

Optical diagnostics of atmospheric pressure discharges

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Optical - mainly spectroscopic - diagnostics applied to atmospheric pressure discharge are discussed in this contribution, with emphasis on the aspects that are peculiar of the environment in which they are carried out, namely the time and space resolution needed and the collision processes in electronic states. A survey of the state of the arts is given, with a detailed description of our contribution to the field.

1. Introduction

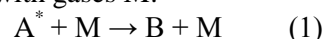
Non-equilibrium atmospheric pressure discharges are nowadays a sufficiently well established issue in both fundamental and applied gas discharges research as to justify efforts in their diagnostic investigation. Applications range from surface modification to flue gas treatment (pollutants removal, hydrocarbons reforming...), plasma assisted combustion and the most recent and challenging “plasma medicine” issues. A wide variety of devices has been developed so far - volume discharges (dielectric barrier or corona type), surface discharges, jets, micro-discharges (i.e. with sub-millimetre dimensions) - all with the common features of being highly transient, strongly influenced by post-discharge and surface processes, collision dominated although non-equilibrium. In the presence of such characteristics, the development and application of optical diagnostics is then devoted to both the search for new or improved techniques and to the assessment of good practice for classical ones. Optical diagnostics are imaging and spectroscopic techniques. Time resolved imaging, in the nanosecond time scale, is used to visualize the breakdown mechanism, mainly in the streamer case. Spectroscopic diagnostics are basically Optical Emission Spectroscopy (OES), Laser Induced Fluorescence (LIF) and absorption, in its various version of resonant, broad-band (BBAS) cavity enhanced (CEAS), cavity ring-down (CRDS). Quantities accessible to spectroscopic diagnostics are gas temperature, electron density, electric field and density of transient species – radicals and electronic metastable states. Systems investigated can be both specially designed discharges, such as single streamer volume/surface DBDs, or applicative systems. The former type of discharge is used for studies on the physics of breakdown mechanisms at high pressure, and presents the technical challenge of accurate synchronization to

the discharge event for high resolution time resolved measurements. The second type of discharges is often a sum of many randomly occurring micro-discharges events over a large volume/surface that cannot be synchronized to any instrumentation. The measurement is then a spatio-temporal average over the line of sight and temporal gate of the detector, including a mix of discharge and post-discharge processes.

In this lecture we shall point out the peculiarities of optical diagnostics in atmospheric pressure discharges, survey the state of the arts with a description of our own contribution to the field.

2. Collision processes in electronic states

In both OES and LIF the observable quantity is some emission originating from an electronically excited state. Collision-induced transformations of electronic states are processes in which the initial A^* state in a gaseous system is taken to another state B by collision with gases M:



In these processes any added gas M is effective, and the kinetics is characterized by the bimolecular rate constant k_M , or by the corresponding cross-section σ_M . The effectiveness of various M gases is largely variable, depending upon the way M participates into the transformation, by exchanging translational energy and momentum only, or putting into play resonances of own electronic states, or through a chemical reaction. Rate constants values can be different by many orders of magnitude, starting from values larger than $10^{-9} \text{ cm}^3 \text{ s}^{-1}$, down to $10^{-15} \text{ cm}^3 \text{ s}^{-1}$, and can have a strong A^* vibrational state dependence. We distinguish three categories:

Rotational Energy Transfers (RET). RET collisions at ATP are very fast, such that in most cases the rotational distribution is a Boltzmann one with $T_{\text{rot}} = T_{\text{gas}}$. This is nevertheless not always true, as it is the case of OH 3064 Å system, that in

particular conditions reveals strongly non-equilibrium rotational distributions of the OH($A^2\Sigma^+$) emitting state [1,2]. Also LIF processes can be heavily affected by RETs: in the typical duration of a pulsed tuneable laser, about 10 ns, hundreds of RET collision occur, affecting the rotational redistribution, and then the saturation condition.

Vibrational Energy Transfers (VET or vibrational relaxation). VET collisions are usually slow in ground states, and normally do not affect ground state distributions of transient species (radicals). They can be fast in electronically excited states, depending on the availability of collision partners with resonant v-v effects. We have encountered three such cases. The $N_2(C^3\Pi_u, v)$ in a N_2 discharge, that shows large vibrational relaxation rates [3], and the $CN(B^2\Sigma^+, v)$ in a $N_2 + CH_4$ discharge, for which VET rates are low [4], and the $OH(A^2\Sigma^+, v)$ [2].

