Title: High-Temperature Non-Equilibrium CO_2 Kinetic and Radiative Processes

Abstract

CO_2 kinetic and radiative vibrational state-to-state processes (STS) are explored in this work. Better insights into these processes may lead to more efficient spacecraft design for Mars atmospheric entries, and better understanding on the dynamics of physical-chemical processes for CO_2 plasma sources

The kinetic models developed in this work include an extension of the Forced Harmonic Oscillator (FHO) theory to the collisional dynamics of triatomic molecules. The FHO does not suffer from many shortcomings such as First Order Perturbation Theories such as SSH, while remaining computationally affordable, making it a very attractive theory at contemporary level. Other improvements to the state of the art include a better accounting of the dissociation pathways and the modelling of the excited $^3B_2$ state. Other important chemical processes in CO_2 gases and plasmas were accounted for, and in particular the reaction $CO_2 + O \longleftrightarrow CO + O_2$ was studied extensively, since it is found to significantly contribute to the decomposition of CO_2 and may as well play a key role in recombination processes through the inverse $CO + O_2$ reaction. Strong evidence of CO_2 dissociation being a two-step process through this Zeldovich reaction is found, either from the bibliography research, and from the state-specific kinetic simulations carried out in this work. The obtained model was compared to available experimental shock-tube data, outperforming macroscopic chemistry models, and reproducing the observed experimental trends of decreasing characteristic dissociation times, while showing a reasonable agreement absolute values comparisons between experimental/synthetic decomposition times.

Contemporary radiative databases for carbon dioxide are not tailored for full spectrum calculations necessary for atmospheric entry spacecraft design. To this end, the well-known rovibrationally specific CDSD4000 database for CO_2 was refitted, using well known spectroscopic polynomial expressions, to obtain a vibrationally specific database. The presented method may be applied to databases for any arbitrary linear polyatomic molecule, yielding vibrationally specific data with the correspondingly compact data size, more performance friendly than detailed databases such as CDSD. The refitting procedure introduces some loss of detail since fitted polynomials cannot reproduce data with full accuracy. Once alternative methods for computing broadening effects are accounted for, the refitted database, dubbed CDSDv, is able to reasonably reproduce calculated and experimental spectra found in literature, particularly in the 4.3 μm spectral region the most significant contributor to the radiative features of CO_2 Infrared radiation.

In the last chapter of this work, several venues for improvement of both the kinetic and radiative model are discussed at length.

Keywords: CO_2, non-equilibrium, databases, radiation, kinetics