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State-to-state dissociation–recombination and chemical exchange rate coefficients in excited diatomic gas flows

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Abstract

In this paper, simple analytical state-to-state rate coefficients for the dissociation–recombination and chemical exchange reactions are presented on the basis of kinetic theory in nonequilibrium excited diatomic gases. They take into account the excited vibrational and electronic states of the chemical species and are expressed according to the preferential character of the chemical reactions. Evolution of these rate coefficients varying according to the translational temperature, bringing into play molecules CO and C_2, are discussed.

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Keywords: State-to-state rate coefficients; Nonequilibrium gas flow; Dissociation; Recombination; Chemical exchange; Vibrational excitation; Electronic excitation; CO; C_2

1. Introduction

The knowledge of the behavior of reactive and radiative nonequilibrium gas flows remains necessary important for a deep understanding of plasma chemistry, atmospheric physics, lasers physics, chemical technology and other fields. It was shown in particular starting from theoretical and experimental studies, that there is a presence of a strong coupling between the internal states of species and chemical reactions [1]. Indeed, one shows that values of the rate coefficients related respectively to vibrational energy exchanges and the dissociation process are of the same order of magnitude on a broad range of temperatures [2–6].

This consequence challenges the majority of multi-temperature models because they are all based on various quasistationary distributions over vibrational populations. At the same time, these multi-temperature models treat often the radiative processes part in an uncoupled way while considering a Local Thermodynamic Equilibrium (LTE) assumption. Those which can lead to significant errors in the evolution of the macroscopic parameters of gas flows, by knowing that the radiative lifespan of the excited chemical species are of the same order of magnitude as the characteristic times of the vibrational energy exchanges and the chemical processes.

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This report resulted also in the rapid development of a state-to-state approach in the kinetic, transport and dynamics fields of real gas flows [1,7]. This approach was extended in the Ref. [8] to take into account the strong coupling between the physico-chemical and radiative processes.

The state-to-state model consists in describing the gas flow starting from its macroscopic parameters, which are the translational temperature, the gas velocity and number densities of the atomic and molecular population levels. These macroscopic parameters are controlled by the momentum and the total energy conservation equations solved simultaneously by the equation of detailed vibrational-chemical-radiative kinetics. It is thus important to calculate with precision the term of production of this last equation. It is given according to the rate coefficients of all processes who lead to the nonequilibrium character of the gas flow, in particular those related to the chemical reactions.

In the case of dissociation processes, we can note that most reliable reactive cross section data come from quantum and quasi-classical calculations [9–16]. These data concern the molecular systems containing H_2, D_2, OH, H_2O, N_2, and other species including excited electronically states. But the number of dissociation reactions remains limited and the direct use of these precise approaches in computational fluid dynamics is possible only by exploiting computing grid technologies [17–19], which at the present time are still under development.

Simpler but less accurate models are thus used in numerical simulations, like those of Marrone–Treanor [20] and of Macheret [21]. However, these models can be used only when the molecules remain in their ground electronic states, which is not the case at high temperature. Indeed, the presence of molecules on their excited electronic states comes from the Vibration–Electronic energy exchanges [22], quantified by their semi-empirical rate coefficients given in Refs. [23,24].

Therefore a generalization of the Marrone–Treanor model was proposed in Ref. [25] to allow the dissociation of the molecules on their excited electronic states. This model gives analytical expression of the dissociation and recombination rate coefficients according to the vibrational and electronic states of the molecules, while taking into account the nonpreferential and preferential dissociations.

These analytical expressions are used for a numerical application of a high enthalpy reactive and radiative COgas flows behind a shock wave [26]. The gas mixture is initially in ambient temperature with a pressure of 500 Pa and the shock speed is 5200 m s^{-1}. The temperature behind the shock reaches approximately 13 000 K. Results obtained show us that dissociation of the molecule on their excited electronic states have an important contribution to the evolution of the macroscopic parameters of the gas flow. However, this numerical application has considered only the CO dissociation as chemical reaction and the related rate coefficients can be used only if the atoms composing the diatomic molecule remain on their ground electronic state. Let us note that in Ref. [27], the necessity to take into account the strong coupling between the physicochemical and radiative processes in order to evaluate with a better precision the evolution that the macroscopic parameters of this gas flow has was shown. Indeed, the radiative lifespan of the CO molecules on its $A^1\Pi$ excited electronic state is of the same order of magnitude as the vibrational energy exchange and chemical collision processes.

However, under the above initial conditions of this CO gas flow, Ramjaun [28] shows in experiments the presence of the radiative system of Swan bands behind the shock. This result proves the existence of the C_2 molecules in their excited electronic states $d^3\Pi$ and $a^3\Pi$. Fairbain [29] suggests that these C_2 molecules come starting from the following chemical exchange process:

$$\mathrm{CO} + \mathrm{C} \leftrightarrow \mathrm{C}_2 + \mathrm{O}, \tag{1.1}$$

while considering the dissociation of these molecules,

$$\mathrm{C}_2 \leftrightarrow 2\mathrm{C}. \tag{1.2}$$

At the same time, let us note the work of Wallaart et al. [30], which studied a CO/Ar/He mixture excited by a laser with pressure of 115 Torr at moderate temperatures. They observed several radiative systems such as that of Swan $\left(d^3\Pi - a^3\Pi\right)$, of Deslandres-d'Azambuja $\left(C^1\Pi - A^1\Sigma\right)$, of Fox-Herzberg $\left(\mathrm{e}^3\Pi - a^3\Sigma\right)$ and of Milliken $\left(D^1\Pi - X^1\Sigma\right)$. These radiations prove the existence of C_2 molecules in their $C^1\Pi$, $\mathrm{e}^3\Pi$ and $D^1\Pi$ excited electronic states.

According to work of Kirby and Liu [31], carbon atoms which can generate these three electronic states by recombination (1.2) must be all excited. These excited atoms can also play a great part in the effectiveness of the chemical exchange (1.1) when the CO molecules become excited, as Piar [32] suggests based on work of Mikulecky and Gericke [33].