Numerical modelling of the CO_2 dissociation in gas discharges including full vibrational kinetics

Vladislav Kotov

Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung - Plasmaphysik (IEK-4), 52425 Jülich, Germany

The plasma chemical conversion $CO_2 \rightarrow CO+\frac{1}{2}O_2$ has been extensively studied in the last decade in view of its application for production of synthetic fuels (Power-2-X). Numerical models is one of the tools which help to understand and optimize the conversion process. Since the total number of vibrational and ro-vibrational states $CO_2\left(v_1, v_2^l, v_3\right)$ up to dissociation energy D=5.5 eV is $\approx 10^5$ it would be numerically prohibitive to include them all into a state-to-state kinetics scheme. Therefore, various reduced approaches exist. In the present work a 'two-modes' approximation [1] based on the assumption of fast equilibration between the symmetric stretching and bending is used. Vibrational states with the same good quantum number $v_s = 2v_1 + v_2$ are gathered together resulting into ≈800 combined states $CO_2\left[v_s, v_a = v_3\right]$ in total.

The model has been benchmarked against the results of the shock tube studies. For conditions of thermal relaxation behind the shock fronts a good agreement between the numerical calculations and the semi-analytic model [2] has been found for translational-rotational temperatures $T \leq 1500$ K. In that temperature range the model can be adjusted to match exactly the experimental vibrational relaxation times. The dissociation process itself is represented in the model by introducing the unstable states with energies larger than D. This approach is backed by a relatively good agreement found between the model calculations and the rate of the process $CO_2 + M \rightarrow CO + O + M$ obtained in shock tubes [3, 4].

The model is applied to the conditions of microwave discharges. Evaluation of the maximum energy efficiency η achievable under those conditions by the purely vibrational mechanism of dissociation will be discussed. In particular, η is found to be very sensitive with respect to the temperature T, e.g. η around 50 % which can be theoretically achieved at T=300 K (degree of ionization 10^{-5}) completely vanishes at $T > 600$ K.

References

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