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# In situ LIF and ex situ CRDS applied to NO measurement in flames: probe perturbation and absolute quantification

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## Abstract

Flame-sampling experiments allow describing the species profiles as function of the height above the burner. However, the so-measured species profiles are perturbed by the heat losses due to the probe, and/or species losses inside the probe. In order to attempt to clarify the perturbations induced by a microprobe, NO species profiles were obtained in a stoichiometric low-pressure flame by using in situ and ex situ measurements. An unperturbed NO species profiles was measured locally by LIF. Two shapes of microprobes were used to perform ex situ measurements by CRDS after gas probe sampling. The comparison of the profiles shows that the profiles obtained after probe sampling are shifted downstream, and that the absolute mole fraction of NO may be drastically affected during the sampling.

## Introduction

Gas sampling and subsequent analyses are convenient for measuring the chemical composition of gases in combustion devices. The design of the probe is one of the important factors that has to be considered for obtaining accurate measurements. One can distinguish cone probes and microprobes. Cones are characterized by a large area-ratio. Cone sampling is generally associated to molecular-beam mass spectrometry detection. Thanks to the pressure drop and the molecular beam which is generated downstream (supersonic flow), reactions are suddenly cooled down preventing the recombination of the short-lived radicals. However, one of the main drawbacks is the perturbation generated by the cone in the flame and in the probe (flow distortions, heat losses, efficiency of the quenching of chemical reactions). Comparison of experimental species profiles obtained either in situ or after probe sampling highlights spatial distortion of the species profiles, and depending on the cone, divergences of the absolute mole fractions have been observed [1,2]. To restrain the flame perturbations in counterflow diffusion flames, gases can be probed through a fused silica capillary tube. However, its introduction generates disturbance identified by comparing non intrusive measurements with those obtained after gas sampling [3].

Microprobes are routinely used to probe gas samples in flames or in Jet Stirred Reactors (JSR) for further analysis by Gas Chromatography for example. As mentioned by Heitor and Moreira [4], the sampling flow rate and the size of the suction orifice are set as a compromise between the required low pressure to achieve aerodynamic quenching of chemical reactions and the minimum flow rate for the chemical analyzers. Biordi et al. [5] showed that depending on the size of the orifice and the angle of the tip, the species profiles may be affected not only in their shape but also in their absolute mole fraction values. Kramlich and Malte [6] have modeled the pressure and temperature variations inside the microprobe by considering one-dimensional gas flow conditions. They have simulated the NO into

NO<sub>2</sub> conversion within the tip by taking into account reactions which can occur at the wall and in the gas phase. They found a good agreement with the experimental measurements of NO and NO<sub>2</sub> performed after gas probe sampling in a JSR apparatus. Colket et al. [7] have developed a gas-dynamic model to describe the gas flow and heat transfer inside the probe. They concluded that an aerodynamic quenching is unlikely to occur in microprobes but, chemical quenching rates may be sufficient to freeze reactions. In an atmospheric flame seeded with NO, Zabielski et al. [8] have compared the NO concentration measured in the burned gases either by in situ optical absorption or after probe sampling by chemiluminescent analyzer. No major discrepancies related to processes occurring in probes have been identified. Recently, Li et al. [9] measured NO in flames seeded with NH<sub>3</sub> either by using Laser Saturated Fluorescence calibrated by the NO addition method or by using a chemiluminescent analyzer after gas probe sampling. They observed a difference of NO amounts of 5-7% between the two techniques. They evoked the possible conversion of NO into NO<sub>2</sub> in the probe through recombination reactions in presence of O-atoms as proposed in [10]. Schoenung and Hanson [11] have compared the absolute mole fractions of CO measured either in situ by laser absorption or after gas probe sampling by using a non-dispersive infrared analyzer. Based on these measurements, they have indirectly observed some conversion of CO into CO<sub>2</sub>. They have analyzed the difference of the absolute mole fractions from the chemical equilibrium predictions of CO/CO<sub>2</sub>, and from the aerodynamic model proposed in [7]. They recommended working with reduced pressure downstream the probe (around 50 mbar).

