

Vibrational Kinetics in a Nanosecond Discharge Afterglow in Air

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Abstract. In this paper we study a kinetic model to simulate an air plasma afterglow. In the frame of Plasma Assisted Combustion (PAC), a preliminary investigation of the influence of air excited species in chemical reactions chain is performed. We compare the temporal evolution of the vibrational temperature of excited N₂ measurements performed with CARS technique with a numerical 0D simulation. Calculations reproduce experimental behaviour and propose a possible interpretation.

I. INTRODUCTION

In recent decades an active interest has been shown for applications of non equilibrium plasmas to combustion. Many laboratories in Europe, US and the former Soviet Union have achieved combustion improvements by using plasma technologies, in particular nanosecond discharges due to their energy-efficient excitation of mixtures. Major effects have been noticed in the reduction of the delay time of combustible mixtures, along with auto ignition [1] and stabilisation [2] of flame in lean mixtures. Ignition and combustion of supersonic flows have also recently shown strong benefits from plasma pre-treatment. Different mechanisms have been proposed in the literature to explain the observed effects and to build on the experiments, but a complete understanding of the principles is still lacking.

The aim of our work is to develop a tool for the numerical simulation of the discharge and after-glow phenomena in a pulsed discharge scheme, with an emphasis on kinetics and plasma phenomena, in order to understand the role of plasmas in the combustion processes.

The complexity of the physics, due to several physical phenomena simultaneously taking place such as gas discharge, hydrodynamics and chemical kinetics, makes the complete analysis very challenging. To describe accurately such situation some simplifications have to be introduced. Despite the simplified approach, this study should allow to pinpoint the chemical species that plays a fundamental role in the kinetic mechanism of the discharge.

It is well known that vibrational excitation of molecules increase the rate of chemical reactions, but the rate coefficients for those reactions are not well known. In this study we start the development of a vibrationally-specific chemical kinetic scheme for air, and validate it against CARS measurements taken in a discharge afterglow. In particular we account for vibrational-vibrational (VV) and vibrational-translation (VT) reactions.

II. EXPERIMENT OF REFERENCE

We decided to use as experiment of reference a CARS investigation of a nanosecond pulse discharge in air performed at ONERA in the Department of Physics [3]. Scientific community has showed interest on non thermal plasma technique, like the repetitively nanosecond pulse discharge [4], as catalyst in combustion. It is somehow related to his versatility: non equilibrium condition, no pressure restrains, high energy particles. Even if this work latest goal is the investigation of the PAC, we decide to simulation first an air discharge. The justification on this choice resides on the extremely complexity of the problem, and on the major importance of the air as a component of the mixture.

A sketch of the experimental set-up is presented in figure (1). The system consists of a nozzle for the injection of methane/air mixtures, with two stainless-steel needles 3 mm apart placed at the exit. In order to create a nanosecond discharge, a high voltage pulse generator has been employed (50 ns FWHM, 10-40kV amplitude and 100 Hz max pulse repetition frequency). This set of experiments has been done in a single shot mode. Different lasers have been employed into CARS hardware system. A detailed explanation of the measurements system is given elsewhere [3].

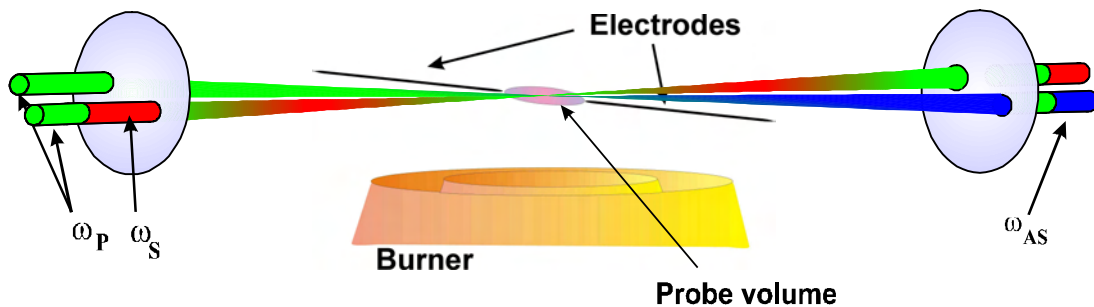


Figure 2 A sketch of the experimental set up and the lasers system for CARS measurements.

The central goal of this set of experiments is the measurement of the temporal evolution of the vibrational and rotational temperature of N_2 in the afterglow of a pulsed discharge. The results of CARS investigation are represented in the figure (2). Those data will be the object of our simulations.

