Advances in the optical diagnostics of kinetic processes in atmospheric pressure dielectric barrier discharges

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Abstract. Dielectric barrier discharges at atmospheric pressure have recently received a growing interest because of their potentially advantageous use in a number of applicative fields, in both their main classes of ‘volume’ and ‘surface’ geometric arrangements. From a diagnostic point of view, the high pressure regime adds problems relevant to an enhanced role of collision quenching, vibrational and rotational relaxation, while maintaining many of the demands of a highly non-equilibrium system for a detailed characterization of its degrees of freedom. In addition, filamentary DBDs are intrinsically pulsed systems, in which the electron impact excitation is confined in small space regions and very short time intervals, such that a prominent afterglow phase, both spatial and temporal, is present in the discharge volume, and kinetic processes involving long-lived species, chemi-luminescent reactions, recombinations (aided by the large pressure) can competitively come into play in the excitation of electronic states. We have applied our ensemble of diagnostic methods, based on time resolved emission and laser spectroscopy, to the investigation of elementary kinetics in DBDs. Here we present our last two years results that include: Optical-Optical Double Resonance (OODR)-LIF measurements of $N_2(A^3Σ_u^+)$ density, in a volume DBD that is of relevance in the debate upon the mechanisms for establishing the glow regime; OODR-LIF and emission study on a Masuda type surface discharge; measurement of $N_2(C^3Π_u, v)$ quenching and vibrational relaxation rate constants and its relevance to nitrogen Second Positive System emission diagnostics at atmospheric pressure; kinetics of $CN(B^2Σ^+, v)$ formation and violet system emission in $N_2$-CH$_4$ discharges. The latter issue shows in addition a correlation between emissions and surface status (i.e. the presence of a deposit) that is a clear monitor of a gas-surface interplay.

1. Introduction
Dielectric Barrier Discharges (BDB) at atmospheric pressure (ATP) are discharges in which at least one electrode is covered by a dielectric layer, i.e. it is not in direct contact with the gas. The simple consequence of such an arrangement is that, after the breakdown, charge accumulation on the dielectric surface prevents the corona-to-spark transition and, finally, stops the discharge itself if the voltage does not increase continuously. If an AC voltage is supplied to the electrodes, the discharge starts again when the applied electric field is reversed. As a consequence a non-equilibrium regime with low gas temperatures is intrinsically maintained without the need for complex pulsed HV supplies. Strong non-equilibrium at ATP and simple design make then DBDs very attractive for a wide variety of applications. These range from well...
established industrial applications like ozone generation, CO$_2$ lasers, excimer lamps, to promising ones like polymer surface treatment, pollution control, hydrocarbons reforming, plasma assisted combustion, aerodynamic flow control, plasma display panels. It is not our aim in this short paper to report exhaustively on the physics and applications of DBDs: good reviews are largely available in the literature [1, 2, 3, 4, 5]. Rather, since we are interested in the diagnostic investigation of the microscopic kinetics occurring in DBDs, a field that is often neglected in the literature, we will remind and highlight those peculiarities that are of importance for both diagnostics and kinetics.

Various discharge geometries have been realized, that can be divided into two main classes: volume discharges, in which the two electrodes are faced to each other and the discharge burns in between, and surface discharges, in which the electrodes are on (or embedded in) the same dielectric slice and the discharge burns in a thin layer above the surface. In most cases the discharge is made of a group of microdischarges distributed in time and space, and the current looks like that shown in figure 1, in presence of a sinusoidal applied voltage. This is what is commonly referred to as the filamentary regime. DBDs’ operating frequencies range from 50 Hz to 500 KHz, and operating voltages from few KV to few tens of KV, depending of course on the gas and on the electrodes geometry. Microdischarges properties depend solely on the gas composition, pressure and geometry, and this means that an increase of the discharge power results simply in an increase of the number of microdischarges. A simple geometrical scaling is then allowed, i.e., for example, doubling the electrodes area will result in a doubling of the current/power, provided the external circuit is able to supply sufficient power. We will see that, from the point of view of discharge kinetics, such an idea is over-simplified when dealing with long living species that depend on the history of the discharge, i.e. on how much time/how many cycles the gas mixture has been exposed to the discharge.

