

## Optical diagnostics in dielectric barrier discharges at atmospheric pressure\*

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*Abstract:* Our recent work on optical emission spectroscopy (OES) and laser-induced fluorescence (LIF) applied to dielectric barrier discharge (DBD) at atmospheric pressure (ATP) is reported. The interplay of discharge kinetics and diagnostic techniques features is evidenced, with emphasis on collision processes that, with their variety of state-to-state characteristics and rate constants, determine the observation of a peculiar collision-dominated non-equilibrium system.

*Keywords:* dielectric barrier discharges; laser-induced fluorescence; optical emission spectroscopy; plasma chemistry; plasma diagnostics.

### INTRODUCTION

Atmospheric-pressure (ATP) discharges are at present a well-established issue in the plasma chemistry community, but, in spite of the large amount of publications, the application of optical methods to the diagnostics of kinetic processes is rarely found in the literature. This can be ascribed to both historical and technical reasons. Research on these devices is, in its actual massive form, quite recent, and only few among the many possible applications are well established, so that it is probably not yet time for a strong need for a more profound understanding of these devices. The technical reason is that the collision regime at ATP and the reduced discharge dimensions impose severe limits/difficulties to the application of optical diagnostics. This is true not only for complex laser diagnostics like laser-induced fluorescence (LIF), but also for simple optical emission spectroscopy (OES), that is influenced by collision quenching of the emitting electronic states [1]. As a result, spectra are strongly “modulated” by emission yields that are quite different from those of the collisionless case.

Dielectric barrier discharges (DBDs) are intrinsically pulsed discharges, and in most operating conditions they run in a filamentary regime, in which thin microdischarges fill only a small part of the discharge volume. The result is the coexistence of discharge and post-discharge regimes in which, in the average volume, energy transfers, chemi-luminescent, recombination, and plasma-surface processes can compete with electron impact processes in the production of observable spectroscopic emissions. The vast majority of cases that can be found in the literature concerns the use of OES applied to DBD processing devices without time resolution, by which emitting species can be identified, but it is clear that elucidation of the mechanisms producing the emissions is of fundamental importance for the use of OES data in the understanding of the discharge kinetics and even simply for process monitoring.

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Analysis based on non-time-resolved OES results is often insufficient to this end, and a combination with other techniques is necessary. In [2], for example, OES and surface analysis were combined to interpret emission spectra in a DBD for silane-based coatings. Nitrogen emissions have been used for the estimation of electron temperature [3] or of the reduced electric field  $E/N$  [4,5]. To this end, collision-radiative models are necessary that require a detailed knowledge of the collision processes occurring in the electronic states. Full-time resolution was achieved by a sophisticated cross-correlation spectroscopy technique, applied to single-microdischarge devices, in [6,7]. Important details on the microdischarge space and time evolution were achieved in such a way, but real discharge processing devices, made of many uncorrelated microdischarges, cannot unfortunately be investigated by this technique. Non-emitting species measurement must be achieved by other techniques. Classical absorption (non-time-resolved) was applied to the detection of NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and O<sub>3</sub> in [8] and of CF<sub>2</sub> in [9], and two-photon LIF to the measurement of oxygen atoms in [10] and nitrogen atoms in [11]. We have explored this realm, touching many of the issues described above by a multidagnostic approach with time-resolved optical diagnostics, applied to common DBD devices. In this paper, we will briefly review our recent results on

- the use of N<sub>2</sub>(C) emission (SPS) for electron temperature estimation by a collision-radiative model, with a complete characterization of the collision processes in the N<sub>2</sub>(C,v) manifold [12];
- optical-optical double resonance (OODR) LIF for N<sub>2</sub>(A) metastable detection [13];
- a combination of time-resolved emission and laser spectroscopy for the investigation of CN violet system emissions in a N<sub>2</sub>-CH<sub>4</sub> discharge [14]; and
- the detection of CH in a He-CH<sub>4</sub> discharge, an archetype of all the difficulties one has to face when trying to detect a radical in this kind of discharge [15].

