

Behavior and Modelling of the Vibrational-to-Translational Temperature Ratio at Long Time Scales in CO₂ Vibrational Kinetics*

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Non-thermal microwave plasma reactors can efficiently split the CO₂ molecule. However, big challenges remain before this technology becomes a feasible industrial technology. Computer modelling can be very useful to tackle such challenges. Detailed kinetic modelling is commonly used to get insights into the complex vibrational kinetics of CO₂ as vibrational excitation is strongly related to the energy efficiency in the dissociation process. The vibrational-to-translational temperature ratio has been identified as a key variable to achieve high energy efficiencies and has also been used to simplify detailed CO₂ vibrational kinetics, notably reducing the number of species and reactions required to model the non-thermal plasma.

In this work, we have used a reaction kinetics model to study the vibrational kinetics of CO₂ plasma under the different conditions typically used in CO₂ dissociation experiments in non-thermal microwave plasmas and we showed that Treanor-like vibrational distribution functions can be obtained at low gas temperatures even if vibrational-to-translational (VT) relaxation is included in the calculations. We have also pointed out that symmetric sublevels can play an important role in defining the vibrational distribution function. In fact, at some conditions the vibrational temperature can almost double when VT relaxation of symmetric sublevels is accounted for in the model.

A timescale analysis of the collisional processes based on the first asymmetric vibrational level was performed to get insights into the behavior of the vibrational kinetics. It was found that, in general, vibrational-to-vibrational (VV) relaxation is the fastest process and VT relaxation of asymmetric levels is the slowest process throughout the studied conditions. Moreover, it was found that the VT relaxation of symmetric sublevels limits the

intermode vibrational-to-vibrational (VV') relaxation process. Likewise, at high temperatures, the VT relaxation of asymmetric levels is hindered by the VT relaxation of symmetric sublevels, particularly the VT relaxation of asymmetric sublevels that proceed through the formation of symmetric sublevels b or c. Symmetric sublevels are formed in VV' and VT relaxation reactions. Their subsequent VT relaxation takes place in a descending ladder fashion, being the relaxation of the lowest level a the slowest step in the process. Therefore, it is concluded that the relaxation of symmetric sublevels slows down the relaxation of asymmetric levels and can lead to Treanor-like vibrational distribution functions and higher vibrational temperatures.

We also showed that, while T_V may increase with the gas temperature, the ratio T_V/T decreases with the gas temperature in the studied range of electron temperature and density values. It was also shown that above certain values of gas temperature, the VT relaxation is dominant; no vibrational excitation is attained and thus $T_V = T$. At sufficiently high electron densities, the limit at which the ratio T_V/T becomes 1 is when thermal equilibrium is reached and $T_e = T = T_V$.

Furthermore, we demonstrated that the behavior of the ratio T_V/T with increasing gas temperatures can be fitted to an expression that incorporates the Landau-Teller temperature dependence of VT relaxation (See Figure below). The fittings were evaluated by computing the Adjusted R-square and the Root Mean Square Error (RMSE), yielding both very good results in the gas temperature range of 300-1500 K. Within this temperature range, the average Adjusted R-square is higher than 0.99 and the average Root Mean Square Error (RMSE) is smaller than 0.22. It is to be noted

however, that at temperatures higher than 1500 K, the quality of the fittings decay, although the trends remain correct and the fitted curves approximately match the results of the vibrational kinetics model. This expression can therefore be used to approximately predict the ratio T_v/T at timescales longer than $\sim 10^{-5}$ s, as VT relaxation proceeds and the gas temperature increases, particularly for ionization degrees greater than 10^{-6} and gas temperatures lower than ~ 1500 K.

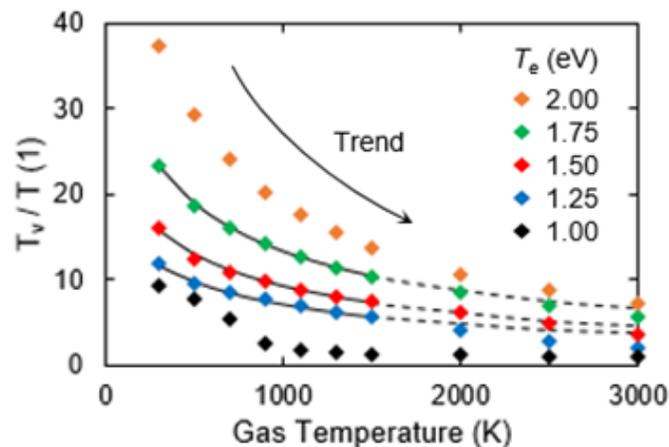


Figure: The long time scale behavior of the vibrational-to-translational temperature ratio in a CO₂ microwave plasma can be described by a simple function of temperature:

$$T_v/T = \frac{A}{T} \exp\left(\frac{B}{T^{1/3}}\right) \text{ with } A \text{ and } B \text{ being fitting parameters.}$$

As the gas temperature increases the non-thermal degree decreases in a very similar way for all electron temperatures. However, at a very low ionization degree ($T_e=1$ eV), the rates of vibrational excitation are also very low and for temperatures higher than ~ 1000 K the VT relaxation completely dominates and $T_v=T$ (see black diamonds).

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Sergio Moreno received his mechanical engineer degree at the Universidad Industrial de Santander in Colombia. After 5 years working in the design, construction, and operation of process plants, he moved to the Netherlands where he received his MSc in mechanical engineering with a

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Andrzej Stankiewicz received his MSc in chemical engineering from Warsaw University of Technology and PhD from the Industrial Chemistry Research Institute in Warsaw. He is Full Professor and Chair of Process Intensification at Delft University of Technology, the Netherlands, and former Director of TU Delft Process

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Georgios Stefanidis is Professor at the National Technical University of Athens (NTUA). He holds a Diploma in Chemical Engineering from NTUA and a PhD degree in the same field from the University of Gent. He has co-authored over 100 peer review publications in the broad field of Process Intensification, mostly focusing on alternative energy forms

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