Typical parameters of the microdischarges are: duration 1- 20 ns, filament radius 50-100 $\mu$m, electron density $10^{14}$-$10^{15}$ cm$^{-3}$, electron temperature 1-10 eV. Filaments then carry large

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig1}
\caption{Voltage and current in a filamentary N$_2$ DBD, with 2 mm electrodes gap. The average current is several times lower than peak microdischarges current.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig2}
\caption{Voltage and current in a N$_2$ APTD, with 1 mm electrodes gap. The discharge current is superimposed to the electrodes displacement current.}
\end{figure}
electron energy and density, but they fill a very small fraction of the discharge volume and for a very short time. In other words, in the average volume two phases coexist: short intense and small discharges and large time and space afterglows. Even a time-resolved (gated) observation cannot discriminate between the two, and the measurement will be an average over the two phases. The only case in which a discrimination has been possible is that reported in [6], [7], in which a special geometric arrangement was able to produce a single filament discharge whose emissions were observed by cross-correlation spectroscopy. Within a restricted range of parameters the DBD can exist in a diffuse mode, that can be an Atmospheric Pressure Glow Discharge (APGD) or an Atmospheric Pressure Townsend Discharge (APTD), the latter being found in nitrogen discharges (see [8] and references therein). The current is continuous, like in figure 2, and the discharge is diffuse. Due to the discharge spatial uniformity, this operating mode is very attractive for surface treatment applications. Its appearance seems to be linked to the survival of a sufficient charge density between two discharge cycles (voltage half-cycles), likely due to the presence of long-lived electronic excited (metastable) states. It is then a case in which microscopic kinetics can determine the macroscopic behavior of the discharge and can have a heavy influence on the applicability of DBDs to material processing. The APGD is still a mixture of temporal discharge and post-discharge regimes, but, contrary to the filamentary case, the two regimes can be discriminated by a gated measurement synchronized to the applied voltage.

2. Experimental approach

Our optical diagnostic approach to the study of discharge kinetics includes a set of time-resolved emission and laser spectroscopy tools:

- **Laser Induced Fluorescence (LIF)**, for the detection of non-emitting transient species, i.e. radicals (ground state) and electronic metastable states. LIF is essentially and absorption measurement, in which the state under observation (lower state) is pumped to an electronic upper state by absorption of laser photons through a resonant transition. The observable quantity is the fluorescence light emitted by the upper state after absorption. We have applied LIF in the following three configurations:
  (i) LIF excitation spectra - laser wavelength scan, fixed full/partial fluorescence detection). Used for the determination of ro-vibrational distributions of the lower state;
  (ii) LIF fluorescence spectra - spectrally resolved fluorescence detection at fixed laser wavelength. Used for the determination of collision phenomena in the upper state (electronic quenching and vibrational relaxation);
  (iii) fixed laser wavelength and fluorescence detection, for analytical purposes, i.e. the determination of relative/absolute concentrations of transient species and their evolution in the discharge/post-discharge cycles;

- **Emission spectroscopy**, for the detection of emitting species, and in particular:
  (i) high/medium resolution (up to few angstrom bandpass) for the determination of ro-vibrational distributions of the emitting state;
  (ii) low resolution - single spectral feature (for example a full molecular band) detection, for the monitoring of the relative population of the emitting state and its evolution in the discharge/post-discharge cycles.

The recording of the time evolution of spectroscopically observable quantities is the basis for the application of a method, that we have largely employed in our past research in low-pressure discharges, for the identification of microscopic processes taking place in the discharge. In practice, if we have a reaction:
\[ A + B \xrightarrow{k} C + M \]  

(1)

whose reactants (A and B) and at least one product (C) are observable, the following relationships involving the temporal evolution of A, B and C holds:

\[ [C](t) \propto [A](t)[B](t) \]  

(2)

The verification/negation of such a correlation gives strong indication that reaction (1) is/is not the dominant mechanism for the production of the observable specie C. Note that the absolute concentration of A, B and C needs not to be known, but only their relative temporal evolution is required. A typical application example is the pooling reaction:

\[ N_2(A^3\Sigma^+ + u, v') + N_2(A^3\Sigma^+ + u, v') \xrightarrow{k_2} N_2(C^3\Pi_u, v'') + N_2(X^1\Sigma_g) \]  

