

TIME RESOLVED LIF MEASUREMENTS FOR THE STUDY OF NO REMOVAL : INFLUENCE OF H₂O

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1 Introduction

The necessity to reduce urban atmospheric pollution has motivated a growing interest for NO removal by non thermal plasmas, using electron beam or pulsed discharges [1-11]. In the most cases the studied polluted gases were either nitrogen[1,3,9] or air-like mixtures[1,8,10] or air-like with some amounts of moisture[2,4,5,7] and/or hydrocarbons[6]. The vast majority of experimental results devoted to NO removal at atmospheric pressure are obtained using either corona or dielectric barrier discharges. Such filamentary discharges are strongly non homogeneous and their understanding require altogether spatially and time resolved modeling and experiments [8].

On the other hand, we have developed a time-resolved laser-induced fluorescence (LIF) diagnostic of the NO-removal in a pre-ionized homogeneous discharge [9], i.e. without density nor temperature gradients, using the photo-triggering technique. This technique allows to measure specie densities in the temporal post-discharge after one homogeneous pulsed excitation, so that experimental results can be more confidently compared to predictions of a 0D-model, i.e. a model which have a spatially homogeneous kinetic description of the cleaning process. This model is fully self-consistent and describe both kinetics during the discharge and the post-discharge [10]. We first reported the influence of electrical parameters (energy and reduced electric field) on the NO removal efficiency in the N₂/NO mixture [9]. Then, the influence of hydrocarbon (C₂H₄) addition was determined [11]. We showed that dissociation of NO through collision with the metastable state N₂(a¹Σ_u⁻) play the main part in the NO-removal process in homogeneously excited N₂/NO mixture, and, that a de-excitation process of N₂(a¹Σ_u⁻) by C₂H₄ explains that the NO-removal efficiency decreases when ethene is added to the mixture. Estimation for the rate coefficient value of this reaction, closed to the known value for methane [15], was also deduced from our results. In this study, the influence of water is investigated on the NO removal efficiency.

2 Experiment and modeling

2.1 Experiment

A comprehensive description of the photo-triggered pulsed discharge operating mode has been previously given[10]. The electrodes are directly connected to an energy storage unit (C=17.44 nF in our device) charged up to a voltage V₀. Once the desired voltage value has been reached, the gas breakdown is achieved through photo-ionization of the gas mixture by UV-photons which are produced by an auxiliary corona discharge located at the bottom of the main discharge. The circuit inductance (6.5 nH) is minimized in order to reduce the current pulse duration (50 ns). As a result, a volume V_{dis}=50 cm³ can be homogeneously excited at each shot. The total pressure of the studied mixtures has been fixed to 345 Torr, with NO and C₂H₄ maximum concentration values respectively equal to 1000 ppm and 5800 ppm. The V₀ value can be chosen up to 40 kV, which corresponds to a maximum specific deposited energy, E_{dep}, equal to 240 J/l; E_{dep} is defined by E_{dep}=C.V₀²/(2.V_{dis}).

The LIF diagnostic was performed by using a tunable pulsed laser Datachrom 5000 from Quantel. The Nd:Yag laser emission, frequency doubled, pumped a mixture of rhodamines 590 and 610 dyes to generate emission around 574 nm. The resulting frequency was doubled in a KDP crystal and then mixed to the 1064 nm wavelength to give an emission around 226 nm, corresponding to the NO(A²Σ→X²Π) excitation transition. Fluorescence was observed at 248 nm. The output signal of a photo-multiplier was recorded on a boxcar synchronized with the laser shot. Figure 1 present a typical LIF spectrum of one NO rovibrational line, before the discharge, and 200 μs after the discharge shot. More details about this time resolved technique, and about validation of the LIF diagnostic on NO, can be found in a previous publication [9].

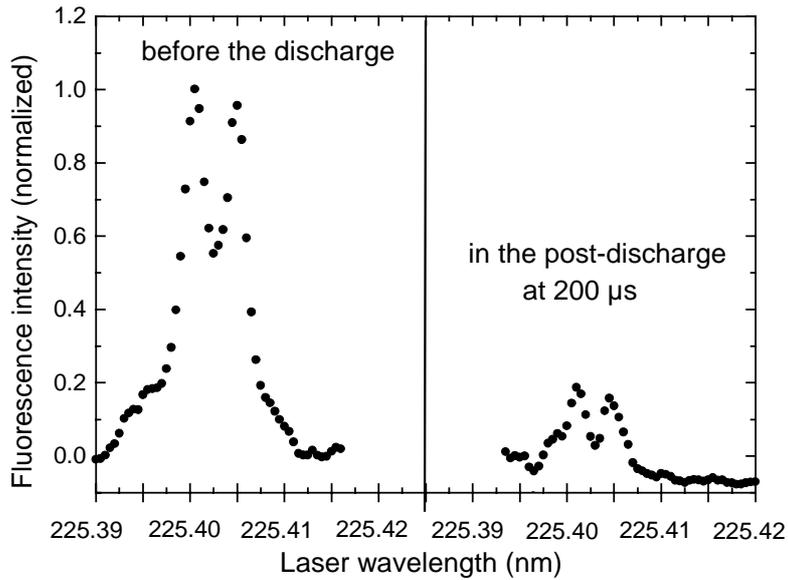


Figure 1 : LIF spectrum of NO before and 200 μ s after the discharge shot. 375 Torr, 25 kV, 109 J/l.