The question of the microprobe disturbance in the flame structure analysis frequently arises. The flame temperature profile is an input data which is required for the chemical flame modeling. In order to match the experimental and the simulated species profiles, it is generally necessary to shift the temperature profiles downstream. On the contrary, such shift is not required

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for modeling the in situ species profiles [12]. In order to identify the perturbation generated by the microprobe, the present work aims to compare in situ and ex situ measurements of flame species profiles. NO species was chosen because it is very sensitive to possible kinetic reactions that may occur inside the probe, and it is measurable locally and after gas probe sampling.

NO species can be measured by using in situ Laser Induced Fluorescence (LIF). This well-known technique allows measuring in situ species in relative mole fraction with a high sensitivity and spatial resolution. In case of NO species, the relative mole fraction can be converted into absolute one by adding small known amounts (same order than the expected native NO) of NO in the premixed gases [13,14]. The NO standard addition method relies on the main assumption that there is no NO-reburning in the flame. This aspect was verified in particular in lean flame [14].

The line-of-sight pulsed-CRDS (Cavity Ring-Down Spectroscopy) technique has already been applied to measure NO species. In situ measurements can be perturbed by the fact that NO being a stable species present in the burned gases may persist in the cold gases surrounding the flame as shown in low-pressure flames [15]. In atmospheric flames, Sepman et al. [16] have performed NO measurements by using pulsed-CRDS. They were suffering from a strong background signal due to CO<sub>2</sub> and H<sub>2</sub>O absorption around 226 nm. Evertsen et al. [17] have quantified NO in absolute mole fraction after sampling gases at the exhaust of a diesel engine. These studies [15,17] were undertaken by probing weak absorption transitions to avoid saturation effects [18,19]. These effects will be discussed later in the paper.

The present work aims to identify the microprobe perturbation effects in the flame. Species profiles of NO in a stoichiometric low pressure flame of CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> obtained either in situ by LIF or ex situ by CRDS were compared one to each other to highlight the probe perturbation in the flame. The absolute mole fractions determined in the burned gases by two techniques are also discussed. NO-LIF was calibrated in situ in the burned gas of a stoichiometric low pressure flame by using the NO standard addition method. Results were compared to NO mole fraction measured after gas probe sampling by using pulsed-CRDS technique applied in an external absorption cell.

## Experimental setup

### Low pressure burner and gas supply

Experiments were undertaken in a stoichiometric laminar CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> premixed flame stabilized at 5.33 kPa (40 Torr) on a 6-cm diameter bronze water-cooled McKenna burner. Volumetric flow rates (in standard (273.15K, 1.013×10<sup>5</sup> Pa) L/min, slpm) of the gas mixture are 0.48/0.96/3.35 for CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> respectively. An additional line with a low range Mass Flow Controller (MFC, 0.1 slpm) is connected to the premixed gases inlet of the burner to seed the mixture with known amounts of

NO from a commercial preparation of 2001 ppmv NO diluted in N<sub>2</sub> (standard 1 with ±2% precision). The temperature profile of the flame has previously been obtained by NO-LIF thermometry [20]. Details concerning the burner and gas supply were given in [21].

The burner enclosure is equipped with different optical accesses allowing in situ laser diagnostics (LIF). For the in situ measurements, the height above the burner (HAB) is defined by the distance between the laser axis and the burner surface. For the probe sampling measurements, it is defined by the distance between the microprobe tip and the burner surface.

### Probe sampling and absorption cell

Gas sampling was performed through quartz microprobe in order to perform ex situ measurements of NO molecule by using pulsed-CRDS technique in an external absorption cell. Two shapes of microprobe were examined. They are designed with a tip angle extended to a cylindrical tube over a total length of 50 mm. This first section is connected to a second tube with an inner diameter of 9.8 mm. Both are opened with a 200 μm diameter orifice. The first microprobe is very sharp with an inner tip angle about 10°, and an area ratio of 255 (microprobe 1). The second one has an inner tip angle about 20°, and an area ratio of 750 (microprobe 2).

