Relaxation of excited states calculated with CoRaM-Air, the CORIA's Collisional-Radiative model for air

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A nonlinear time-dependent 2T collisional-radiative model for air plasmas has been developed. The model consists of 13 species: N_2, O_2, Ar, N, O, NO, N_2^+, O_2^+, N^+, O^+, NO^+, Ar^+ in their ground state and major electronic and vibrational excited states, and electrons. Many elementary processes are considered which allow the calculation of the states relaxation during either dissociation/ionization or recombination situations.

During the atmospheric entry of a spacecraft, the hypersonic flow is converted into a high enthalpy flow through a shock wave: the temperature reached during this phase induces the dissociation of the molecules and the ionization of the gas [1]. The gas is therefore converted into plasma. The related complex chemistry involves a lot of radicals and ionized species. In the case of an Earth's atmospheric entry, the species produced may be: N_2, O_2, Ar, NO, N, O, N_2^+, O_2^+, Ar^+, NO^+, N^+, O^+, and e^-. The behaviour of this mixture is complex and is now far from being completely understood. In addition, the characteristic hydrodynamic times scales are short, which prevents a complete relaxation of the flow: this flow is therefore in non-equilibrium [2]. In this context, the chemistry of the flow plays a key role, for example in the radiative flux transferred to the spacecraft and in the recombination processes taking place on the fuselage. To avoid any damaging, a thermal protection system is used. Its sizing and its characteristics depend on the chemistry of the flow: this chemistry has therefore to be well understood.

From shock tubes experiments, it is possible to identity a global chemical mechanism, which means a set of main reactions involving the species composing the flow [3]. This global chemical mechanism is valid only over the pressure and temperature ranges over which experiments have been performed, and in ionization and dissociation conditions. Other experiments can also be performed in simplified conditions also in shock tubes in the purpose of identifying some global rate coefficients related to main reactions involved in the previous global chemical mechanism [4]. These two kinds of data (global rate coefficients and global chemical mechanisms) can be only used over the pressure and temperature ranges related to their identification: they fail to model other situations. This approach is therefore limited and other tools have to be used.

Theoretical approaches may be useful. The power of computational means is now sufficiently high to envisage massive calculations including numerous excited states. In this context, two types of studies can be done. The first type concerns the calculation of the global rate coefficients by a state-to-state approach. By comparison with the rates derived from experimental results obtained for example in shock tubes, the elementary cross sections or rate coefficients between particular excited states can be verified indirectly [5]. It is therefore useful to have close collaborations with the quantum chemists' community. The amount of elementary data constitutes often a limitation of this type of approach. However, this approach is a promising way owing to the rapid increase of the quality, the accuracy and the systematic aspect of this type of calculation.

The second type concerns the study of the complete chemistry of a complex mixture by a state-to-state approach taking into account a sufficiently high amount of excited states of the different species involved. The related detailed chemistry allows the prediction of the behaviour of the complex mixture particularly in strong non-equilibrium conditions. The specific behaviour of a given excited state can be also identified and compared to experiments. This allows a partial validation of the approach. The validation of theoretical approaches sometimes comes up against the difficulty to derive ground states population densities from experiments. Their determination requires indeed complex experimental

means (laser induced fluorescence, absorption, Raman scattering, etc.) or is sometimes very difficult owing to the species considered (atomic oxygen for example). By optical spectroscopy, information is easily derived on excited states: in this case, a partial validation of the detailed chemistry can be obtained from the comparison between the experimental and theoretical behaviour of the excited states.

In this context, we have elaborated a theoretical tool able to:
- derive global rate coefficients,
- reproduce the complex chemistry of mixtures in non-equilibrium conditions

in the case of the Earth's atmospheric re-entries. This tool is based on the elaboration of a Collisional-Radiative (CR) model taking into account:
- 13 different species (N_2, O_2, Ar, NO, N, O, N_2^+, O_2^+, Ar^+, NO^+, N^+, O^+, and e^-),
- 350 excited (electronic and vibrational) states of the previous species,
- $\approx 10^6$ elementary processes.

This model is named CoRaM-Air. Heavies are assumed in Maxwell-Boltzmann equilibrium with the temperature T_A and electrons with the temperature T_e. No equilibrium assumption is made concerning either the electronic or vibrational excited states: the CR model is therefore vibrational and electronic specific.

CoRaM-Air may be used in dissociation and ionization situations, or in recombination situations. The model is implemented in a temporal code providing the evolution in time of the mixture whose pressure and temperatures conditions are suddenly modified. Figure 1 illustrates the evolution in time of the population densities calculated in a typical dissociation situation.
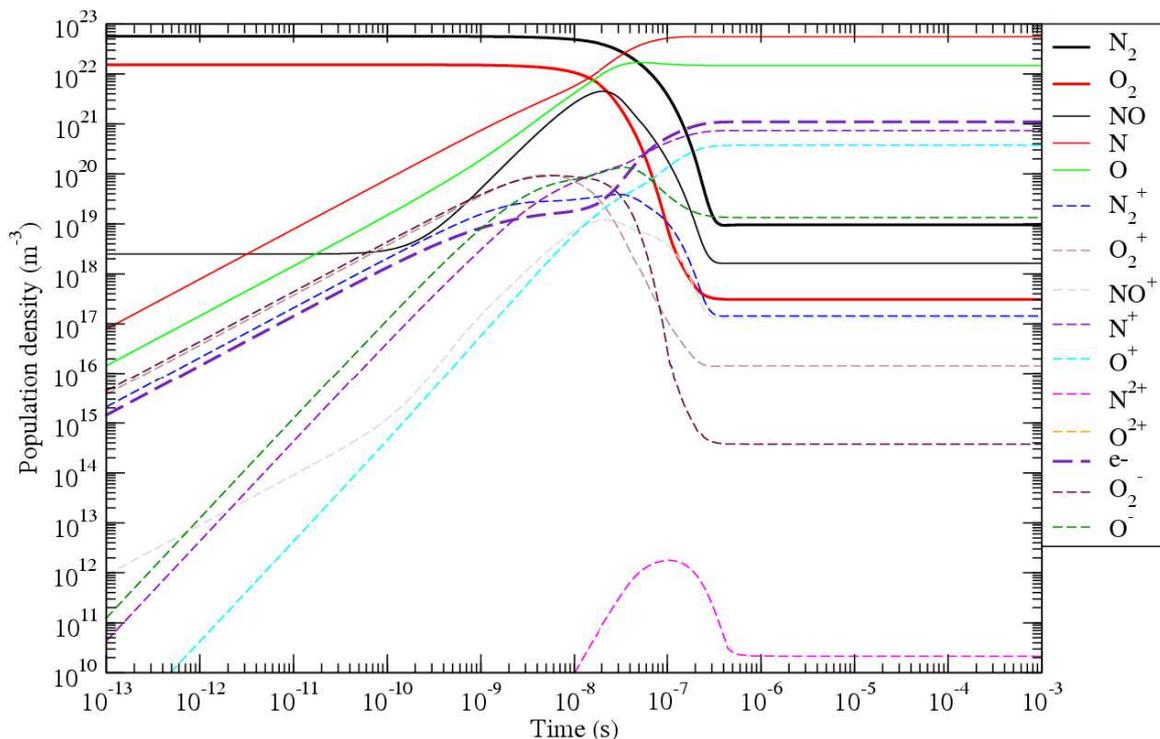

Figure 1. Time evolution of the species considered in CoRaM-Air for the dissociation – ionization situation from (300 Pa, 200 K, 200 K) to (15000 Pa, 7000 K, 15000 K) for the conditions (p, T_e, T_A).

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