LIF diagnostics in volume and surface dielectric barrier discharges at atmospheric pressure

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Abstract. In this paper we review our recent work based on Laser Induced Fluorescence (LIF) diagnostics applied to Dielectric Barrier Discharges (DBD) at atmospheric pressures. Emphasis is given to the main issues that have to be faced in this application through the detailed description of the most difficult case, that of CH LIF detection. The application to kinetic studies of LIF diagnostics is then illustrated through the application of LIF to the CN radical and of Optical-Optical Double Resonance (OODR) LIF to the measurement of $N_2(A^{3}\Sigma_u^+)$ metastable.

1. Introduction

Atmospheric pressure dielectric barrier discharges are at present a well established issue in the plasma chemistry community, but, in spite of the large amount of publications, the accurate application of optical methods to the diagnostics of kinetic processes is still in its infancy. This can be ascribed to both historical and technical reasons. The technical reason is that the collision regime at atmospheric pressure (ATP), and the reduced discharge dimensions (the inter-electrode gap in particular), impose severe limits and difficulties to the application of optical diagnostics. This is particularly true for Laser Induced Fluorescence (LIF). On the other hand application of LIF is necessary when ground state transient species must be looked for. Optical Emission Spectroscopy (OES), infact, is rarely applicable as a monitor of ground states species. In our recent studies on OES in dielectric barrier discharges, we have found a number of examples in which observable emissions are due to excitation of electronic states by energy transfers with metastable molecules (NO-$\gamma$ System, nitrogen Herman Infrared System [1, 2] dissociative excitation (CH 4300 Å System [3]), recombination reactions (CN violet System [4]). In such a way that a relationship between emission features and the corresponding ground-state molecules cannot be established. Absorption techniques would be eligible for ground state molecules measurement, and are free of collision quenching problems, but dielectric barrier discharges are highly transient systems, whose study requires time-resolved measurements. To date, absorption techniques, do not have the necessary time resolution. In this talk we will present our recent work on the application of LIF to dielectric barrier discharges at ATP, starting with the most difficult case we have encountered, that of LIF detection of CH radical [3]. We will illustrate it first as a benchmark of all the difficulties that can be encountered in LIF application to ATP DBDs. We will then describe our most
complex and successful achievement, the detection of nitrogen triplet metastable \( N_2(A^3\Sigma^+_u) \) by Optical-Optical Double Resonance (OODR) LIF, a case in which it has been possible to obtain the absolute calibration of the LIF measurement by means of a method based on optical emission [1]. Such technique has also been applied to a surface dielectric barrier discharge [2, 5], a device that is particularly hostile for any optical diagnostic method. Finally we will address the detection of CN radical, and its use in combination with optical emission spectroscopy [4], that clearly shows how much LIF, with its good time resolution, is useful for kinetic studies.

2. CH LIF detection

The LIF measurements of CH density at atmospheric pressure has been addressed in combustion research. Almost all possible transitions involving the three electronic states \( A^2\Delta, B^2\Sigma^- \) and \( C^2\Sigma^+ \) have been employed to this end (see, for example [6], [7], [8] and references therein). In spite of the difficulties due to the low emission yield of the excited states, particularly increased by the pre-dissociative character of B and C states, densities as low as \( 10^{11} - 10^{12} \) \( \text{cm}^{-3} \) have been detected in atmospheric pressure flames [8], and even planar-LIF has been demonstrated in [9]. We have attempted CH radical detection by LIF in He-CH\(_4\) and N\(_2\)-CH\(_4\) mixtures. We have been able to detect a measurable LIF signal in He-CH\(_4\) only, finding a low signal strictly restricted to the active discharge time region [3]. LIF detection of CH in a Dielectric Barrier Discharge (DBD) at atmospheric pressure is in fact an archetype of all the difficulties that can be encountered in the application of this spectroscopic technique. These difficulties are relevant to the discharge kinetics, the discharge device structure, the CH molecular structure, the kinetics of CH electronic states at atmospheric pressure. We examine these issues in detail. Low average CH densities are expected, due to its high reactivity and to the pulsed and spatially inhomogeneous nature of the discharge. Filamentary discharges are a sum of short and tiny microdischarges that fill a small part of the volume for a short time. CH, produced by electron impact in the microdischarges, does not fill the entire discharge volume, due to its high reactivity/short lifetime, resulting in low average densities. The LIF setup must then be regulated for maximum sensitivity.