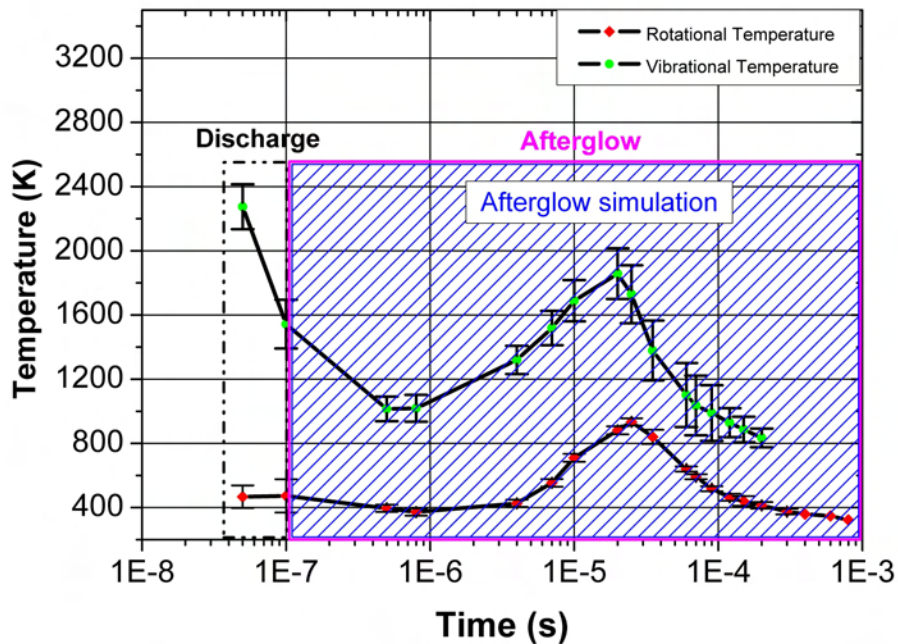


Figure 2 Temporal evolution of the vibrational (green dot) and Rotational (red rhombus) temperature by using CARS Measurement.

III. KINETIC MODEL OF THE AFTERGLOW

As stated in the foregoing paragraph, our goal is to develop a complete kinetic model in order to reproduce the evolution on time of T_{vib} (Figure 2). Because of the interference between CARS signal and electron population in the discharge, measurements have been taken at $t > 40$ ns. This means that the first temperature measurement ($t = 70$ ns) still belongs to the discharge. To circumvent the complexity of simulating two regimes, discharge and afterglow, we will deal at first with the afterglow (blue dashed part of fig. 2).

The "T0" for the simulations presented is approximately $T = 10^{-7}$ s after the beginning of the discharge.

The kinetic model for the afterglow is composed by a set of chemical reactions taking part between the byproducts of the discharge. In order to consider the interaction between vibrationally excited species and the rest of the medium we properly calculated reactions rate. This results, eventually, in a scheme counting for 1400 reactions and 96 species.

Since from the referenced experiment we do not have, so far, information about species concentration we are forced to make certain assumptions. We begin with recovering the amount of energy deposited in the investigated volume from

electrical characteristics. We assume that most of the energy goes into dissociation and ionization, leading to the creation of atomic nitrogen and oxygen together with the respectively ions, and electronic vibration excitation ($N_2(A,v')$, $N_2(B,v'')$, $N_2(C,v''')$, with v',v'',v''' vibrational level). To justify our assumption, we can recall the correlation between the fraction of total power dissipated by different modes and the reduced field [5]. In the table (1) are listed reactions and species considered in the kinetic model.

The information on the initial vibrational level population of N_2 at the beginning of the afterglow is partially given by the CARS measurements. The vibrational temperature measured is that between the $v=0$ and $v=1$ levels:

$$T_{vib} = \frac{E_1 - E_0}{\ln\left(\frac{n_0}{n_1}\right)} \quad (4)$$

with the usual notations. Thus it does not give information on the distributions of levels with $v > 1$.

In order to explain the variations of vibrational temperature measured, we propose that, early on in the afterglow, the population of the higher vibration levels is not in equilibrium with the 0 and 1 level, as in figure (4).

This could be due to quenching/recombination of excited states/atoms preferentially down to the low vibrational levels, if the vibrational states are all distributed with $T_v = 5000$ K at the end of the discharge . This explanation is consistent with the very fast decrease observed in the early afterglow in the measurements (Figure 2), which is much faster than VV or VT transfers.

