Study of the electron kinetics in He/CH_4/CO_2 mixtures for Syngas production

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This report discusses the electron kinetics in He/CH_4/CO_2 mixtures as a necessary step to model the production of Syngas in cold or warm plasmas. In particular the influence of helium concentration, gas and vibrational temperatures and product (CO and H_2) concentration on the electron velocity distribution function (*evdf*), transport parameters, collision frequencies and fractional power losses is analysed in detail. The effect of the population of vibrational levels on the *evdf* is taken into account by considering both super-elastic collisions and electronic excitation and ionization from vibrationally excited levels, mechanism usually neglected in electron kinetic studies in CH_4 and CO_2.

Introduction

Due to the demand for fuels that are cheaper, less polluting and with high exploitation life expectancy, research on the production of hydrogen from natural gas is of great importance. However solutions need to be found for the efficient storage and transport of hydrogen. Complex hydrocarbons with a high ratio of hydrogen atoms/molecule can be used for this purpose. Non-thermal plasmas at atmospheric pressure have been studied for the conversion of mixtures of methane and production of Syngas (H_2 and CO mixture) [1]. The gas mixtures studied include methane with an oxidant (in general O_2 or CO_2) with or without the admixture of a rare gas [2].

Until now most of the studies have been experimental and only recently the plasma chemistry has been modelled [3] showing that a rich and complex chemical kinetics takes place in these mixtures. The study of the electron kinetics is a key factor to understand what happens in these mixtures and a necessary step to develop a full kinetic model.

In this work we expand a preliminary study [4] of the electron kinetics in He/CH_4/CO_2 and He/CH_4/O_2 mixtures and obtain results that further contribute to the interpretation of the experimental results and allow us to identify the main processes and energy transfer channels.

Method

We solve the electron Boltzmann equation for a swarm moving in a constant electric field in a hydrodynamic regime. In these conditions the electron velocity distribution can is expanded in terms of the powers of the density gradients. The corresponding expansion coefficients are obtained using a numeric method based on the discrete ordinates S_n [5] and solving the Boltzmann equation in a (v,θ) grid. With this approach we obtain two sets of transport parameters, *flux* and *bulk* [6] where the former correspond to the transport parameters obtained neglecting non-conservative processes and the later include an explicit contribution from non-conservative processes in the gas (ionisation and attachment).

We used the recommended data on electron collision cross for helium and carbon dioxide from [7] while methane cross sections were based on [8, 9], updated with recent results and adjusted to swarm data [4]. The population of vibrational levels is taken into account in super-elastic collisions and on electronic excitation and ionisation following the treatment in [10]. This populations are usually neglected for non-thermal plasmas for molecular gases with more than two atoms as at room temperature no significant population of these levels is observed. However, at discharge systems used for methane conversion (coupled catalytic-DBD discharges systems and “warm” plasmas systems), the vibrational temperature can be sufficiently high that a significant vibrational population is present [11].

Results

We have obtained the isotropic component of the electron energy distribution function, *flux* and *bulk* transport parameters, the rate coefficients for selected processes and the fractional power losses as function of the electric reduced field and we have studied the influence of the helium concentration, the gas and vibrational temperatures and products concentration (CO and H_2) on these results.

As expected, the electron energy distribution is significantly shifted to higher values as the helium concentration increases. As a result, and in spite of the reduction of methane concentration, the collision frequencies for methane dissociation increase. Figure 1 shows the shift to lower reduced electric fields of the collision frequency for dissociation of CH_4 into CH_3 when the helium concentration. Similar shift is also seen for the ionisation and attachment coefficients and in carbon dioxide. These results are in good agreement with the experimental results reported in [2].

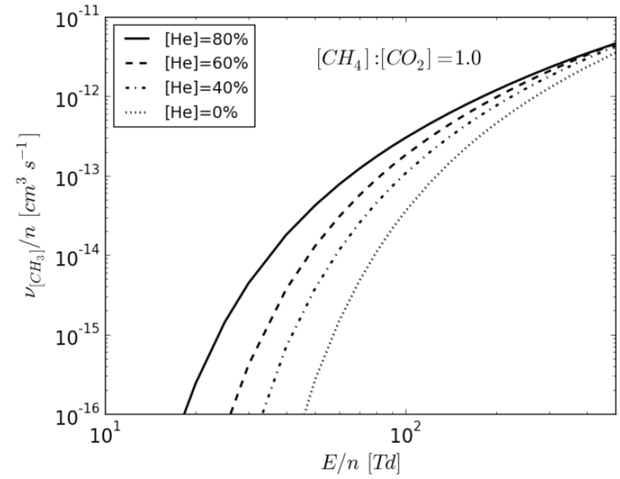

Fig. 1: Variation of the density-normalized collision frequency for dissociation of CH_4 into CH_3 as a function of the reduced electric field, in mixtures with different concentration of helium.

The results show that a significant increase on methane and carbon dioxide dissociation (and formation of Syngas) can be obtained with the admixture of a rare gas and the energy efficiency in these discharges can be improved if the population of vibrational levels is sufficiently high to influence the dissociation processes.

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