INFLUENCE OF WATER ON NO REMOVAL BY NONTHERMAL PLASMA IN N₂/H₂O:NO MIXTURES

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Abstract

Influence of water vapour on NO removal has been studied using a large volume homogeneous pulsed discharge coupled with a time resolved LIF measurement of the NO density, in N₂/H₂O/NO mixtures at a total pressure of 460 mbar. Experimental results emphasises that NO removal is strongly reduced when H₂O is added to N₂/NO. A kinetic explanation is given using predictions of a self-consistent 0D model: the NO removal rate is mainly determined through loss mechanisms balance for nitrogen metastable singlet states, i.e. collisions with NO and H₂O molecules.

1. Introduction

Pulsed discharges, dielectric barrier or corona, are amongst the considered techniques for atmospheric pollutant removal [1]. However these discharges are strongly non-homogeneous so that spatially and temporarily resolved optical diagnostics are difficult to handle and can be hardly compared to predictions of 0D kinetic models. In previous works [2,3], we have used an homogeneous photo-triggered discharge [4] (UV-corona pre-ionised) to study NO removal in N₂/C₂H₄/NO mixtures, both experimentally and theoretically. We showed that dissociation of NO through collision with singlet metastable states of N₂, in particular N₂(a¹Σ⁺u⁻), play the main part in NO destruction 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 [5], was deduced from our results. We proceed on the influence of H₂O on NO removal in N₂/H₂O/NO mixtures.

2. Experiment and modelling

A comprehensive description of the photo-triggered pulsed discharge operating mode has been previously given [6]. 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 \( V'_{\text{dis}} = 50 \text{ cm}^3 \) can be homogeneously excited at each shot (electrodes gap : 1 cm). The total pressure of the studied mixtures has been fixed to 460 mbar, with NO and \( \text{H}_2\text{O} \) maximum concentration values respectively equal to 1000 ppm and 2.5 %, at ambient temperature. The \( V_0 \) value can be chosen up to 40 kV, which corresponds to a maximum specific deposited energy, \( E_{\text{dep}} \), equal to 240 J/l; \( E_{\text{dep}} \) is defined by \( E_{\text{dep}} = C.V_0^2/(2.V_{\text{dis}}) \). 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 \( \text{NO}(A\Sigma \rightarrow X^2\Pi) \) 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. More details about this time resolved technique, and about validation of the LIF diagnostic on NO, can be found in a previous publication [2].

Our 0D-model [7] predicts time evolutions of chemical specie densities on a large time scale, typically from 1 nanosecond up to 1 second 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 [8]. Input parameters are: initial voltage applied to the electrodes, capacitance \( C \) of the storage unit and circuit inductance \( L \), gas pressure and composition. The time 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 1. Energy deposition in the plasma is well known for each value of parameters.

![Figure 1 - Time evolutions of the discharge current and of the voltage across the capacitors. Full lines : measurements. Dot lines : predictions. Voltage of the auxiliary discharge for pre-ionisation is also plotted. Pure nitrogen at 460 mbar.](image-url)
3. Results

In figure 2 are plotted examples of the measured (points) and predicted (line) NO density time evolutions for an initial value, \([\text{NO}]_0\), equal to 1.1×10^{16} \text{ cm}^{-3} (1000 \text{ ppm}) and for \(E_{\text{dep}}=92 \text{ J/l}\), either in the \(\text{N}_2/\text{NO}\) mixture (experimental points : squares) or with addition of 2\% \(\text{H}_2\text{O}\) (circles).

![Figure 2 - Typical time evolutions of NO concentration after one discharge in \(\text{N}_2/\text{NO}\) and \(\text{N}_2/\text{H}_2\text{O}/\text{NO}\) mixtures for a specific deposited energy of 92 \text{ J/l}. Symbols : measurements. Line : prediction for \(\text{N}_2/\text{NO}\).](image)