(3)

The \( N_2(C) \) state is responsible of the intense Second Positive System (SPS) emission. The nitrogen triplet metastable can be measured by LIF. If SPS evolves in time as the square of the metastable density (LIF signal), reaction (3) holds. More in detail, the time correlation method is used in this case to look for the time interval, typically the deep post-discharge, in which SPS emission is due to reaction (3). Another example is the energy transfer:

\[ N_2(A^3\Sigma^+_u, v') + NO(X^2\Pi) \xrightarrow{k_1} NO(A^2\Sigma^+ + v'') + N_2(X^1\Sigma_g) \]  

(4)

whose occurrence can be verified again by comparing the time evolution of NO-\( \gamma \) system emission (from NO(A) state) to \( N_2(A) \) (LIF) and NO(X) (LIF) time evolutions.

Peculiarities of spectroscopic diagnostics at atmospheric pressure are tied to an increased influence of collision processes with respect to the low-pressure case (see [9] and references therein), that involve the ro-vibrational manifolds of the electronic states we are looking at. Three collision energy transfers have to be considered:

(i) **Rotational Energy Transfers** (RET). 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 collision occur, affecting the rotational redistribution, and then the saturation condition.

(ii) **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 energetically contiguous electronic states. We have encountered two different such cases. The \( N_2(C^3\Pi_u, v) \) in a \( N_2 \) discharge, that shows large vibrational relaxation rates, and the CN(\( B^2\Sigma^+, v \)) in a \( N_2 + CH_4 \) discharge, for which VET rates are low.

(iii) **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:

\[ Y = \frac{A}{A + \sum_i [Q_i]k_i} \]  

(5)

where \( A \) is the Einstein coefficient of the observed transition(s), \([Q_i]\) is the density of the i-specie quencher and \( k_i \) is the i-specie quenching rate coefficient. 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 \( \text{N}_2(B^3\Pi_g) \) 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 \( \text{N}_2(C^3\Pi_u) \) at ATP is about \( 10^{-2} \), by virtue of a two orders of magnitude larger radiative rate. As a consequence, while at low pressure, where electronic quenching is not large (below 1 Torr) 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 emissions, that we have observed in our investigations on nitrogen - methane/benzene DBDs. Two intense systems are observed at low pressure, the violet and the red system, coming from \( \text{CN}(B^2\Sigma^+) \) and \( \text{CN}(A^2\Pi_i) \) states respectively. Also in this case, \( \text{CN}(B) \) state has a roughly two orders of magnitude larger radiative rate (about \( 1.5 \times 10^7 \) s\(^{-1} \)) than \( \text{CN}(A) \) state (some \( 10^5 \) s\(^{-1} \), depending on the band [11]). At ATP practically only the violet system shows intense emissions.

3. OODR-LIF on \( \text{N}_2(A^3\Sigma_u^+) \)

The classical single-photon LIF scheme for the detection of \( \text{N}_2(A) \) involves the FPS \( \text{N}_2(B-A) \) transitions, both for excitation and detection [12]. As we have seen the quantum yield for fluorescence from the B-state is very unfavorable at ATP, 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:

\[
\begin{align*}
N_2(A^3\Sigma_u^+, \nu'' = 0) + h\nu_{L1} &\rightarrow N_2(B^3\Pi_g, \nu' = 3) + h\nu_{L2} \rightarrow \\
&\rightarrow N_2(C^3\Pi_u, \nu) \rightarrow N_2(B^3\Pi_g, \nu') + h\nu_F
\end{align*}
\]

Figure 3. Potential energy diagram of the three nitrogen triplet states involved in the OODR-LIF scheme (6). The red and blue upward arrows indicate the photon absorption on FPS and SPS transitions. In the figure level \( \nu=2 \) is excited, that is the case of the scheme used for \( \text{N}_2(A, \nu''=0) \) density measurement. Downward arrows indicate the direct (thick blue) and collision fluorescence (thin blue) (see text).