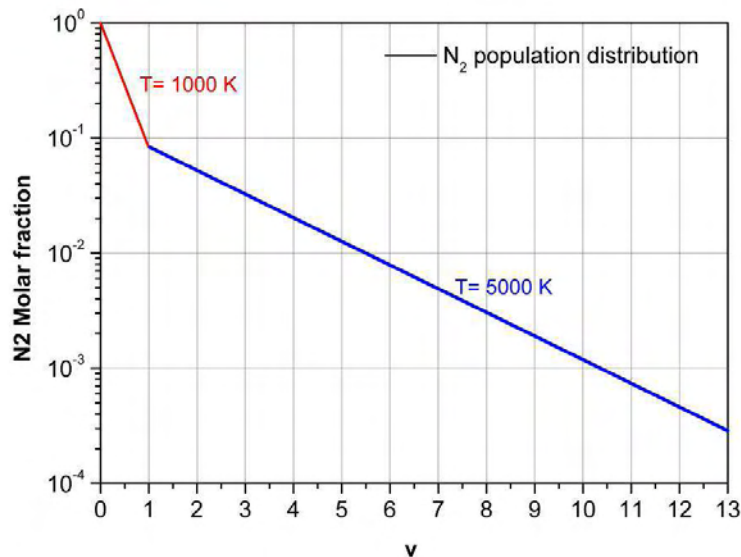


Figure 3 Assumed initial condition for the population of the nitrogen vibrational levels.

In summary, our model is based on the following hypothesis:

- initial condition for neutral specie concentration

- N₂ - O₂ 80% dissociated
- excited species concentration
- N₂ - O₂ 10% Ionized & 10% Excited
- initial temperatures
- $T_v(n_0, n_1) = 1000 \text{ K}$
- $T'_v(n_2, \dots, n_i) = 5000 \text{ K}$
- $T_g = 1000 \text{ K}$
- reaction scheme is reported in the table 1.

A modified version of the CHEMKIN software was used for the chemical kinetics calculations.

Species created by the discharge	Species created by the afterglow	Reactions
O, N N ₂ ⁺ , O ₂ ⁺ , O ⁺ , N ⁺ O₂(X³Σ_g⁻; 1 ≤ v ≤ 13) N₂(X¹Σ_g⁺, A³Σ_u⁺, C³Π_u, 1 ≤ v ≤ 13)	NO, NO ₂ , N ₂ O NO ⁺ , NO ₂ ⁺ , N ₂ O ⁺ NO(X²Π_{1/2}; 1 ≤ v ≤ 13)	Associative ionization Dissociative recombination Dissociation Recombination 3 body recombination Charge exchange Quenching Radiative decay Predissociation Inverse predissociation Vibrational relaxation Vibrational energy transfer

IV. RESULTS AND DISCUSSION

In figure 4, the simulated vibration temperature (black line) and the experimental temperature (red line) are presented. The two lines show a similar behaviour, although time scales are different.

A detailed analysis of the simulated results reveals that the reactions responsible for the ramping-up of the temperature between v=0 and v=1 are the VV and VV' processes. This is followed by VT relaxation toward Boltzmann equilibrium at the gas temperature.

Figure 5 shows the temporal evolution of the concentration of the first three vibrational levels of N₂. The temperature of the initial condition corresponds to

the black line. For the reasons stated in the foregoing section, the population at the starting point of the simulation, $t= 100$ ns, is not in equilibrium.