2.2 Modeling

Our 0D-model predicts time evolutions of chemical specie densities on a large time scale, from 1 nanosecond up to 1 millisecond following the gas mixture pre-ionization. This model couples the solution of the Boltzmann equation for the electrons, the kinetic equations for the excited and ionized states of heavy particles, as well as for radicals, and the electrical circuit equations. The Boltzmann equation is solved numerically in the steady-state approximation using algorithms developed by Ségur and Bordage [12]. Input parameters are: initial voltage applied to the electrodes, capacitance C of the storage unit and circuit inductance L , gas pressure and composition. The temporal evolution of the gas temperature is also taken into account through the resolution of the energy conservation equation. Concerning electrical parameters, there is a very good agreement between calculated and experimental discharge voltage and current, as shown in figure 2, so that energy deposition in the plasma is well defined.

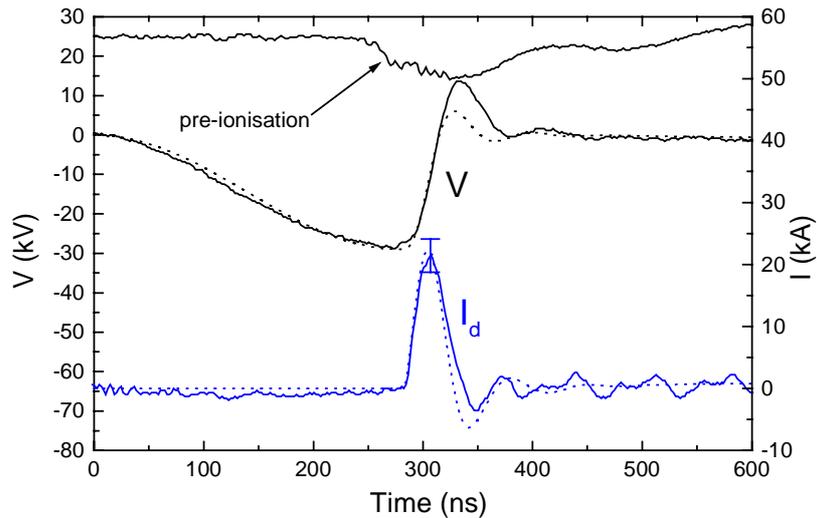


Figure 2 : time evolution of current and voltage during the discharge. 345 Torr, 29 kV. Solid curves = experiment; dots = model.

3 Results and discussion

In figure 3 is plotted the measured (points) and predicted (lines) NO density time evolutions for an initial value, $[\text{NO}]_0$, equal to $1.1 \times 10^{16} \text{ cm}^{-3}$ (1000 ppm), and for $E_{\text{dep}} = 92 \text{ J/l}$, either in the N_2/NO mixture (experimental points : squares) or with addition of 2% H_2O (circles).

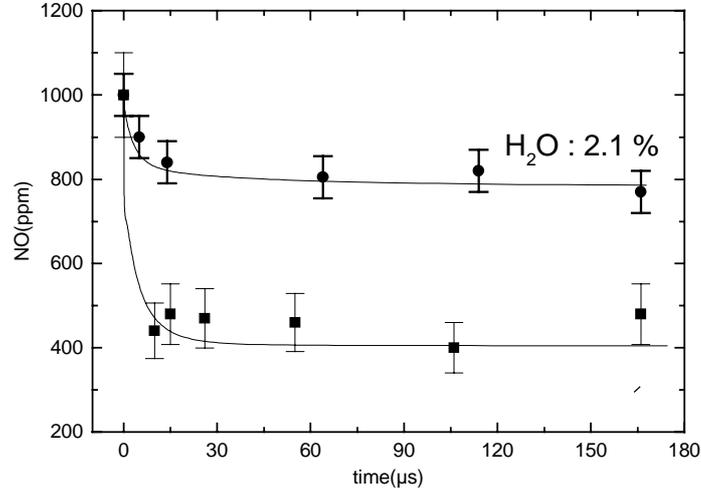
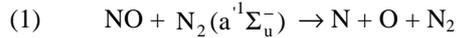


