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Vibrational kinetics in CO2 plasmas: checks and balances

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A joint experimental and modelling investigation is carried out in order to check the validity of commonly accepted assumptions underlying the vibrational kinetics of CO_2 plasmas and the accuracy of rate coefficients frequently used in plasma modelling. To this purpose, new dedicated experiments are designed to allow an easy access to a variety of diagnostics and an unambiguous comparison with numerical simulations. The system of election is a DC glow discharge, operating either in pulsed or continuous regimes, at pressures around the Torr, currents of a few tenths of mA, in a Pyrex tube of radius 1 cm, in pure CO_2 and in a variety of gas mixtures including CO_2-N_2, CO_2-CO and CO_2-O_2. In-situ Fourier transform infrared spectroscopy is used to measure the gas temperature, the characteristic vibrational temperatures of CO and the various CO_2 vibration modes, as well as the CO and CO_2 concentrations in the plasma, while actinometry and high-resolution two-photon absorption laser induced fluorescence are used to measure the oxygen atom concentrations and loss frequencies. To interpret the experimental results, a comprehensive self-consistent kinetic model is developed, coupling the electron, vibrational, chemical and ion kinetics.

A careful model development and validation strategy, strongly supported by benchmark experiments, has been pursued in recent years. It has provided, for instance, the validation of a set of reactions and rate coefficients describing the relaxation of vibrational energy in the afterglow [1] and the input of vibrational energy in an active discharge [2] in low-excitation conditions where dissociation is negligible, the demonstration that the characteristic temperatures of the effective symmetric (which includes the Fermi resonant states) and bending modes in those conditions are very nearly the same [2], the determination of the electron impact dissociation rate coefficient [3], and the development of a reaction mechanism for O_2 and for vibrationally cold CO_2 plasmas [4,5].

The body of knowledge built in [1-5] creates the conditions to take a further step: a new set of experimental data allowing the development of a detailed and carefully validated self-consistent model describing the electron and heavy-particle kinetics, including the neutral and ion chemistry and a comprehensive CO_2 vibrational kinetics in a fully developed plasma. The validity of first order perturbation Schwartz-Slawsky-Herzfeld

(SSH) and Sharma-Brau theories [1,2] to calculate vibrational energy exchange rate coefficients is checked and discussed in light of the new results. It is shown that vibrational kinetics is important in shaping the electron energy distribution function. Furthermore, it is established that, depending on the operating conditions, different phenomena are critical to determine the vibrational distribution functions of CO_2, such as deactivation of vibrationally excited states at the wall and vibrational-to-translation energy exchanges in CO_2-O collisions, respectively for the lower and higher pressures considered. Therefore, no single mechanism takes universal control over the vibrational kinetics. As these two processes are often overlooked in discharge models, the corresponding predictions of vibrationally-driven dissociation from these models are likely to be significantly overestimated.

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