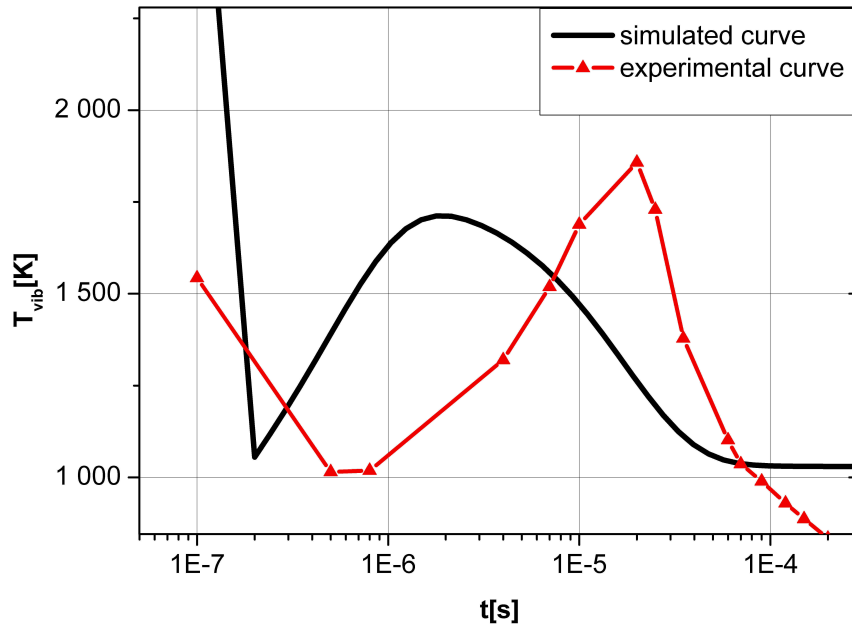


Figure 4 Temporal evolution from 100 ns to 100 μ s of the vibrational temperature calculated (black line) and measured experimentally (red dots and line).

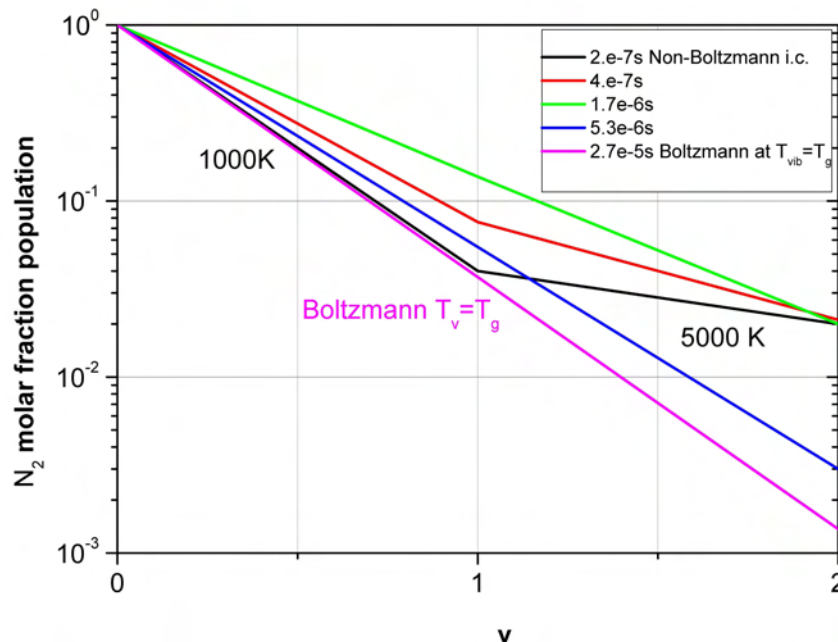


Figure 5 Temporal evolution of the distribution function for the vibrational population of N_2 $v=0,1,2$. The black line represent the initial conditions and the pink one is the result at the equilibrium

If we now consider the population at 200 ns (red line), the concentration of the level 1 is increased comparing to the level 0, up to a maximum reached at approximately 1 μ s. This corresponds to an enhancement of the vibrational temperature. The point of maximum concentration of the level 1 coincides with reaching the Boltzmann equilibrium. To explain this behaviour it is necessary to recall some vibration mode characteristics. Since we are considering a single quantum VV mode of harmonic oscillators, the exchanges of energy between successive levels are resonant. Therefore the total number of quanta is conserved and the steady state concentration is Boltzmann. Moreover, the relaxation time for VV' and VV reactions is faster than the VT stage, then the distribution of the population will reach first a Boltzmann equilibrium at a certain temperature and then it will relax to the gas temperature.

These results are preliminary, and the inaccuracies of reaction rate together with the limited experimental information may have lead to the discrepancy in time scales between the experiment and the calculations. Further work is needed to clarify this point.

Moreover, the chemistry of the excited states may be fundamental in explaining the initial non equilibrium in the vibrational distribution, and measurement of excited states concentrations during the discharge and early afterglow are planned in the near future.

V. CONCLUSION

In this paper we simulate the temporal evolution of the vibrational temperature of a nanosecond pulse discharge in air. The purpose of our analysis is to gain some insights in the chemical mechanisms during a nanosecond pulse discharge. We are particularly interested in the investigation of the influence of vibrational excited molecules in the kinetic mechanism of the afterglow. For this reason we formulate a vibrationally-specific kinetic scheme. Preliminary results are presented in the foregoing section, with hypothesis on the concentrations and distribution. They are in relative agreement with the experimental one.

The model needs to be completed with a more precise reaction mechanism including the model of the discharge. In addition, more experimental work will be done in order to eliminate the assumptions and better characterize the discharge.

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