Such a scheme takes advantage of the two orders of magnitudes larger quantum yield of C-state at ATP. The scheme is also depicted in figure 3. Following the photons absorption, fluorescence is observed from the same excited \( \nu \)-level (direct fluorescence) and from all the vibrational levels lower than \( \nu \). The latter is the consequence of vibrational relaxation and we will call it collision fluorescence. Direct fluorescence has been used for both electronic quenching rate constants measurement and for \( \text{N}_2(A) \) OODR-LIF density measurements, while collision fluorescence has been used for vibrational relaxation rate constants measurements.
3.1. Collisions in the (C, v) manifold

The Second Positive System of N\textsubscript{2} is frequently used for optical diagnostics of gas discharges. In particular it can be used to infer the electron temperature T\textsubscript{e} and the ground state N\textsubscript{2}(X) vibrational temperature, T\textsubscript{v}, and it has often been used for modeling tests of N\textsubscript{2} discharge kinetics (see [15] and references therein). Discharge parameters are inferred from the (C, v) measured vibrational distributions in a condition in which C state is excited predominantly by electron impact (i.e. in the discharge), whose collision cross sections are well known. Relative measured vibrational distributions in a condition in which C state is excited predominantly by kinetics (see [15] and references therein). Discharge parameters are inferred from the (C, v) function, but could be described by the empirical function:

\[ K(P) = A_0 + k_\infty P - (k_0 - k_\infty) P / (1 + P/P_0) \]  

with \( A_0 = (2.7298 \pm 0.0116) \times 10^7 \) s\(^{-1}\) (the radiative rate); \( k_0 = (2.22 \pm 0.56) \times 10^6 \) Torr\(^{-1}\)s\(^{-1}\); \( k_\infty = (4.144 \pm 0.046) \times 10^5 \) Torr\(^{-1}\)s\(^{-1}\); \( P_0 = (0.87 \pm 0.26) \) Torr. In the limits \( P \rightarrow 0 \) and \( P \rightarrow \infty \) (in practice \( P \ll P_0 \) and \( P \gg P_0 \)) equation (7) becomes, respectively:

\[ K(P) = A_0 + k_0 P \]  

\[ K(P) = A_0 + (k_0 - k_\infty) P_0 + k_\infty P \]  

In practice, then, for pressures above few Torr, a linear dependence on P is empirically valid, with a rate constant equal to \( k_\infty \) and an ‘effective’ radiative rate given by \( A_0 + (k_0 - k_\infty) P_0 \).

We did not extend this study to the other v \( \geq 1 \), but, if a non-linear dependence analogous to the v=0 case occurs, the Stern-Volmer plots in the range 2-35 Torr reasonably represent the P \( \rightarrow \infty \) situation, with the radiative rates equal to the ‘effective’ one defined above.

**Table 1.** Recommended rate constants for vibrational relaxation, \( k_{\text{vw}} \) and total collision quenching \( k_\text{q}^V \) of N\textsubscript{2}(C\textsuperscript{3}Π\textsubscript{u}, v) by collision with N\textsubscript{2}. Rate constants are in units \( 10^{-11}\) cm\(^3\)s\(^{-1}\). Empirical radiative rates \( A_v \) are also reported (in \( 10^7\)s\(^{-1}\)) (see text).

| w/v | 0 | 1 | 2 | 3 | 4 |
|-----|---|---|---|---|---|
| 0   | - | 1.19\(\pm\)0.13 | 0.528\(\pm\)0.043 | 0.734\(\pm\)0.072 | 0.736\(\pm\)0.067 |
| 1   | - | - | 0.763\(\pm\)0.094 | 0.464\(\pm\)0.059 | 1.02\(\pm\)0.093 |
| 2   | - | - | - | 0.360\(\pm\)0.034 | 0.285\(\pm\)0.036 |
| 3   | - | - | - | - | 0.105\(\pm\)0.037 |
| \( k_\text{q}^V \) | 1.24\(\pm\)0.06 | 3.14\(\pm\)0.21 | 4.28\(\pm\)0.21 | 6.34\(\pm\)0.27 | 9.86\(\pm\)0.46 |
| \( A_v \) | 2.91\(\pm\)0.015 | 2.67\(\pm\)0.02 | 2.72\(\pm\)0.03 | 2.62\(\pm\)0.03 | 2.36\(\pm\)0.07 |
We then report in Table 1 the rate constants and radiative rates that, according to the previous discussion, can be empirically used for the calculation of the quenching rate by a linear law above a pressure of a few Torr.