The sum of these investigations has shown that DBD devices possess unique features that come up from a combination of high-pressure and highly non-equilibrium conditions that at first sight may look as a contradiction. We will review our work on optical diagnostics, by which we mean basically OES and LIF, from the point of view of these DBD peculiarities.

## THE ROLE OF COLLISIONS IN OPTICAL DIAGNOSTICS

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  $\sigma_M$ .

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 its 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<sup>-9</sup> cm<sup>3</sup> s<sup>-1</sup>, down to 10<sup>-15</sup> cm<sup>3</sup> s<sup>-1</sup>, and can have a strong A\* vibrational state dependence. We distinguish three categories:

*Rotational energy transfers* (RETs). RET collisions at ATP are very fast, such that even the rotational distribution of fast radiative electronic states is a Boltzmann one with  $T_{\text{rot}} = T_{\text{gas}}$ . Also, LIF processes can be heavily affected by RETs: in the typical duration of a pulsed tunable laser, about 10 ns, hundreds of RET collisions occur, affecting the rotational redistribution, and then the saturation condition.

*Vibrational energy transfers* (VETs 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 res-

onant  $v$ - $v$  effects. We have encountered two such cases. The  $N_2(C^3\Pi_u, v)$  in a  $N_2$  discharge, that shows large vibrational relaxation rates [12], and the  $CN(B^2\Sigma^+, v)$  in a  $N_2 + CH_4$  discharge, for which VET rates are low [14].

*Electronic quenching.* The process by which a collision removes the electron from the excited-state manifold (sum over all final products). It determines the fraction of the excited-state population that can be observed through photon emission, that is given by the emission yield

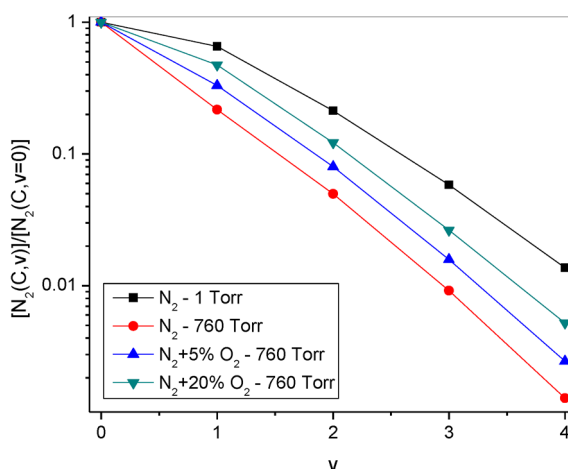
$$Y = \frac{A}{A + \sum_M [Q_M] k_M} \quad (2)$$

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  $10^5 \text{ s}^{-1}$ , 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 color 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 the  $CN(B^2\Sigma^+)$  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 emission 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 if OES has to be used for diagnostic purposes. The most detailed example is that of SPS emission, and its use as a diagnostic of the electron energy distribution function (EEDF). The  $N_2(C^3\Pi_u, v)$  states, from which SPS bands originate, are excited by electron impact in a discharge. A simple collision-radiative model gives the time evolution of the C-state populations  $C_v$  [3]:

$$\frac{dC_v}{dt} = n_e \sum_{j=0}^{10} k_{vj}^{XC} X_j - \left( k_v^Q X + A_v \right) C_v + \sum_{w=v+1}^4 k_{vw} X C_w \quad (3)$$