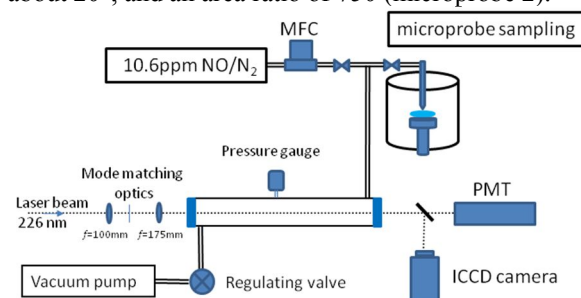


Fig. 1. CRDS setup with the standard gas and the probe sampling introduction to the cell.

The absorption cell of 39.5 cm long is ended by two mirrors. Gases are injected through a Teflon tube either from the probe gas sampling or from a commercial preparation of 10.6 ppmv NO diluted in N<sub>2</sub> (standard 2 with ±5% precision) as shown in Fig. 1. In order to prevent the adsorption/desorption phenomena at the wall, gases in the cell are in continuous flowing. The pressure was stabilized at the desired value by using an automatic regulating valve (Leybold, CMOVE1250). The gas temperature was controlled by a thermocouple (type K) at the inner wall of the cell.

### Laser techniques

Two laser techniques were implemented in this work; in situ LIF, and ex situ pulsed-CRDS. The pulsed laser system consists of a seeded frequency-doubled Nd:YAG laser (Q-smart) pumping a dye laser (Quantel TDL90+). Wavelengths around 226 nm were provided by doubling the fundamental dye radiation (around 572 nm) and by mixing it with YAG residual radiation at 1064 nm. The spectral laser bandwidth at 226 nm was estimated to be around 0.12 cm<sup>-1</sup>.

LIF and CRDS signals were collected through a photomultiplier tube (PMT) (Photonis, XP2020Q) and recorded on a digital oscilloscope (LeCroy HDO4000, 12-bit vertical resolution, 1GHz bandwidth, 1.25 GS/s). During spectrum acquisition, laser wavelength (fundamental) was scanned at a rate equal to  $0.25 \text{ pm s}^{-1}$  and signals were averaged over 15 laser shots. For the species profiles measurements, signals were averaged over 300 laser pulses. Signals from the scope and the step motor of the dye laser were transferred in real time on a PC, and treated with Labview programs.

#### *In situ LIF*

The laser beam was introduced unfocused parallel to the burner surface and shaped using a horizontal slit of  $300 \text{ }\mu\text{m}$  height in front of the burner enclosure and parallel to the burner surface. The LIF signal was collected by a two-lenses system ( $f=200$  and  $f=350 \text{ mm}$ ) and focused on the entrance slit of a  $0.5 \text{ m}$  monochromator (SpectraPro 2500i). The entrance slit ( $550 \text{ }\mu\text{m}$  width,  $10 \text{ mm}$  height) was parallel to the laser axis. The magnified image of the entrance slit in the vertical axis matches the size of the laser height in the flame, corresponding to the spatial resolution ( $300 \text{ }\mu\text{m}$ ). The output slit was adjusted to obtain a collection bandwidth of  $9 \text{ nm}$ , centered at  $246 \text{ nm}$  in order to collect the complete (0-2) vibrational band of NO.

The relative NO mole fraction profiles were obtained by prompt-LIF in the linear regime of fluorescence. The prompt-LIF signal is measured at the peak value of the temporal LIF signal. As the LIF signal is proportional to the rotational population, conversion into relative mole fraction has been completed by dividing the signal by the Boltzmann fraction  $f_B(J'',T)$ , easily calculated using the experimental temperature data [20]. Since NO is a stable species, the relative mole fraction can be converted into absolute mole fractions by using the standard addition method [13,14]. In order to limit the impact of the temperature uncertainties on the Boltzmann factors calculation, NO was probed along the line  $Q_2(26.5)$  ( $225.58 \text{ nm}$ ) for in situ LIF measurements. The spectroscopic parameters of NO proposed by Reisel et al. [22] were adopted in the present work.

