Topic number: 1

A Complete Multiquantum State-to-State Model for the Fundamental States of N_2, O_2 and NO

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1 Introduction

Recently, there has been a renewed interest in the development of accurate state-resolved databases for the simulation of V–T, V–V and V–D exchange processes. Indeed, such heavy-impact processes play an important role in the dynamics of gas discharges or other plasmas sustained by electron-impact reactions, or even a predominant role in plasmas excited by heavy-impact processes (such as shockwaves). The modelling of the behavior of the latter type of plasmas is relevant for applications such as spacecrafts atmospheric entries, and fostered the need for more improved heavy-impact models [1].

Indeed, the traditional approach of considering simplified First Order Perturbation Methods such as the SSH approach only allows obtaining rates that are valid at translational temperatures lower than 1000K, and considering simplified dissociation models such as the ladder climbing model which, although satisfactory at low temperatures, underestimates dissociation at higher translational temperatures, as it is unable to account for multiquantum transitions [1].

Another important issue, that has been quite overlooked in the past, is the selection of an adequate manifold of vibrational levels. Traditional approaches rely on polynomial expansions for the level energies, often forgetting that the validity range of such fits remains far beyond the quantum number of the dissociation limit. Recently, it has been shown that a more sensible and accurate approach implies using more detailed potential reconstruction methods and retrieving adequate vibrational level energies from the resolution of the radial Schrödinger equation over said potentials [2].

In this work we present a complete dataset of state-resolved reactions for N_2–N_2 and O_2–O_2 collisions, using The Forced Harmonic Oscillator (FHO) theory [3], and considering upgraded manifolds of vibrational energies. Complementary rates, proposed by other research groups, are also discussed.

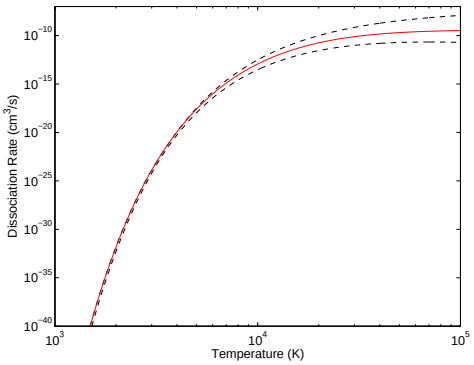
2 N_2–N_2 and N_2–N exchange processes

61 N_2 vibrational levels have firstly been recalculated considering the accurate potential proposed by LeRoy [4]. The FHO method has then been applied considering a Morse intermolecular potential with the parameters $\alpha = 4\text{Å}^{-1}$ and E=200K. For N_2–N collisions we consider the dataset from Esposito et al. [5], obtained using a QCT method. If the collisional partner is O instead of N, or O_2 instead of N_2, a simple scaling law accounting for the differences in molecular masses, is applied, given that the intermolecular interaction potentials are not assumed to differ sensibly.

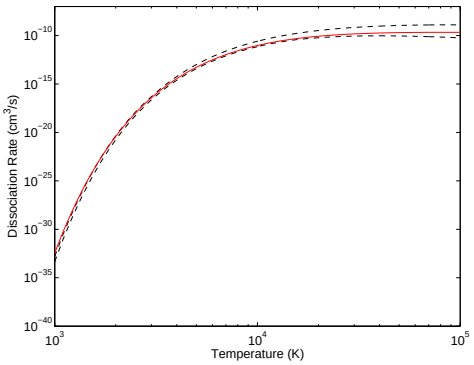
3 O_2–O_2 and O_2–O exchange processes

46 O_2 vibrational levels have firstly been recalculated considering a RKR potential [2]. O_2 molecules have a long-range interaction potential which can be approximated by a larger well in a Morse internuclear potential. This potential well has been iterated until a best-fit is obtained with

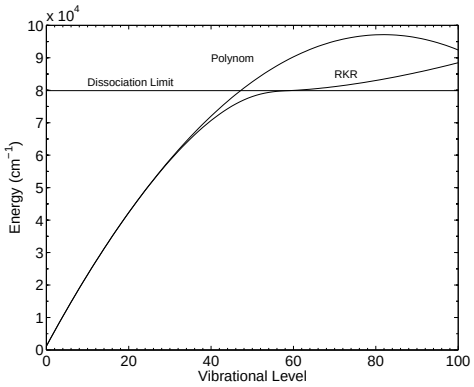
thermal dissociation rates (see Fig. 1(b)). The parameters $\alpha = 4\text{Å}^{-1}$ and E=370K yield such an optimized fit. For O_2–O collisions we consider the dataset from Esposito et al. [6], also obtained using a QCT method. Once again the same scaling laws are considered if the collisional partner is N or N_2 with the exception that for O_2–N_2 collisions, the potential well is considered to be E=200.



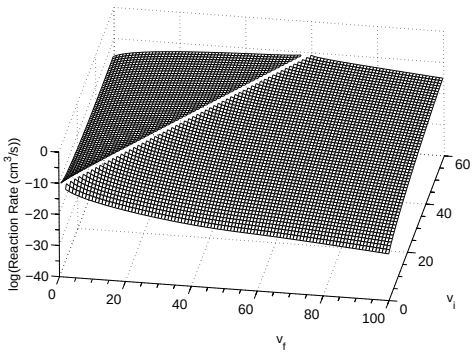
(a) Comparison of the reduced thermal dissociation rate of the FHO dataset for N_2–N_2 collisions and the upper/lower bounds of experimental rates.



(b) Comparison of the reduced thermal dissociation rate of the FHO dataset for O_2–O_2 collisions and the upper/lower bounds of experimental rates.



(c) Comparison of the vibrational level energies of the ground state of N_2, using a polynomial expansion and a potential reconstruction method.



(d) Multiquantum V–T dataset for N_2–N_2 collisions at T=10,000K.

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