where  $k_{vj}^{XC}$  is the electron impact rate coefficient for  $(X, j) \rightarrow (C, v)$  excitation that depends on the EEDF,  $k_v^Q$  is the collision quenching rate coefficient,  $A_v$  the radiative rate,  $k_{vw}$  is the vibrational relaxation  $(C, w) \rightarrow (C, v)$  rate coefficient. The collision features of  $N_2(C, v)$  in a  $N_2$  bath were measured in great detail in [12], where state-selective excitation by OODR-LIF allowed, for the first time, a clear and accurate measurement of the vibrational relaxation process, that, in this case, is quite strong. At steady state, and being the electron density  $n_e$  generally unknown, relative  $C_v$  populations are determined by the ratio of excitation and quenching processes. The quenching in  $N_2$  is a monotonically increasing function of  $v$  ranging, at ATP, from  $3.3 \times 10^8 \text{ s}^{-1}$  to  $2.4 \times 10^9 \text{ s}^{-1}$  ( $v = 0-4$ ). The characteristic time for reaching steady state is of the order of 10 ns. DBDs running in a diffuse regime (glow-APGD or Townsend, APTD [16]), have discharge current time evolutions in the  $\mu\text{s}$  time scale, so that  $C_v$  populations are certainly in a local (temporal) steady state with the changing discharge conditions. A filamentary discharge is instead a sum of short microdischarges, each lasting a few tens of ns. Local steady state is then impossible, but if the light emission is measured with (integrated in) a temporal gate much larger than the emitting state lifetime, it is easy to demonstrate by simple calculations that the relative  $C_v$  populations (i.e., the vibrational distribution) deduced from the integrated emissions are the same as those obtained by the steady-state model, that can be then applied to this purpose also to the filamentary discharge case [15]. Few calculations, reported in Fig. 1, show the effect of collisions on the  $C_v$  dis-



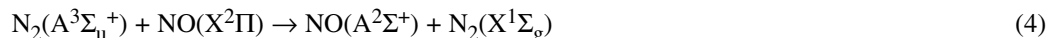
**Fig. 1**  $N_2(C,v)$  vibrational distributions calculated by the steady-state solution of eq. 3 at different conditions, showing the effect of  $v$ - and mixture-dependent quenching rate constants.

tribution on a constant excitation arrangement, given by Maxwellian EEDF at  $T_e = 3$  eV. In pure  $N_2$  the comparison of distributions at 1 Torr and at ATP clearly evidences the effect of the  $v$ -dependent rate constants. Addition of  $O_2$ , whose quenching rate coefficients are much larger but with a smooth  $v$ -dependence, tend to cancel out the effect of the  $v$ -dependence of  $N_2$  rates. This example illustrates how, from the optical diagnostics point of view, ATP DBDs are collision-dominated not because collisions push the system toward equilibrium, but in the sense that the state-to-state nature of collisions strongly influences the internal states distributions.

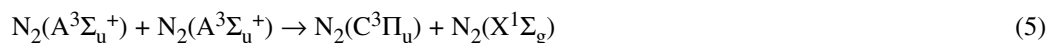
### WHAT CAN BE DEDUCED FROM OES?

Monitoring plasma parameters and kinetic processes by OES is desirable because of the simplicity of the technique that, besides the relatively low cost of the equipment, does not require a special design of the discharge hardware, as it is in the case of LIF. 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. We have already seen the possibility of using SPS emission to gain insights into the EEDF, but it is clear that  $N_2(C,v)$  excitation contains integral (through the excitation rate) information on the EEDF shape for energies larger than about 11 eV. A further piece of information can be added by looking at first negative system emission from the  $N_2^+(B)$  state, whose excitation threshold is about 18.5 eV. But in this case, the collision quenching of  $N_2^+(B)$  is not known with great accuracy. Among the many emissions we have analyzed along our DBD studies, none of them, with the notable exception of SPS, has been found to be produced by electron impact. Discussion of such cases follows.