#### *Ex situ pulsed-CRDS*

Measurements of NO were performed in an external absorption cell. The quasi-plane cavity ( $39.5 \text{ cm}$  long) is ended by two highly reflective mirrors (Layertec GmbH,  $25 \text{ mm}$  diameter,  $-6 \text{ m}$  radius of curvature, reflectivity $>0.993$ ). Typically, the empty ringdown decaytime was equal to  $200 \text{ ns}$ . As shown in Fig. 1, the laser beam was shaped with a system consisting of a  $100 \text{ }\mu\text{m}$  pinhole aperture and two lenses ( $f=100$  and  $f=175 \text{ mm}$ ) in order to match approximately the  $TEM_{00}$  transverse mode of the optical cavity. At the exit of the cell, a beamsplitter allows reflecting a fraction of the light towards an ICCD camera for controlling the perfect alignment of the cavity [23]. The transmitted light was collected by a PMT in front of which a 226-Corion filter was placed, to measure the temporal CRD signal. Ringdown decaytime was determined from an exponential fitting procedure over  $800 \text{ ns}$  [20], which

correspond to 4 times the off-resonance decay. By using a 12-bit vertical resolution system, the on-resonance decay as low as  $130 \text{ ns}$  (fitting period/6) can be reasonably measured [24].

The absolute species concentration of NO was calculated from the integrated spectral absorptivity determination  $A(\omega)$  by using CRDS technique according to Eq. (1) [25].

$$A(\omega) = \int L(\omega)d\omega = (\pi e^2/m_e c^2) f_{J''J'} N_{tot} f_B(J'', T) l_s \quad \text{Eq. (1)}$$

where  $L(\omega)$  are the net losses per pass along the absorption length  $l_s$  (in cm),  $m_e c^2/\pi e^2$  is equal to  $1.13 \times 10^{12} \text{ cm}^{-1}$ ,  $f_{J''J'}$  is the rotational oscillator line strength for absorption, and  $N_{tot}$  is the total population of NO (in molecule  $\text{cm}^{-3}$ ). Due to the relatively important ratio between the laser bandwidth and the Doppler linewidth of NO at  $300\text{K}$  (close to 1.2), the mono-exponential behaviour of the ringdown decay can be easily affected with the increase of the absorbance [18,19]. To prevent this, NO was probed along the line  $^S R_{21}(7.5)$  (at  $225.87 \text{ nm}$ ) which is weak enough to properly measure the absorbance of NO at room temperature. By considering the radiative lifetime of  $201 \text{ ns}$  [22],  $f_{J''J'}$  was calculated equal to  $8.226 \times 10^{-5}$ .

## Experimental results

### Validation of the pulsed CRDS setup

The procedure of quantification by CRDS was validated by introducing the commercial preparations of NO diluted in nitrogen in continuous flowing in the cell, under controlled temperature and pressure. First, the gas standard 1 (2001 ppm NO) was diluted with nitrogen (from 5 to 30 ppm in  $\text{N}_2$ ). The dilution was undertaken through 2 MFC implemented in the inlet gas lines of the burner set-up. The cold diluted preparation was injected in the burner enclosure from which it was probed through the microprobe 1. This arrangement allows controlling the mixing efficiency of the gases in the burner inlet line. The pressure in the cell was maintained at  $1.3 \text{ kPa}$ , allowing varying the NO concentration from 2 to  $8.10^{12}$  molecule. $\text{cm}^{-3}$ . Second, using the gas standard 2 (10.6 ppm NO), the concentration of NO was varied from  $1.5$  to  $10.10^{12}$  molecule. $\text{cm}^{-3}$ , by changing the pressure in the cell from  $0.5$  to  $4 \text{ kPa}$ , independently of the burner set-up. Figure 2 shows the determined concentration as function of the known injected concentration of NO in the absorption cell. Regardless of the procedure, the evolution of the measured NO concentrations with the injected ones is identical. This indicates the absence of NO losses in the sampling line or inside the probe tip using a non reactive mixture of  $\text{NO}/\text{N}_2$  at room temperature.