Figure 2 emphasizes that the stationary state for NO is obtained very quickly, 10 \(\mu\text{s}\) or less, without water in the mixture and within 20 \(\mu\text{s}\) with water addition. The measured NO-removal efficiency, at the stationary state, is 60 \% without \(\text{H}_2\text{O}\) in conditions of figure 2, but it decreases to 30 \% with \(\text{H}_2\text{O}\). Hence addition of water limits drastically the NO-removal. Such a result has also been obtained when a light hydrocarbon, for example ethene [3], is added to the \(\text{N}_2/\text{NO}\) mixture. Close examination of model predictions reveals that, in \(\text{N}_2/\text{NO}\) [3], main reaction pathways for NO-removal are:

\[(1) \quad \text{NO} + \text{N}_2(a') \rightarrow \text{N} + \text{O} + \text{N}_2\]

where \(\text{N}_2(a')\) represents singlet metastable states, with a rate coefficient \(k_1=3.3\times10^{-16} \text{ cm}^3\text{s}^{-1}\) [5,9], and

\[(2) \quad \text{N} + \text{NO} \rightarrow \text{O} + \text{N}_2\]

with a rate coefficient \(k_2=3.1\times10^{-11} \text{ cm}^3\text{s}^{-1}\) [10]. When \(\text{H}_2\text{O}\) is added to \(\text{N}_2/\text{NO}\), we believe on the possibility of the de-excitation collision:

\[(3) \quad \text{N}_2(a') + \text{H}_2\text{O} \rightarrow \text{products}\]

which could explain the decrease of the NO-removal efficiency owing to the decrease of \(\text{N}_2(a')\) density. This reaction is invoked here for the first time in studies about NO removal plasma technology.

457
In figure 3 is displayed the evolution, versus the H$_2$O concentration and for same other conditions than in figure 2, of the ratio between the NO density measured 160 μs after the current pulse, i.e. at a time for which chemical equilibrium is well achieved, and the initial NO density before the discharge, $\alpha = [\text{NO}](160 \, \mu s)/[\text{NO}](t=0)$. Figure 4 presents the evolution of $\alpha$ against the specific deposited energy at a H$_2$O concentration of 0.45 %.

![Graph showing NO density ratio vs H$_2$O concentration](image)

**Figure 3** - NO density at 160 μs after the discharge versus the initial density (t=0), as function of the H$_2$O concentration for a specific deposited energy of 92 J/l and for $[\text{NO}](t=0) = 1.1 \times 10^{16}$ cm$^{-3}$ (1000 ppm). Symbols: measurements. Lines: predictions taking into account

![Graph showing NO density ratio vs specific deposited energy](image)

**Figure 4** - NO density at 160 μs after the discharge versus the initial density (t=0), as function of the specific deposited energy, for a H$_2$O concentration of 0.45 % and $[\text{NO}](t=0) = 1.1 \times 10^{16}$
cm$^3$ (1000 ppm). Symbols : measurements. Full lines : predictions taking into account reaction (3).

Using of a kinetic scheme without reaction (3), given by dotted lines in figure 3, leads to underestimate $\alpha$, i.e. to overestimate NO-removal efficiency, with respect to experimental results. Measurements clearly show that this efficiency rapidly decreases when the H$_2$O concentration increases. Such a phenomenon is well predicted for a rate coefficient $k_3$=3.0x10$^{-10}$ cm$^3$/s for reaction (3). As shown both in figures 3 and 4, a very good agreement is reached between model and experiment for this value of $k_3$, which has been deduced from comparison of our measurements and model results on a large range of water concentration and specific deposited energy values. Figure 4 also emphasises that the NO-removal efficiency increases when the deposited energy increases, which is explained in great part by the increase of N$_2$(a') density created by the discharge.

Initial NO concentration has been also varied in order to verify the consistency of our kinetic modelling. In figure 5 are plotted predicted and measured time evolutions of NO density in conditions of figure 2, but for two values of the initial NO concentration, 425 ppm and 1000 ppm, for a H$_2$O concentration of 2 %.

![Figure 5](image.png)

**Figure 5** - Time evolutions of NO concentration after one discharge in N$_2$/H$_2$O/NO mixture, with 2 % of water for a specific deposited energy of 92 J/l. Symbols : measurements. Lines : predictions with reaction (3).

Excellent agreement is achieved between LIF measurements and model predictions but only if reaction (3) is taken into account.

4. Conclusions

Dissociation of NO through collisions with singlet metastable states of nitrogen play the main part in the NO removal process in homogeneously excited N$_2$/NO [3]. As a result, addition of water vapor to that mixture leads to a decrease of the NO removal efficiency owing to de-excitation collisions of singlet states with H$_2$O. Rate coefficient value for this
process is $3.0 \times 10^{-10}$ cm$^3$s$^{-1}$, close to the one previously measured for collisions of singlet states with light hydrocarbons [3,5].

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