*NO- $\gamma$  system.* This emission, that is typical of  $N_2$  discharges containing even traces of  $O_2$ , is known to be produced, at low pressure, by the energy transfer

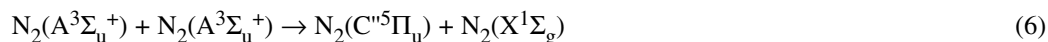


We have shown in [13] that this is true also in a DBD at ATP. By the way, the SPS too, in the post-discharge, is produced by an energy transfer process involving the nitrogen metastable, the pooling reaction



It was then possible to identify a time region, in the post-discharge between two current cycles, in which the ratio of SPS and NO- $\gamma$  emissions is proportional through a known constant to the ratio  $[N_2(A)]/[NO]$ , giving a way to calibrate OODR-LIF on  $N_2(A)$ .

*Herman infrared system (HIR).* This emission,  $N_2(C''^5\Pi_u \rightarrow A'^5\Sigma_g^+)$ , was demonstrated to be due again to the pooling reaction in a  $N_2$  surface DBD [17].



*CN violet system.* The violet system,  $CN(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ , is a prominent emission in  $N_2$  discharges containing hydrocarbons. In our investigations on  $N_2$  (or Ar) +  $CH_4$  or  $C_6H_6$  we were attracted by two features. First, the vibrational excitation of  $CN(B)$  was largely supra-thermal; second, the emission was observed even in the absence of hydrocarbons in the gas feed, but in the presence of a surface deposit previously produced by a discharge with hydrocarbons in the gas feed, indicating an emission produced with the aid of species coming from the surface. Further analysis by LIF indicated a weak vibrational relaxation in the  $CN(B^2\Sigma^+, \nu)$  manifold. We found that two processes, both giving rise to a very large vibrational excitation, were responsible for violet system emission and concluded that one of these is the recombination



while the other one is likely



*CH 4300 Å system emission,  $CH(A^2\Delta \rightarrow X^2\Pi)$ .* We have recently investigated this emission in  $N_2$ - $CH_4$  and He- $CH_4$  mixtures in order to assess the possibility of extracting information on CH radical from its emissions [15]. Analysis of the intensity ratios between SPS and  $CH(A)$ , and between FNS and  $CH(A)$ , has instead shown that  $CH(A)$  excitation is not achieved by electron impact on CH but by dissociative excitation of  $CH_4$ . In particular, in  $N_2$ - $CH_4$  and in He- $CH_4$ , respectively:



Summing up the whole of these experiences, we conclude that the mixed discharge/post-discharge regime of a DBD, and the generally low average electron density, results in emission spectra that are far from being dominated by electron impact on the corresponding ground state. The relationship between the emission and the corresponding radical is then not at all straightforward, and sometimes even nonexistent. Use of emission features as a process monitor, even if empirically sound, could instead be wrong when used as a tool for interpreting the corresponding mechanisms.

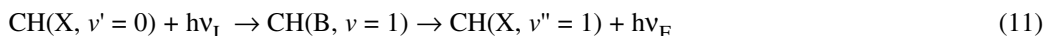
## LASER-INDUCED FLUORESCENCE

Knowledge on ground-state transient species must be looked for through more sophisticated techniques. LIF possesses the requisites of sensitivity and time resolution, and is often penalized by the collision quenching of the fluorescing electronic state. Absorption techniques do not suffer such shortcoming but, at present, do not have the proper time resolution. The most difficult case we have encountered is that of CH LIF detection, a benchmark of all the difficulties that can be encountered in LIF application to ATP DBDs. These are related to:

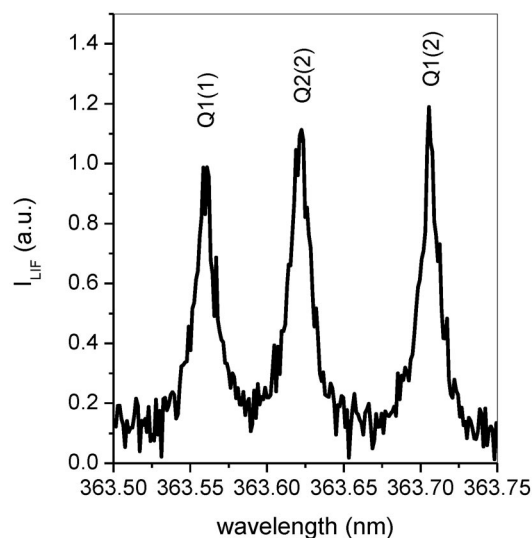
- *The discharge kinetics:* low average CH densities are expected, due to its high reactivity and to the pulsed and spatially inhomogeneous nature of the discharge.
- *The CH molecular structure:* all available electronic transitions [ $CH(A-X)$ ,  $CH(B-X)$  and  $CH(C-X)$ ] are strongly diagonal, limiting the choice of an efficient excitation-detection scheme in which the detected fluorescence band is different from that chosen for laser absorption.

- *The CH electronic states kinetics:* the collision quenching due to the high discharge pressure, and the pre-dissociative nature of the CH electronic states strongly lower the fluorescence yield.
- *The discharge hardware structure:* the small dimensions, of the order of the laser beam ones, and the fluorescing nature of the materials employed, are a big concern in an LIF experiment, due to the resulting strong diffused light that is superimposed to the true LIF signal.

We have applied the following excitation-detection scheme:

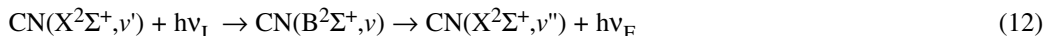


that gives the best combination of diagonal/off-diagonal absorption/emission coefficients, to a He-CH<sub>4</sub> discharge, getting a low but measurable signal (Fig. 2). The final findings show a very low CH density strictly confined into the time interval in which discharge electrons are active [15].



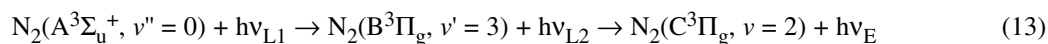
**Fig. 2** LIF excitation spectrum (fixed full-band detection and scanning laser wavelength) in the spectral region used for CH detection. The  $Q_1(2)$  rotational line has been chosen for maximum signal.

A better fate concerned our attempt to detect CN radical by the following scheme [14]:



With  $v-v' = 0$  and  $v-v'' = -1$ . Strong signal detection allowed LIF excitation scan along the vibrational bands with good rotational resolution, and also the measurement of fluorescence spectra by intensified CCD detection. The latter measurement allowed us to assess the weak vibrational relaxation in the CN(B,v) manifold. That is weak also in the CN(X,v) manifold, as demonstrated by excitation spectra that revealed high vibrational excitation also in the CN ground state. The CN time evolution measured by LIF, finally, helped in the assessment of processes 7 and 8 for CN violet system emission.

We have achieved the best results for LIF as an analytical tool in [13], where OODR-LIF was applied to the detection of N<sub>2</sub>(A<sub>3</sub>Σ<sub>u</sub><sup>+</sup>) in a volume DBD and, after the calibration already described, to its absolute density measurement. The same technique was then applied to a surface DBD in [17]. The following excitation detection scheme was chosen:



with two laser beams at about 685 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  $10^{13} \text{ cm}^{-3}$ , in close agreement with the calculations reported in [16].

## CONCLUSIONS

The whole of these studies shows that DBDs at ATP are

- highly transient,
- strongly influenced by post-discharge and surface processes,
- non-equilibrium–collision-dominated systems (in the sense we have clarified in the text), and
- a field where much research work on diagnostics has still to be done.

The collision quenching of emitting states, by collision with several collision partners, is still poorly known. The EEDF in filamentary discharges is still an issue, but of great importance for OES measurement interpretation. The excitation of emitting states must be investigated case by case, if correct information from OES has to be achieved. Time-resolved LIF and absorption techniques must be massively applied for both transient species monitoring and interpretation of OES measurements.

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