For NO concentration lower than  $6 \times 10^{12}$  molecule  $\text{cm}^{-3}$  (corresponding to net losses per pass equal to  $2 \times 10^{-3}$  at the peak transition), the measured concentration was found in very good agreement with the injected one (linear fit with a slope equal to 0.97). At higher concentration of NO, the measured value is slightly lower than the injected one. When the absorption coefficient

increases with the increase of the NO concentration, the ringdown decay is no more mono-exponential, yielding to an apparent decrease of the measured NO concentration, a drawback well described in [18,19]. In order to ensure that we were working in the appropriate range of concentrations, the pressure of the probed gas in the cell was maintained at 1.333 kPa (10 Torr with a reading accuracy of 0.01 Torr), and the maximum mole fraction of NO should not exceed 18.5 ppm. The uncertainties for measuring the NO concentration in the CRD cell have been estimated to be  $\pm 14\%$  due to the pressure gauge (0.5% f.s.), the spectroscopic parameters (2%), and the statistical error for CRD measurements (6%), additionally of those due to the mixture dilution and preparation (5%).

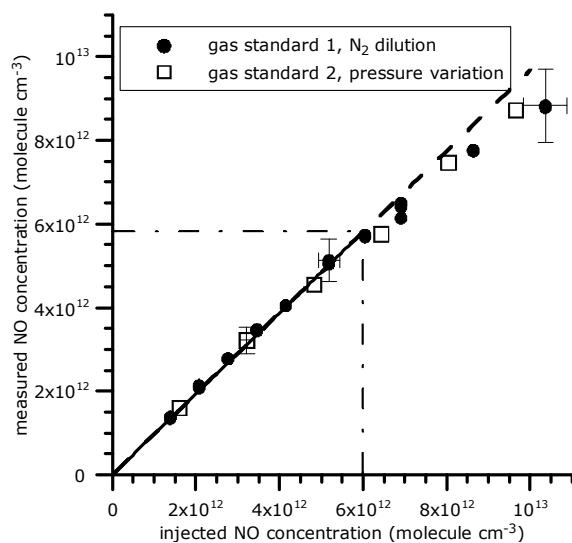


Fig. 2. Calibration of NO in the CRD cell at room temperature (300K). The slope of the fitted linear line is equal to 0.97.

#### NO calibration in the burned gases

The absolute calibration of NO was performed in the flame at HAB=20 mm with different approaches either by LIF or by CRDS. The first one was undertaken in situ from the standard addition method by LIF. The others were undertaken after gas sampling using CRDS.

##### *In situ LIF*

The prompt-LIF signal of NO by exciting the  $Q_2(26.5)$  transition was converted into absolute mole fraction by using the standard addition method detailed in [14,21]. For that, NO was substituted to  $N_2$  in the premixed gases within a small range of mole fractions (0 to 40 ppm) by using the gas standard 1 and the same arrangement of the RDM as previously. Figure 3 shows the variation of the prompt-LIF signal as function of the known mole fractions of NO added in the premixed gases. By extrapolating the linear fit to  $y=0$ , the native NO mole fraction in the flame was found equal to  $10.6 \pm 1.1$  ppm. The overall uncertainty was estimated to be  $\pm 10\%$ , due to the pressure gauge and MFC accuracies (0.5% f.s. for each apparatus), the standard gas preparation (2%), linear regression (1%), and statistical error for LIF measurements (5%).

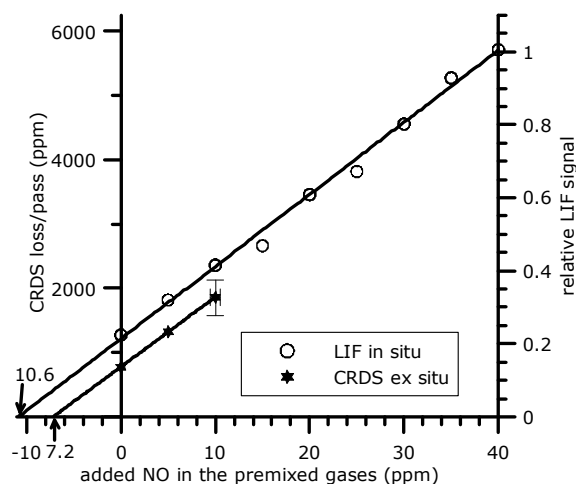


Fig. 3. NO calibration in the flame from NO addition in the premixed gases by using in situ LIF or ex situ CRDS.

