Vibrational Kinetics in a Nanosecond Discharge Afterglow in Air

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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.

2. Experiment of reference
In order to study the role played by the vibrationally excited species during an air afterglow, we used a set of measurements on the evolution of the vibrational temperature.

A sketch of the experimental set up, performed at ONERA in the Physics and Instrumentation Department, is presented in figure (2). 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 diagnostics is given elsewhere [1]. The central goal of this set of experiments was to investigate the vibration temperature of an air pulse discharge afterglow. As reported in [1], the temperature information was obtained from the ratio of the intensity line emitted from the level v=0 (ground state) and v=1 (first vibrating energy level) of N₂. The results of CARS investigation are represented in the figure (1).

Fig.1 Temporal evolution of the vibrational (black line) and rotational (red line) temperature by using CARS measurement.

We can divide the temperature evolution line mainly in 3 parts. The region A, corresponding to early afterglow from 50 ns to 1 µs, shows a sudden reduction on T_vib, which translates into a significant increase of the concentration of the v=0 level with respect to the v=1 level. In region B, the temperature ramps up, recovering almost the same value showed at the end of the discharge. Finally, in region C, T_vib relax towards T_rot. Just for the sake of completeness, we recall that CARS measurements have been taken during a pulse afterglow, no electrical field is present and in addition experiments were performed in one single shot mode. The comprehension of such behavior is particularly challenging. The trend of T_vib is extremely interesting, because it shows a way to reheat (region B), even during the afterglow, nitrogen vibrating species. These represent a source of energy that can be available after the electrical pulse. An exhaustive interpretation of the experimental results demands an accurate numerical study. It results evident that there is a mutual influence between vibration excited species and the rest of the gas. In order to explain the behavior of T_vib evolution we assemble a complete kinetic model to simulate plasma afterglow. Nevertheless, a preliminary investigation on the nanosecond pulse discharge first is mandatory to establish
the initial condition for the afterglow. We will start then by describing the discharge model. As a first interpretation of figure 1, we can associate the sudden drop of temperature to a fast reaction involving excited nitrogen molecules and nitrogen ground state molecules. Then, a phenomenon of rearranging of vibration quanta towards a condition of equilibrium (Boltzmanian) could explain the increasing of temperature, until eventually collisions with gas at ambient temperature drops $T_{vib}$ towards $T_{gas}$.

4. Kinetic scheme

During the discharge the most important chemical reactions are represented by electron impact on the main air constituent $N_2$ and $O_2$.

\[
\begin{align*}
A + e^- & = A^* + e^- \\
A + e^- & = A + 2e^- \\
A + e^- & = A + A + e^- \\
A + e^- & = A(v) + e^- 
\end{align*}
\]

The air discharge products consist mainly of 33 species. In particular, we include in the model just the species fulfilling the following conditions: reasonable lifetime, respect with time step integration, and a noticeable influence on the discharge chemistry.

In the selected group appear, electronically excited $N_2$ ($A\,^3\Sigma_u^+, B\,^3\Pi_g, C\,^3\Pi_u$), vibrationally excited $N_2$ ($v=1,..,11$), metastable molecular and atomic oxygen, $O_2$ ($a\,^1\Delta_g$, $b\,^3\Sigma_g^-$), $O$ ($^3\Sigma, ^1\Pi$), positively and negatively charged particles $N_2^-$, $N^+$, $O^-$, $O_2^-$, $O^+$, and NO are produced by a fast recombination of the plasma species. The inclusion of excited oxygen $O_2$ ($a\,^1\Delta_g$) is fundamental to explain the electron detachment from $O^-$ in the afterglow.

Vibrational excitation cross sections for $N_2$ were calculated by Pierrot et all[2], while the rest of rate coefficient are taken from Capitelli[3] and Gudmundsson[4]. The state-to-state vibration model allows us to investigate the effect of excited species on the overall discharge. We assume that the electron temperature is fixed at 35000K, and we used Maxwellian reaction rate. The Maxwellian assumption will be verified at a later time, but is not irrelevant given the large electric field (300 Td). The set of first order differential equations is solved with a 2-temperature CHEMKIN software, modified to allow electron temperature to be different from gas temperature. Kinetics
calculations are presented in figure 3.

Fig 3 Temporal evolution of species concentration in air pulse discharge, $T_e=35000 K$, $T_g=300$. Dashed red line corresponds to electron concentration.

The kinetic mechanism adopted for afterglow simulation comprehend the reactions of recombination of electrons, ions and atoms, besides electron attachment and detachment, radiative decay, collisional de-excitation, charge exchange, etc... Even thought the knowledge on vibrational energy dependence of chemical reaction rate is mostly unknown, the effects on chemistry dynamics is particularly strong, especially for endothermic processes [4]. At this purpose, we cite a pioneering work done by Bose et all. [5,6] on the determination of the degree of dependence of Zeldovich reactions to nitrogen vibrational excitation.

5. Results and discussion

Fig 3 shows the temporal evolution of specie concentration. The dashed line represents the evolution of electron concentration. The major products of the pulse discharge are excited atomic oxygen, excited nitrogen, atomic oxygen ions, ozone and atomic oxygen. If we analyze the plasma composition at different instant, we can notice that it takes approximately 10 ns to start producing high efficient electron impact collision. From 10 to 13 ns the concentrations of major air species start to decrease effectively on behalf of plasma byproducts. We found that the simulation fulfills at $t=13$ns the two conditions adopted as the start of the afterglow: energy deposited by the electrical field and vibration temperature. (The solver treats in a different way reactions between electrons and gas at $T_e$, and reaction between the different species at $T_g$). Most of the energy injected during the discharge goes into excitation more than dissociation or ionization.

We suppose that at $t=1 \mu s$ (beginning of region B) the $N_2$ ground state is overpopulated respect to $N_2$ excited states. We don’t know yet, which are the reasons why temperature dropped, but this agrees with overpopulation of the ground level. In fact,

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

An increment of $n_0$ is equivalent to a decreasing of $T_{vib}$. We can additionally show it by means of the VDF (fig5). Our assumption it is not confirmed yet, because a complete and exhaustive model for the afterglow is still developing. Preliminary results of the evolution of the vibration temperature in an air afterglow are presented in fig 6.
The similar trend showed by both temperature characteristics is important for partially justifying the assumption made on the overpopulation of the nitrogen ground state at $t_0=1\mu s$. Thanks to the effect of redistribution of vibrational quanta associated to VV and VV' process $T_{vib}$ show an increment up to 1700K. A subsequent relaxation through VT collision is responsible for the temperature collapsing. Further work is needed on the kinetic model to explain the timescale difference between the two curves.

6. Conclusion
In this paper we are particularly interested in the investigation of the influence of vibrational excited molecules in the kinetic mechanism of the afterglow. A kinetic model of the discharge is assembled in order to infer the proper initial condition for the afterglow. A state-dependent mechanism is created to investigate the mutual interaction between excited vibration levels of nitrogen and the rest of species created by the discharge. The results of afterglow simulation are preliminary.

References