A drawing of the discharge apparatus is reported in figure 1. Inter-electrode spacings are 5 mm, in He-based mixtures, and 1.5 mm in N\(_2\) based mixtures. The small dimensions, of the order of the laser beam ones, and the fluorescing nature of the materials employed, are a big concern in a LIF experiment, due to the resulting strong diffused light that is superimposed
to the true LIF signal. Strong direct laser scattered light calls for a LIF excitation-detection scheme with different bands, allowing spectral separation of the LIF signal from the scattered laser. With the requirement of maximum sensitivity, however, another type of indirect laser scattered light comes into play. The hardware materials of the discharge apparatus irradiated by spatial ‘wings’ of the laser beam produce a broadband fluorescence, at wavelengths larger than the laser one, that cannot be completely filtered out, unless the LIF detection wavelength is lower than the laser one, that, as we will see in the next, is not the actual case. The spatial wings of the laser beam are produced by diffusion from all the beam manipulation optics and from the discharge vessel windows. Careful alignment and spatial cleaning of the laser beam can minimize, but not remove completely this indirect scattering. The cleaning of the laser beam is obtained by diaphragms made of black-anodized aluminium, two of which are placed inside the discharge vessel (see figure 1).

Figure 2. LIF excitation spectrum showing the region chosen for laser absorption. The simulated spectrum is shown for wavelength identification only. Simulations are calculated by LIFBASE [10].

![LIF excitation spectrum](image1.png)

Figure 3. Fluorescence spectrum measured by ICCD. The position of $N_2$ Second Positive System (SPS) emission bands superimposed to the LIF band is marked (simulation by LIFBASE).

![Fluorescence spectrum](image2.png)

All available electronic transitions, $CH(A^2Δ \rightarrow X^2Π)$, $CH(B^2Σ^- \rightarrow X^2Π)$ and $CH(C^2Σ^+ \rightarrow X^2Π)$ are strongly diagonal, limiting the choice of an efficient excitation-detection scheme in which the detected fluorescence band is different from that chosen for laser absorption. This is of fundamental importance since, as we have seen, the amount of direct and indirect laser scattered light is quite large. We have chosen the following scheme:

$$CH(X^2Π, v = 0) + hν_L \rightarrow CH(B^2Σ^-, v = 1) \rightarrow CH(X^2Π, v = 1) + hν_F$$

(1)

that gives the best combination of diagonal/off-diagonal absorption/emission coefficients. In particular the $Q_1(2)$ rotational line is pumped with $λ_L=363.798$ nm, and the observation is made with the monochromator centered at about 405 nm. Direct laser scattered light is suppressed by additional use of a bandpass interference filter. Part of the indirect discharge materials fluorescence, that is broadband, instead, enters the spectral observation window. Finally, nitrogen Second Positive System emission bands fall within the fluorescence observation window.
window. These represent a tolerable background in He-based mixtures, where air impurities are present, but, in N\textsubscript{2} based mixtures such a background becomes overwhelming, preventing any LIF signal detection. In figure 2 and figure 3 LIF excitation and fluorescence spectra are shown respectively, measured in a He+0.14\%CH\textsubscript{4}, showing the correct attribution of the measured signal to CH LIF and the low useful signal extracted from the SPS background.

The collision quenching of CH(B) state by N\textsubscript{2} and By He is not known. It has been measured only for methane air combustion mixtures. It could be relatively slow if we imagine an analogy with CH(A) state quenching whose rate constant is 2.7 \times 10^{-13} \text{cm}^3\text{s}^{-1} by N\textsubscript{2} [11], and much lower by He [3]. Nevertheless CH(B, v=1) state is predissociative, with predissociation onset at the rotational level N'=7. Even if we excite a lower rotational level by laser absorption, fast rotational energy transfers (RET) quickly bring excitation beyond the predissociation limit. In [7] calculations keeping RETs into account gave a fluorescence quantum yield for N'=2, due to predissociation only, of 4.13 \times 10^{-3} at T=1200 K, and 3.75 \times 10^{-3} at T=1900 K. Due to the temperature and mixture dependence of collision processes, extrapolation to our case is difficult, but it is reasonable to imagine, in our conditions, a fluorescence quantum yield lower than 10^{-2}.