##### *Ex situ after gas probe sampling by CRDS*

Gases were continuously sampled from the flame at HAB=20 mm. The 2 microprobes were tested. The determined concentration of NO by using CRDS was converted into mole fraction knowing the temperature (room T) and pressure (10 Torr) in the cell. NO mole fraction was quantified from the measurement of the integrated spectral absorptivity of transition  $S_{R_{21}}(7.5)$ , according to Eq. (1). With the microprobe 1, the measured mole fraction of NO after gas sampling was found equal to  $6.7 \pm 0.7$  ppm, much lower than the value obtained by LIF. With the microprobe 2, the NO mole fraction was determined equal to  $11.4 \pm 1.1$  ppm, in very good agreement with the value obtained by LIF calibrated by NO addition.

With the microprobe 1, further investigations were undertaken to identify the source of the discrepancies between the absorptivity measurements performed with both microprobes. First, the standard addition method (with the gas standard 1 in the premixed gases) was applied similarly to what was performed during the LIF calibration. Figure 3 shows the variation of the losses per pass as function of the NO added in the premixed gases. Here, the NO addition was limited to 10 ppm to ensure that the CRD measurements were satisfyingly performed (in the linear regime of absorption). The mole fraction of NO was found equal to  $7.2 \pm 1.0$  ppm, in good agreement with the value previously obtained from the integrated spectral absorptivity (6.7 ppm). Second, small amounts of NO were added to the sampling line just after the microprobe. No evidence of NO losses in the sampling line could be seen. The overall uncertainty was estimated to be  $\pm 15\%$  (for measurements performed with NO addition) and  $\pm 10\%$  (without NO addition).

In the burned gases, (HAB=20 mm), the absolute mole fraction of NO obtained by CRDS after gas sampling with the microprobe 2 is close to the one derived from the addition NO in LIF, respectively equal to  $11.4 \pm 1.1$  and  $10.6 \pm 1.1$  ppm. This consistency suggests that the NO-reburning which could affect the standard

addition method is negligible, and that the NO losses are very weak inside the microprobe 2 and in the sampling line. On the contrary, the values of the NO mole fractions determined by CRDS (with different methodologies) with the microprobe 1 are 40% lower than with the one measured with the microprobe 2. This suggests that the NO losses occur inside the tip of this microprobe during the sampling of the burned gases at flame temperature.

#### Calibrated NO profiles and discussions

In situ and ex situ NO profiles were measured as function of HAB after exciting the molecule at the peak of the selected transition ( $Q_2(26.5)$  in the flame or  $S_{R_1}(7.5)$  in the CRD cell). Figure 4 presents the three NO profiles independently obtained in the studied flame as previously explained. Each profile is calibrated as follow. The in situ relative LIF profile was corrected for the Boltzmann factor and temperature variations along the flame axis. It was converted into absolute mole fraction at HAB = 20 mm, from the calibrated value obtained by the standard addition method. As a matter of comparison, the NO profile previously obtained in [20] is also reported. One can see that the NO profiles obtained by LIF after several years were found in good agreement one to each other. The ex situ profile obtained with a given microprobe was calibrated by using the integrated absorptivity measurements at 20 mm with this microprobe.

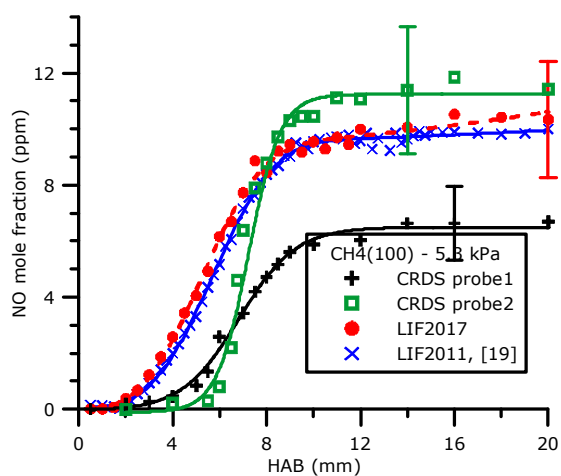


Fig. 4. NO mole fraction profiles in flame obtained either by LIF in situ or by CRDS after gas probe sampling.

