET collisions, infact, the rotational distribution of the excited state, after population of a single level by laser absorption, quickly reaches thermal equilibrium with the gas temperature (see figure 5b). The equilibrium condition depends on the lifetime of OH(A) state. In pure He or Ar the lifetime is as high as to allow hundreds of RET collisions and then the achievement of equilibrium. Addition of molecular gases drastically reduces the lifetime up to a condition in which rotational equilibrium with gas temperature is not ensured.

The main road to LIF thermometry is by recording excitation spectra, obtained by scanning the laser wavelength over a spectral range that includes lines originating from different ground state rotational levels. A good practice requirement is to select, if available, a small spectral interval with a proper group of lines, in order to reduce the scan time, but such that individual lines are still spectrally separated. The choice we made in [1] with these requisites is shown in figure 6. A full scan is made in about 6 minutes, and the scan itself can be used for simultaneous temperature and OH concentration measurements.

6. Results

6.1 Plasma gun

The Plasma Gun developed in the GREMI CNRS/Univerité d'Orléans laboratory has been investigated by OH LIF measurements. Full results are reported in [8]. The gas flow in the jet is He and the effluent jet impinges on various targets, from metal to liquid ones, at 12 mm from the jet orifice. The applied voltage is pulsed HV with pulse duration in the μs time scale and repetition rates of 2kHz. Ambient humid air penetration, water intake from the liquid surface and complex fluid-dynamics make it impossible to predict the gas mixture, which varies in a sub-mm space scale. The laser beam must then be focussed to achieve a spatial resolution of about 0.2 mm, and a
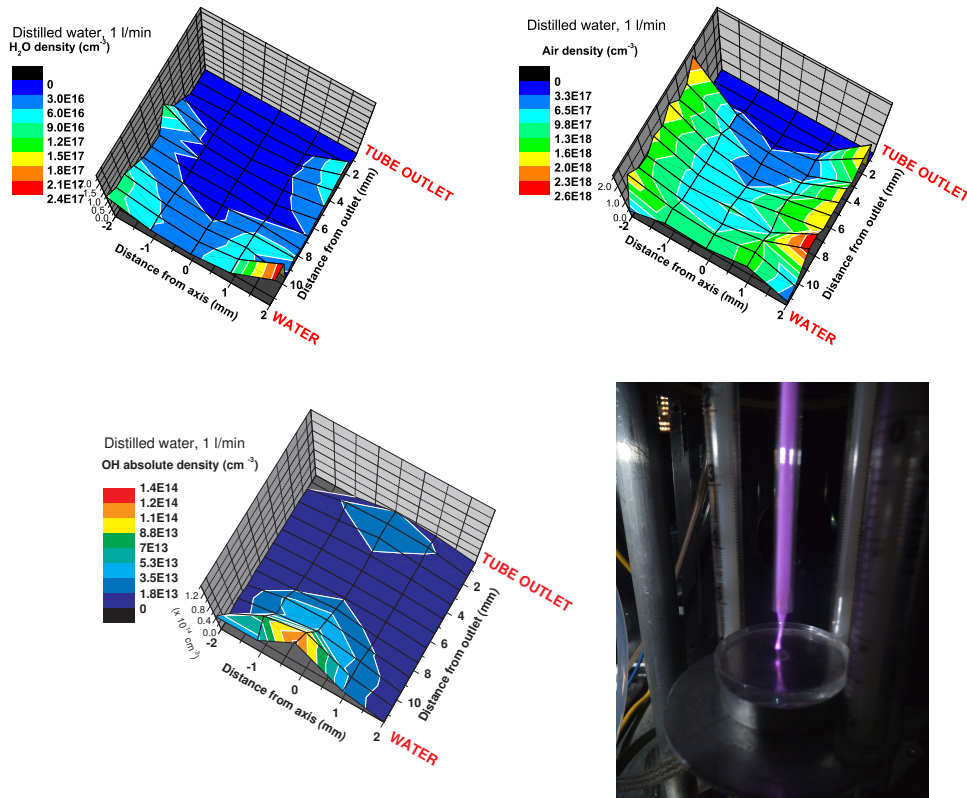
Figure 7: OH, air and water concentrations measured by LIF in a Plasma Gun with distilled water target [8]. A picture of the Plasma Gun impinging on water, in the arrangement for LIF measurements, is also shown.

partial saturation LIF regime must be chosen in order to get sufficient signal. The gas temperature remains low, and the thermometric method of the fluorescence spectrum can be applied in the jet core, giving a temperature of 340 K. No correction of the LIF outcomes for temperature spatial variations is then necessary.

Route 1 is applied for the measurement of local air and water partial pressures from Q and VET rates. Sample results are shown in figure 7 in the form of spatial maps of all measurable densities, in the case of distilled water target. It was observed in [8] that a significant dependence on the target material exists, due to a physical interaction of the plasma plume with the target, and on the mixture changes due to the chemical nature of the target. The goal of a source of radicals independent of the target nature is then not achievable by an APPJ.

The calibration is performed in a cell with known OH density. The cell is a DBD discharge in He-H_2O mixture, inserted in the LIF measurement plane, where OH density is measured by the time-resolved broad-band absorption (TR-BBAS) technique described in [9].

6.2 RF APPJ

A RF APPJ (see figure 1) with He flow interacting with a commercial oilseed target has also been investigated with the purpose of correlating oil oxidation with the density of OH radicals in the jet [1]. Again route 1 is applied giving spatial maps of OH, air and water. Contrary to the plasma gun case, RF excitation is continuos, resulting in a higher temperature of the effluent gas.
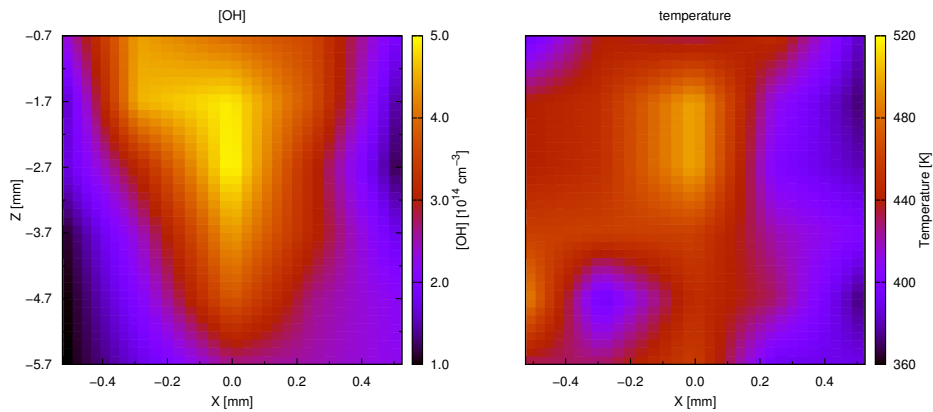
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Figure 8: OH concentration and gas temperature maps measured in a RF APPJ with He flow.

The strategy for temperature measurement must be changed, and we applied the LIF excitation spectrum method of figure 6. Sample results of OH concentration and gas temperature spatial maps are shown in figure 8. Temperatures as high as about 500 K are measured. The calibration, like in the plasma gun case, is made by a cell previously characterized by TR-BBAS [10].

7. acknowledgements

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