Electronic Quenching. It is the process by which a collision removes the electron from the excited state manifold toward any other final product. Electronic quenching determines the fraction of the excited state population that can be observed through photon emission. Such a fraction is given by the quantum yield:

$$Y = \frac{A}{A + \sum_M [Q_M] k_M} \quad (2)$$

where A is the Einstein coefficient of the observed transition(s) and $[Q_M]$ is the density of the M quencher. Quantum yields at ATP can be so low as to suppress (i.e. to make it difficult to detect) some emission systems. A classical case is that of nitrogen First Positive System (FPS), that is emitted by the $N_2(B^3\Pi_g)$ state. Its quantum yield at ATP is about 10^{-4} , due to a quite low radiative rate (some $10^5 s^{-1}$, depending on the band). On the contrary the quantum yield of $N_2(C^3\Pi_u)$ at ATP is about 10^{-2} , by virtue of a two orders of magnitude larger radiative rate. As a consequence, while at low pressure (below 1 Torr), where electronic quenching is not large both SPS and FPS bands are readily observable, and the color of the discharge is orange, at ATP FPS emission is dramatically reduced, only SPS remains intense, and the colour of the discharge turns blue-violet. An analogous case is that of CN. Two intense systems are observed at low pressure, the violet and the red system, coming from $CN(B^2\Sigma^+)$ and $CN(A^2\Pi_i)$ states respectively. Also in this case, CN(B) state has a roughly two orders of magnitude larger radiative rate than CN(A) state. At

ATP practically only the violet system shows intense emissions.

The quantum yield at ATP is strongly dependent on the vibrational level and on the gas composition. A detailed knowledge of the rate coefficients of all the M collision partners is then necessary.

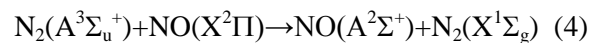
3. Optical Emission Spectroscopy

The spectral analysis of emitted light can be used for rotational (gas) temperature measurements and, with the support of appropriate collisional-radiative (CR) models, for electron density (in an argon discharge) [5] and reduced electric field (E/N in a nitrogen discharge) [6, 7]. The latter makes use of a Boltzmann solver to calculate the EEDF with E/N as a parameter, and compare nitrogen emission spectra of Second Positive System (SPS) and First Negative System (FNS) to those simulated by a CR model. Our contribution to this issue is the measurement of collision processes affecting nitrogen emissions by LIF [3,8]. The electron density can also be measured by Stark broadening [5] and the electric field by Stark polarization spectroscopy [9].

In single streamer discharges the problem of synchronization to the discharge event has been solved by use of the cross-correlation spectroscopy in [10] and by superposition of a fast voltage pulse to the sinusoidal voltage in a coplanar DBD in [11]. In this work, in an Ar discharge, the pre-breakdown phase of the streamer development has been analyzed by time-resolved spectroscopy.

Use of OES for analytical purposes, i.e. for the measurement/monitoring of radicals and kinetic processes, is desirable because of the simplicity of the technique. The information contained in OES spectra is, however, indirect and partial, and calls for a preventive study to ascertain the excitation mechanisms that produce the emissions under study. Among the many emissions we have analyzed along our studies on dielectric barrier discharges, none of them, with the notable exception of SPS, has been found to be produced by electron impact.

NO- γ system. We have shown in [12] that this emission is due in a DBD at ATP to the process

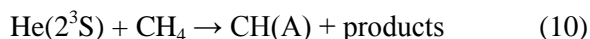
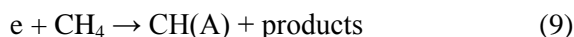


CN violet system. The violet system emission, $CN(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ is a prominent emission in N_2 discharges containing hydrocarbons. In our investigations on N_2 (or Ar)+ CH_4 or C_6H_6 [14] we found that two processes were responsible of violet system emission:



both giving rise to a very large vibrational excitation of the CN(B) state.

CH 4300 Å system emission, CH(A²Δ→X²Π). In N₂-CH₄ and He-CH₄ mixtures CH(A) excitation is not achieved by electron impact on CH but by dissociative excitation of CH₄ [15]. In particular:



in N₂-CH₄ and in He-CH₄ respectively.

In practice the mixed discharge/post-discharge regime of a DBD, and the generally low average electron density, result in emission spectra that are far from being dominated by electron impact on the corresponding ground state of the emitting molecules. The relationship between the emission and the corresponding radical is then not at all straightforward, and sometimes inexistent.

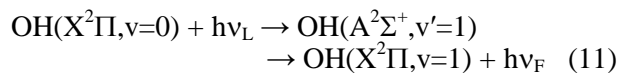
4. Laser induced fluorescence

The best analytical technique for the measurement of transient species in atmospheric pressure discharges is LIF, being it a unique combination of sensitivity, time and space resolution. Time resolution is linked to the laser pulse duration, generally around 10 ns, and volumes of fractions of a mm³ can be easily selected. Its major drawback is that in most cases it requires a calibration for reliable absolute density measurements. We address this issue through two examples, the most complete case of OH and the most complex one of Optical-Optical Double Resonance (OODR) LIF measurement of nitrogen N₂(A³Σ_u⁺) metastable.