3. OODR-LIF on N\textsubscript{2}(A\textsuperscript{3}Σ\textsuperscript{u}\textsubscript{+})

The classical single-photon LIF scheme for the detection of N\textsubscript{2}(A) involves the FPS N\textsubscript{2}(B\textsuperscript{3}Π\textsubscript{g} \rightarrow A\textsuperscript{3}Σ\textsuperscript{u}\textsubscript{+}) transitions, both for excitation and detection [12]. The quantum yield for fluorescence from the B-state is very unfavorable at ATP (order of 10^{-4}), and we already noticed in [13] that at pressures above 1 Torr the LIF signal became difficult to detect. We then proposed in [14] an Optical-Optical Double Resonance (OODR) LIF scheme in which the metastable is pumped to C-state by absorption of two photons resonant with FPS and SPS transitions:

\[ N\textsubscript{2}(A\textsuperscript{3}Σ\textsuperscript{u}\textsubscript{+}, v'' = 0) + h\nu_{L1} \rightarrow N\textsubscript{2}(B\textsuperscript{3}Π\textsubscript{g}, v' = 3) + h\nu_{L2} \rightarrow N\textsubscript{2}(C\textsuperscript{3}Π\textsubscript{u}, v) \rightarrow N\textsubscript{2}(B\textsuperscript{3}Π\textsubscript{g}, v') + h\nu_F \] (2)

Such a scheme takes advantage of the two orders of magnitudes larger quantum yield of C-state at ATP. Following the photons absorption, fluorescence is observed from the same excited v-level (direct fluorescence) and from all the vibrational levels lower than v. The latter is the consequence of vibrational relaxation and we will call it collision fluorescence. We have used the direct fluorescence the measurement of metastable density in a volume [1] and surface discharge [2, 5]. An interesting by-product has been the possibility to measure, from the direct fluorescence, the electronic quenching rate constants, and from collision fluorescence the vibrational relaxation rate constants, of the whole N\textsubscript{2}(C, v) manifold [15, 16]. From the technical point of view, the OODR-LIF solution requires in principle two lasers that must be synchronized within one ns by appropriate electronics. This was the solution adopted in our laboratory. There are nevertheless some possibilities to use a single laser setup. Already in [14], we used a single dye laser setup in which, by accidental misalignment of the cavity, in addition to the principal beam at λ\textsubscript{1}, a spurious mode was produced at about λ\textsubscript{2} = λ\textsubscript{1} + 30 nm. By a BBO crystal it was then possible to produce the mixed wavelength 1/\lambda_{mix} = 1/λ\textsubscript{1} + 1/λ\textsubscript{2}. Tuning the dye for λ\textsubscript{1} ∼ 685 nm we could produce a second beam, naturally synchronized to the first one, at λ_{mix} ∼ 350 nm, implementing the scheme of formula (2). More reproducible arrangements were proposed in [14]. One by a Ti-sapphire laser, whose fundamental wavelength can excite the FPS (1,0) at about 891 nm, with its third harmonic that would fall in the spectral region of the SPS (3,1) band. Another more versatile solution, could be the use of a tunable laser, dye or OPO, pumped by a Nd-YLF laser, whose fundamental wavelength, at 1051 nm, is suitable for absorption from the FPS (0,0) band. The choice of the SPS band for the second photon absorption would be then free. The modeling of the OODR process at atmospheric pressure is an hopeless task, so that the
possibility to deduce absolute densities of the metastable relies upon a calibration strategy. We adopted in [1] the method proposed in [17] by which the metastable density is proportional to the ratio of SPS and NO-γ emission intensities and to the NO density in the post-discharge. We then selected a condition, the post-discharge of a diffuse APTD in pure N₂, in which the LIF sampled volume is the same homogeneous volume from which the emissions come out (note that this is not true in a filamentary discharge). The calibrated OODR-LIF could then be applied to different conditions (discharge and filamentary regime). By applying this strategy we found a metastable density of the order of 10^{13} \text{ cm}^{-3} in the pure nitrogen APTD, a value in close agreement with the calculations of [18]. Addition of small oxygen concentrations to the discharge was observed to induce a transition to the filamentary regime, starting from 250 ppm of oxygen, that appears not to be caused by a marked decrease of the metastable density in the discharge, but rather by a considerable increase of its quenching rate. Such an increase, due to collision quenching by O₂ and O, strongly reduces the survival of the metastable between two discharge events in the voltage cycle, and reduces its ability to reach the surface as well. These observation are consistent with the idea that the APTD regime is sustained by a space charge memory effect due to the nitrogen triplet metastable, as outlined before. We also apply OODR-LIF measurements of the nitrogen triplet metastable to a Masuda-type surface discharge [2]. Surface discharges develop in a thin (order of 100 \mu m) layer above the surface. The laser diagnostic cannot then, for geometrical reasons, probe the discharge layer. We then measured the N₂(A) density at 1 mm from the discharge, in a so-called space afterglow. In addition, the calibration method described above could not be applied since it is based on the measurement of emissions that come instead from the discharge, i.e. from a volume different from that probed by the laser. We then applied the OODR-LIF calibrated in the volume discharge as above, finding a density of about 10^{11} \text{ cm}^{-3} in the afterglow. This afterglow density was traced-back in the discharge, by estimations based on NO-γ emissions, to about 10^{12} \text{ cm}^{-3}, one order of magnitude lower than in the volume discharge. Such a lower density might be explained by larger diffusion losses due to the vicinity of the production zone (the discharge) to the surface. However investigations under modulated regime (T_{ON}/T_{OFF} = (1-10) ms/20 ms) [5] revealed that the upper limit of the metastable density in the space afterglow is about 10^{12} \text{ cm}^{-3}. The density value decreased by increasing the discharge duration T_{ON} with respect to the diffusion time (about 3 ms) of the metastable necessary to reach a steady-state density in the space afterglow. That is likely due to the production of a larger density of quenching products (N, N₂(X,v)). This fact, combined with some difference in the material of the discharge electrodes and of the driving ac frequency, justifies the lower value measured in [2] by running the DBD under continuous regime. An important aspect is that in the space afterglow a stable cloud of metastables is established, which is not modulated by the discharge voltage cycles.

