State-resolved and multi-temperature reactions rate coefficients for modeling CO_2 flows

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For high-speed and high-temperature flow modeling, internal energy relaxation and chemical reactions have to be taken into account for correct predictions of fluid dynamics and heat transfer. Several approaches, different in accuracy and computational complexity can be used for this purpose. Until recently, the most commonly used models were the one-temperature and multi-temperature flow descriptions; in the present time, advanced computational capacities allow applying more accurate state-to-state models for non-equilibrium reactive flow simulations. State-to-state models assume complete coupling of vibrational relaxation and chemical reactions and describe the flow dynamics in terms of master equations for the populations of all vibrational states; this requires significant computational efforts, especially in CO_2 molecules characterized by multiple vibrational relaxation channels. Therefore there is a need for developing new models for the state-resolved rate coefficients of vibrational transitions and chemical reactions that combine relative simplicity in their implementation and integration to the existing codes, high computational efficiency and good accuracy verified by comparisons with experiments or with the data obtained in the frame of trajectory calculations.

In our recent works [1, 2], we developed simple and accurate models for the state-resolved dissociation rate coefficients in diatomic air species based on the comparison with quasi-classical trajectory calculations. After that, based on the same idea, we studied the state-resolved Zeldovich exchange reaction rate coefficients [3]. As a result, an analytical dependence of the activation energy on the vibrational energy of the reactants and products was found. This allows taking into account vibrational excitation of NO molecules formed as a result of exchange reactions. The state-resolved reaction rate coefficients calculated using the proposed model are in good agreement with the latest data of quasi-classical trajectory calculations [4].

While the reactions in air species are comparatively well studied, the situation with carbon dioxide flows is much more complicated. The objective of the present study is to develop simple reliable models for the state-resolved rate coefficients of exchange reactions taking into account excitation of different CO_2 vibrational modes and to identify dominating reaction mechanisms under various conditions. Since the lack of trajectory data does not allow a direct comparison, we generalize the approach developed previously for diatomic species and apply it for carbon dioxide. The state-dependent exchange reaction, dissociation and inter-mode VV-transition rate coefficients are evaluated in a wide temperature range. Then, multi-temperature rate coefficients for dissociation and exchange reactions in CO_2 are calculated by averaging the state-resolved coefficients with different vibrational distributions. In particular, the two-temperature Boltzmann distribution as well as a more realistic three-temperature distributions taking into account fast inter-mode VV exchange between symmetric and bending modes and slow VT relaxation are used. The effect of vibrational excitation of various modes on the reaction rate coefficients is discussed.

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