The shape of the NO profiles obtained by using three experimental approaches differ one from each other. Clearly, NO profiles obtained after probe sampling are shifted downstream. The shape of the NO profile obtained by CRDS is less disturbed by using the microprobe 1 than the microprobe 2 (according to the unperturbed LIF profile). The gradient of the NO profile obtained by CRDS with the microprobe 2 is about 1.8 times sharper than the ones observed with the microprobe 1 or by LIF. This indicates that spatially the flame is less perturbed by the sharp tip. However, both microprobes induce a shift of the reaction zone. Indeed, the inflection points of the NO profiles obtained by CRDS are shifted downstream by 2.2 and 2.6 mm by using the microprobes

1 and 2, respectively. The present observations are in agreement with previous ones [5], indicating that the gradients of the species profiles steepen and are further shifted downstream with the increase of the tip angle.

Here, the microprobes differ by their tip angle and their area ratio, which can affect the efficiency of the quenching of chemical reactions [26], the rate of surface reaction [6], the residence time of the gases in the tip. The flow rate of the sampling gas was found identical with the two microprobes (6.54 sccm) at HAB=20 mm. This corresponds to a mass flow rate equal to around  $1.6 \mu\text{g s}^{-1}$ , in agreement with the recommendations given by Fristrom and Westenberg [27]. The surface/volume ratio of the microprobe 1 is almost twice higher than the one of the microprobe 2. Reactions at the surface are certainly favored in the microprobe 1. Allen [10] described that NO quickly react with O-atoms at the wall, yielding  $\text{NO}_2$ . Meantime, if the aerodynamic quenching in the probe is not efficient, remaining O-atoms will react with  $\text{NO}_2$  yielding back NO. Kramlich and Malte [6] have computed the species variation in the probe along the axis by considering wall reactions for the atoms recombination and gas-phase reactions. Rate of the surface reactions are increasing with decreasing the area ratio (increasing the surface/volume ratio), yielding to a faster recombination of O and H atoms into  $\text{O}_2$ ,  $\text{H}_2$  and  $\text{HO}_2$ . The conversion of NO into  $\text{NO}_2$  is mainly explained by the reaction between NO and  $\text{HO}_2$ .

#### Conclusions

In the present work, NO profiles in a stoichiometric flame were measured by using either in situ LIF or ex situ CRDS techniques. In situ NO-LIF profile was converted into absolute mole fractions from the standard NO addition method. Ex situ measurements were undertaken after probing gases from the flame through a quartz microprobe. Two shapes of microprobes were examined. Gases were sampled in the same conditions of flow rate and pressure inside the probe, and analyzed in an external absorption cell. Absolute LIF calibration was performed in a stoichiometric flame with standard addition method up to 40 ppm.

The unperturbed LIF profile was compared to the ex situ CRDS profiles obtained independently with the two microprobes. In the burned gases, the NO mole fraction value obtained by using CRDS after probing the gases through the sharper microprobe was found 40% lower than the values measured either in situ by LIF or ex situ but with a larger microprobe. This seems to indicate that the quenching (aerodynamically and/or chemically) inside the narrower tip is not as efficient as in the wider one. Reactions at the inner surface of the sharper microprobe are assumed to be more important, promoting the conversion of NO into  $\text{NO}_2$ . NO profiles obtained after probe sampling are shifted downstream. The absolute mole fraction of NO in the burned gases is unaffected when working with a large angle of the tip.



The shape of the species profile obtained with the sharp angle probe is close to the in situ one.

This work shows that the design of the microprobe should be specified in the literature, especially for NO species measurements. Further investigations on the chemical reactivity occurring during the sampling in the gas phase and at the wall would be helpful to fully understand the difference between the two microprobes. Extension of this work to atmospheric flames is intended.

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