Using the complete set of rate coefficients we were able in [15] to fit experimental (C, v) distributions measured in a DBD at ATP, with far greater precision than it was possible with old and incomplete data sets. We also showed that neglecting the vibrational relaxation led to a large overestimation of the electron temperature, and that the fit accuracy achieved by the new set allowed a quasi-independent determination of $T_e$ and $T_v$. Note that the $T_v$ that can be determined by SPS diagnostics is practically only the first level temperature, if the ground state $N_2(X,v)$ excitation is not large, as it is the case at ATP.

3.2. $N_2(A^3Σ_u^+)$ density measurement

The pre-ionization source that causes the establishment of the APTD mode in a nitrogen DBD is believed to be secondary electron emission by $N_2(A)$ metastable impact on the dielectric surface [8]. This idea is based on two facts: a) the strong structural similarity of the APTD - the momentary cathode acts as a source of secondary electrons; b) the oxygen argument - in presence of even small quantities of oxygen, which is known to be a strong $N_2(A)$ quencher, the discharge turns to the filamentary mode. A measurement of $N_2(A)$ density in a $N_2, N_2 +$ small $O_2$ admixtures can then be of help in the understanding of this issue. In [18] we applied the OODR-LIF technique to this end. Absolute density calculations from LIF outcomes is normally a difficult task. In the case of OODF-LIF at ATP it becomes overwhelmingly difficult. Critical points for a modeling of the OODR process are:

(i) multi J-levels excitation. More than one ro-vibronic transition is involved in the laser absorption, so that an accurate knowledge of the lasers spectral profiles is required. A further complication is the non-negligible lorentzian pressure line broadening at ATP.

(ii) account for RET collisions in the B-state manifold. With the RET rate coefficient of $10^8$ Torr s$^{-1}$, 760 RET collisions take place within the 10 ns laser pulse duration.

(iii) RET collisions in the A-state manifold influence the saturation conditions, and should be taken into account as well.

We then applied a calibration method to a selected condition, and then measured the metastable density by the calibrated OODR-LIF in all the desired cases. The selected condition was the post-discharge of an APTD in pure $N_2$, in which we proved that reactions (3) and (4) hold simultaneously. It was then possible to apply the method proposed in [19], by which the metastable density is proportional to the ratio of SPS and NO-γ emission intensities and to the NO density. The proportionality constant contains various terms, among which the ratio $k_1/k_2$ of the rate coefficients of reactions (3) and (4). We introduced two major improvements with respect to [19]. First, NO density was measured by LIF instead of being presumed on the basis of known small NO additions to the gas feed. Second, we adopted an ‘effective’ $k_2$ value that takes into account the strong vibrational relaxation in the calculation of $N_2(C)$ excitation by the pooling reaction.

By applying this strategy we found a metastable density of the order of $10^{13}$ cm$^{-3}$ in the pure nitrogen APTD, with a population of $N_2(A, v=1)$ at most 15% that of $N_2(A, v=0)$. 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 $O_2$ 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 attempted to apply OODR-LIF measurements of the nitrogen triplet metastable in a Masuda-type surface discharge [20]. 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 \( N_2(A) \) 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. Finally the metastable density in the afterglow was traced back to the discharge by estimations based on NO-\( \gamma \) emissions, that, also in this case, are due to reaction (4). We found a metastable density of the order of \( 10^{12} \text{ cm}^{-3} \), i.e. 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.

4. \textbf{CN(B\( ^2\Sigma^+ \)) formation and emission in a \( N_2-\text{CH}_4 \) discharge}

Dielectric Barrier Discharges are good candidates for applications of non-equilibrium plasmas to hydrogen production from hydrocarbons, liquefaction of gaseous fuels, \( \text{CO}_2 \) reforming (removal). Within this framework we approached fundamental studies in a \( N_2-\text{C}_6\text{H}_6 \) [21] and \( N_2-\text{CH}_4 \) DBDs [22], and finding also the formation of a liquid deposit in nitrogen(argon)-methane discharges [23]. The \( \text{CN}(\text{B-X}) \) violet system is, as we have seen, the only prominent emission in atmospheric pressure discharge in nitrogen plus small amounts of hydrocarbons. Its intensity is comparable to that of most SPS bands, and can be readily observed with a non-cooled not-intensified CCD.