4. LIF on CN(\text{X}^2\Sigma^+ )

We addressed in [4] the issue of the CN violet system emission in a N₂-CH₄ DBD. This issue was particularly interesting since the emission revealed a largely supra-thermal vibrational excitation of the CN(\text{B}^2\Sigma^+) emitting state, that looked surprising at high pressure. By the way we had already done the same observation in a N₂-C₆H₆ DBD [19]. Such kind of vibrational distributions had been largely studied in hydrocarbon low-pressure flames (i.e. flowing afterglows at pressures from 1 to few tens of Torr) in the early 60’s, but no trace can be found in the literature of investigations carried out at atmospheric pressure. In [20] active nitrogen flames with a variety of 'fuels' (halogenated hydrocarbons, cyanogen derivatives, CH₄ and C₂H₂) were examined, finding out three different kinds of CN(B) vibrational excitations. In particular the distribution obtained under 'blue flame' conditions showed observable emission up to v=15, with a large population of the v=5-7 levels group. The 'blue flame' distribution was attributed to the reaction:
\[ N^* + CN(X^2\Sigma^+) \rightarrow CN(B^2\Sigma^+, A^2\Pi) + N_2(X^1\Sigma) \] (3)

In [21] \( N^* \) was argued to be the \( N_2(A^3\Sigma^+_u) \) metastable, while in [22] and [23] vibrationally excited nitrogen \( N_2(X, v \geq 12) \) was proposed for this role. In order to investigate the occurrence of reaction (3), and its precursor, we implemented a LIF measurement of \( CN(X^2\Sigma^+) \) according to the following scheme:

\[ CN(X^2\Sigma^+, v') + h\nu_L \rightarrow CN(B^2\Sigma^+, v) \rightarrow CN(X^2\Sigma, v'') + h\nu_F \] (4)

with \( v - v' = 0 \) and \( v - v'' = -1 \). In addition we performed OODR-LIF measurements on \( N_2(A^3\Sigma^+_u) \). Both measurements were not absolute, but only a tracing of the relative time evolution of \( CN \) and \( N_2(A) \) that we used for comparison to the corresponding time evolution of the CN violet system emission. No correlation was found between these three quantities that could justify the effectiveness of reaction (3) that was then excluded as a source of \( CN(B) \) excitation. Note that in this assessment exercise, the time resolution of LIF diagnostics was of fundamental importance. LIF measurements were even more useful since, by inspection of fluorescence spectra it was possible to verify that, even at atmospheric pressure, the vibrational relaxation in the \( CN(B, v) \) manifold was not fast. The vibrational distribution observed from violet system emission were then quasi-nascent, and could be used for the identification of the excitation reaction. We found then finally, and with a significant help from LIF diagnostics, that two processes were active in the emission on CN violet system, namely the recombination \( C + N + M \rightarrow CN(B) + M \) [24] and the reaction \( N + CH \rightarrow CN(B) + H \) [20].

5. Acknowledgements
This work has been made in the frame of CNR-AVCR 2007-2009 agreement

6. References
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