Insight into energy transfer and NO_x synthesis in the afterglow by chemical multi-temperature plasma modelling

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Abstract: A time-dependent 1D multi-temperature model that couples chemical and vibrational kinetics is proposed, offering insights into the NO_x synthesis and energy transfer mechanism during the quenching process of dry air microwave plasma at atmospheric pressure. The model tracks a set of energy transfer channels occurring at different time scales. The predicted optimal energy cost in the model aligns closely with experimental results.

1. Introduction

Plasma-based nitrogen fixation powered by renewable electricity presents a promising alternative to the energy-intensive Haber-Bosch (HB) process, which is associated with substantial CO_2 emissions [1]. A critical aspect of this approach is the afterglow phase of the dissociated air flow, which contains not only the target product, NO_x, but also reactive species such as atomic oxygen and nitrogen. However, research in this area remains limited.

2. Methods

This study investigates the relaxation of gas and vibrational temperatures under various cooling trajectories, which provides deeper insights into the mechanisms of energy transfer and NO_x formation. In reality, the cooling by thermal conductivity can be increased by gas flow turbulence or external factors [2]. To better represent experimental conditions, the model artificially increases the cooling rate derived from thermal conductivity. A Continuous Stirred Tank Reactor and Plug Flow Reactor models represent the plasma and quenching regions, respectively. The generalized Fridman-Macheret method is employed to calculate reaction rate coefficients enhanced by vibrational excitation [3]. Particular attention is paid to the distribution of energy emitted or consumed in chemical reactions between vibrational and other degrees of freedom.

3. Results and Discussion

The temporal evolution of different temperatures in the quenching process is shown in Fig. 1. A higher cooling rate induces a more pronounced non-thermal behaviour both in the onset and latter parts of the quenching process. The investigation of the vibrational energy transfer processes demonstrates that the predominant factor limiting the non-thermal state is the V-T relaxation of N_2 and O_2 molecules due to collisions with O atoms. The V-V process N_2-O_2 is the primary mechanism for increasing the vibrational temperature of O_2 and its decreasing for N_2 during the latter stages of the quenching process. This process becomes more significant under low gas temperature conditions in the plasma region due to its weaker dependence on gas temperature.

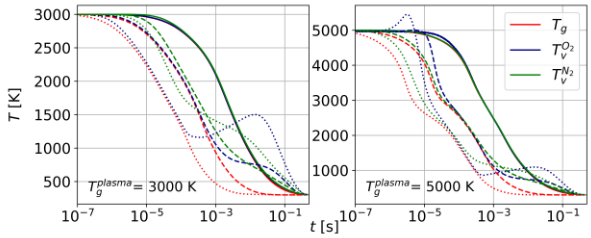

Fig. 1. Evolution of different temperatures as a function of axial distance. T_g^{plasma}, T_g, $T_v^{O_2}$ and $T_v^{N_2}$ represent the gas temperature in the plasma and quenching regions, as well as the vibrational temperatures of O_2 and N_2 in the quenching region. Solid, dashed, and dotted lines correspond to cooling enhanced by factors of 10, 100, and 500, respectively.

4. Conclusion

The optimal cooling rate in the quenching process of microwave plasma depends on the gas temperature in the plasma region: while fast cooling rate can enhance NO_x production at moderate temperatures (3000−4200 K), it becomes less beneficial at higher temperatures due to the reverse Zeldovich reactions. The lowest energy cost for air plasma, calculated at 2.6 MJ/mol under atmospheric pressure, shows good agreement with experimental results [1]. Vibrational non-equilibrium in downstream plays a limited role in enhancing NO_x production under atmospheric pressure. However, incorporating catalysis holds promise for enhancing NO_x formation through the utilization of extra vibrational energy at the end of the afterglow phase, especially at high cooling rates.

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