In our DBD and in both mixtures with benzene and methane we found that the violet system emission shows an unusually large vibrational excitation of \( \text{CN}(\text{B, v}) \) state, that is not normally found in low-pressure discharges. Furthermore, the violet system emission was still present and with even more pronounced vibrational excitation in pure nitrogen fed discharges operated with the dielectric surfaces covered by the brownish, dusty deposit produced after operation with \( N_2-\text{CH}_4 \) feed gas. The production of \( \text{CN}(\text{B}) \) then showed peculiarities typical of chemiluminescent/recombination reactions involving the interplay between the gas-phase and the surface deposits, whose understanding requires a complex diagnostic approach. We addressed this study in a pulsed dielectric barrier discharge (a packet of sinusoidal applied voltage followed by a period of null voltage) by combining the results of the following, time resolved diagnostics [22]:

(i) \text{LIF} on \( \text{CN}(\text{X}) \), to explore the vibrational excitation of the formed cyano radical, to address the issue of vibrational relaxation in the \( \text{CN}(\text{B, v}) \) manifold and to follow the \( \text{CN} \) density time evolution in the discharge cycles;

(ii) \text{OODR-LIF} on \( N_2(A) \), to investigate a possible role of the nitrogen triplet metastable in the \( \text{CN}(\text{B}) \) excitation;

(iii) medium spectral resolution spectroscopy, by gated intensified CCD, to look at the vibrational excitation of \( \text{CN}(\text{B, v}) \) in the discharge and post-discharge at different gas feed compositions;

(iv) low resolution spectroscopy, to follow the time evolution of spectral features in the discharge cycles and correlate it to the time evolution of LIF outcomes.

Both \( \text{CN}(\text{X, v}) \) and \( \text{CN}(\text{B, v}) \) showed a highly supra-thermal vibrational excitation, that is largely more pronounced in the pure \( N_2 \) case than in the presence of \( \text{CH}_4 \) in the gas feed (see figure 4 for the violet system emission case and figure 5 for the \( \text{CN}(\text{B, v}) \) vibrational distributions deduced from the spectra). The vibrational relaxation in both manifolds was found to be weak.
Figure 4. The $\Delta v=0$ sequence of CN violet system in pure $N_2$ (+wall deposit) post-discharge (pD) and in $N_2+0.2\%\ CH_4$ discharge (D).

Figure 5. Vibrational distributions deduced by fitting the spectra of figure 4 [22]. The distributions are normalized to the population of level $v=0$.

The measured vibrational excitation can then be considered to be a ‘quasi nascent’ one, and is then related to the formation mechanisms. Finally a possible role of $N_2(A)$ in the CN(B) excitation could be safely excluded. The combination of all the results converged toward an interpretation involving the presence of two formation mechanisms, one of which is operative preferentially when the discharge is ON, the other being always operative in the voltage packet, and that can be isolated from the other mechanism in the post-discharge. We were able to assign quite safely the post-discharge mechanism to the recombination reaction:

$$C^{(3}P) + N^{(4}S) + M \rightarrow CN(B^2\Sigma^+) + M$$

(10)

and the discharge mechanism likely to the reaction:

$$N + CH \rightarrow CN(B,A) + H$$

(11)

C and CH come someway from the surface in the pure $N_2$ gas feed case, while they can be created, alternatively or in addition, in the gas phase when CH$_4$ is added to the gas mixture. Both mechanisms were found to reach a steady-state after a considerable number of cycles, this number being larger (i.e. slower kinetics) in the $N_2$ case than in presence of CH$_4$ in the gas mixture. The time required for steady-state clearly depends on how the species involved are created, being they extracted someway from the surface or produced in the gas phase. CH, for example, is produced in presence of methane in the discharge mainly by a stepwise process that forms CH$_3$, CH$_2$ and finally CH by successive electron impact events. Such an occurrence is a clear case in which the discharge kinetics can be influenced by the geometry of the discharge and by the gas flow (that determines the time/number-of-cycles the gas mixture is exposed to the active discharge), i.e. a case in which a simple geometrical scaling of the DBD is not correct.
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