Figure 3 : time evolution of NO density after one discharge shot; with water (upper curve) and without (lower curve) ; 345 Torr - 92 J/l

Figure 3 emphasizes that the stationary state for NO is obtained very quickly, 10 μs or less, without water in the mixture and within 20 μs with water addition. The measured NO-removal efficiency, at the stationary state, is 60 % without H_2O , but it decreases to 30 % with H_2O . Hence addition of water limits drastically the NO-removal. A detailed description of the kinetic processes included in the model is far beyond the goal of the present paper. It will be reported in a forthcoming article, and we will focus discussions only on NO-removal mechanisms. Close examination of model predictions reveals that, without water in the mixture, main reaction pathways for NO-removal are :

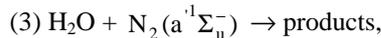


with a rate coefficient k_1 , as discussed below, and



with a rate coefficient $k_2 = 3.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [13]. As far as our knowledge, only two models [4,11] about flue gas plasma cleaning processes take into account reaction (1), which has been also invoked in N_2/O_2 mixture discharge modeling [14]. In a previous paper, the influence of ethene on the NO removal in a $\text{NO}/\text{N}_2/\text{C}_2\text{H}_4$ mixture was studied [11]. It was shown that, similar to addition of water, the addition of C_2H_4 leads to a decrease of the NO removal efficiency. This was interpreted by considering the de-excitation collision of $\text{N}_2(a^1\Sigma_u^-)$ by C_2H_4 (see reaction 3), whose rate coefficient equals to $(4 \pm 2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. A similar process had previously been reported between $\text{N}_2(a^1\Sigma_u^-)$ and CH_4 with a corresponding rate coefficient equals to $(3.0 \pm 0.8) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [15].

As stated before, addition of water leads to a decrease of NO removal efficiency, and we believe on the possibility of the de-excitation collision :



with a rate coefficient k_3 . This reaction is invoked for the first time. Using a kinetic scheme without reaction (3) overestimates NO removal with respect to experimental results. Predicted NO-removal efficiency decreases when the water concentration increases, as well as the measured one. As shown in figure 3, a very good agreement is reached between model and experiment in the case of water admixture for $k_3 = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which has been deduced from comparison of our measurements and model results on a large range of parameter (E_{dep} , $[\text{NO}]_0$, $[\text{H}_2\text{O}]$) values. Such a coefficient value has been validated over a large range of pressure and deposited energy.

References

- [1] - B. Penetrante and S. Schultheis (eds) Non-Thermal Plasma Techniques for Pollution Control, parts A and B, 1993 (Berlin : Springer-Verlag).
- [2] - J. Lowke, and R. Morrow, IEEE Trans. Plasma Sci. **23**, 671 (1995).
- [3] - B. Penetrante, M. Hsiao, B. Meritt, G. Vogtlin, and P. Wallman, IEEE Trans. Plasma Sci. **23**, 679 (1995).
- [4] - O. Eichwald, M. Yousfi, A. Hennad, and M. Benabdessadok, J. Appl. Phys. **82**, 4781 (1997).
- [5] - B. Penetrante, J. Bardsley, and M. Hsiao, Jpn. J. Appl. Phys. **36**, 5007 (1997).
- [6] - W. Niessen, O. Wolf, R. Schruft, and M. Neiger, J. Phys. D **31**, 542 (1998).
- [7] - Y. Mok, S. Ham, and I-S. Nam, IEEE Trans. Plasma Sci. **26**, 1566 (1998).
- [8] – M. Spaan, C. Lukas, V Schultz von der Gathen and F. Dobeles Frontiers in low temperature plasma diagnostics III (Saillon, Switzerland)
- [9] - F. Fresnet, G. Baravian, S. Pasquiers, C. Postel, V. Puech, A. Rousseau, and M. Rozoy, J. Phys. D **33**, 1315 (2000).
- [10] - M. Rozoy, C. Postel, and V. Puech, Plasma Sources Sci. Technol. **8**, 337 (1999).
- [11] - F. Fresnet, G. Baravian, L. Magne, S. Pasquiers, C. Postel, V. Puech, and A. Rousseau, Appl. Phys. Lett **77**, 4118 (2000).
- [12] - P. Ségur, and M-C. Bordage, Proc. XIX ICPIG, ed. J. Labat, pp. 86-107, 1989 (Beograd : University of Beograd).
- [13] R. Atkinson, D. Baulch, R. Cox, R. Hampson Jr., J. Kerr, and J. Troe, J. Phys. Chem. Ref. Data **21**, 1125 (1992).
- [14] - I. Kossyi, A. Kostinsky, A. Matveyev, and V. P. Silakov, Plasma Source Sci. Technol. **1**, 1207 (1992).
- [15] - L. Piper, J. Chem. Phys. **3**, 1625 (1987).