The measurement of OH in an ATP DBD is a model case of the application of LIF to ATP discharges. Due to research in combustion and atmospheric chemistry, the OH(A²Σ⁺, v) electronic states have been largely investigated. Q and VET rate coefficients for the main air constituents, including water, and for some hydrocarbons are known together with their dependence on gas temperature and on the rotational level. (see [2] and references therein). The interest in OH radical in ATP discharges is also great. Many applications of ATP discharges, like waste gas treatment, plasma assisted combustion, plasma medicine and, in

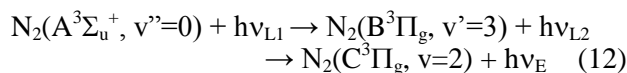
general, plasmas in contact with liquids or discharges in liquid media, deal with gas mixtures with some degree of humidity. Large amounts of OH are formed and can play an important role in the plasma chemistry of the mentioned applications.

The LIF excitation-detection scheme makes use of the transitions of the 3064 Å of OH:



Due to large spectral spacing of the rotational lines and to the absence of strong band-heads, single ro-vibrational transition absorption is possible and advantageous both for signal magnitude and for a good definition of the absorption process. Q and VET rate coefficients are strongly dependent on the colliding gas, and this offers the opportunity to use measured Q and VET rates for the determination of unknown gas mixture compositions where OH LIF is being carried out. This is the case for example of a He plasma jet expanding in ambient air and hitting a liquid surface, in which the gas composition strongly depends on the spatial position due to air penetration into the jet and back diffusion of vapour from the liquid surface. In [2, 16] measurements in He/Ar-H₂O-(N₂) in a pulsed DBD discharge can be found, with LIF calibration by absorption (see next paragraph).

OODR)-LIF was applied to the detection of N₂(A₃Σ_u⁺) in a volume DBD and, after calibration, to its absolute density measurement [12]. The same technique was then applied to a surface DBD in [13]. The following excitation detection scheme was chosen:



with two laser beams at 685 nm and 350 nm. This complex scheme was preferred to the single photon one with FPS transitions only involved, in order to take advantage of the two orders of magnitude larger quantum yield of SPS emissions at ATP. The calibrated LIF gave measured metastable densities of about 10¹³ cm⁻³. A valuable by-product of the OODR-LIF scheme was the measurement of the complete set of electronic quenching and vibrational relaxation rate coefficient of the N₂(C³Π_u, v=0-4) manifold [3], that takes advantage of the selective laser excitation of single vibrational levels.

5. Absorption

Absorption techniques have the advantage of providing absolute outcomes. The sensitivity of absorption techniques, compared to that of LIF, is much lower for single-pass, resonant or broadband,

schemes, and comparable for cavity enhanced laser absorption methods. The space resolution is limited by the line-of-sight nature of absorption. The time resolution is generally low for non-laser schemes, ranging from no resolution to the tens of μs of the BBAS scheme proposed in [17], with pulsed UV LED source and gated CCD detection, to the sub- μs one of [18], where resonant absorption was achieved by a pulsed discharge light source. Pulsed CRDS was pushed up to a time resolution of 50 ns in [19], but at the expense of sensitivity.

The recent appearance on the market of UV LED sources, that can reach wavelengths down to 245 nm, has stimulated a revival of classical absorption techniques for application to ATP discharges, since many radicals of interest for applications have strong electronic transitions in the near UV spectral region [17, 20]. Finally we note that for absolute outcomes in the high pressure case, a knowledge of the pressure broadening of ro-vibrational lines is necessary and must be available in the literature. It can be measured locally if absorption is carried out by a narrowband (below GHz) diode laser.

As a whole, as it is common opinion in combustion research, a combination of LIF and absorption techniques for LIF calibration is the most powerful arrangement for analytic diagnostics also in ATP discharges. In [17] we developed a time-resolved (TR)-BBAS technique for the purpose of LIF calibration on OH radical, but its utility as a stand-alone technique soon came out. Although not much sensitive (lower detection limit about $5 \times 10^{12} \text{cm}^{-3}$) and limited to relatively large discharges (for an absorption length of some cm with single/double-pass path), it is simple and low cost, it gives absolute density values and a simultaneous measurement of the ground state rotational temperature. A development of the technique and its application to studies on OH density evolution in an He-H₂O DBD discharge with small O₂ additions is reported in [21].

6. References

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