Boosting the NO_x production in microwave air plasma: A synergy of chemistry and vibrational kinetics

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Abstract: This study employs a quasi-1.5D multi-temperature model to investigate the role of the non-thermal state in NO_x production at 80 mbar. A set of vibrational relaxation processes, along with heat conduction, is considered to explore energy transfer mechanisms in the discharge and afterglow regions. The analysis identifies the primary factors driving NO_x synthesis. The simulation results show good agreement with experimental data.

1. Introduction

Recently, plasma-based nitrogen fixation has garnered increasing attention, offering the potential to replace the Haber-Bosch process and enable carbon-free fertilizer production [1]. While extensive research has been conducted on experiments involving various plasma types, limited studies have focused on simulation of the plasma region for intermediate pressures of 10-100 mbar.

2. Methods

The quasi-1.5D chemical reactor model is based on a long cylindrical tube represented by a network of five connected plug flow reactor (PFR) models. These five PFR models simulate one plasma region and four concentric outer regions in the radial direction, separately. The model is designed to simulate both the discharge and afterglow regions while incorporating the radial diffusion process. By coupling BOLSIG [2], an electron Boltzmann equation solver, with the open-source combustion library Cantera [3], the model calculates the time-resolved evolution of species concentrations and different temperatures, within a gas-plasma kinetics framework. A generalized Fridman-Macheret method is employed to determine reaction rate coefficients enhanced by vibrational excitation [4]. The calculations were performed for the gas flow of 10 slm and the discharge power of 800 W.

3. Preliminary Results and Discussion

The electron energy is transferred predominantly into the vibrational energy of N_2 molecules in the plasma region. As a result, the peak vibrational temperature of N_2 could reach 7000 K, significantly exceeding the gas temperature, (see Fig. 1), in contrast with the results for higher pressures [5]. The ratio of the vibrational temperature of N_2 to the gas temperature in the plasma centre closely matches the values measured by Gatti et al. [6] in pure N_2 microwave plasma under similar pressure conditions. This pronounced non-thermal state results in an NO mole fraction exceeding 10% in the plasma region. Due to radial concentration gradients, a part of NO generated in the plasma region can diffuse outward. In the cooler outer regions, the lower gas temperatures inhibit NO destruction via reverse Zeldovich reactions, thereby increasing overall NO production.

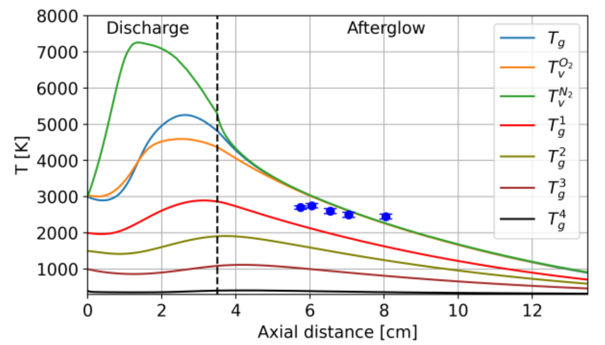

Fig. 1. Evolution of different temperatures as a function of axial distance. T_g, $T_v^{O_2}$ and $T_v^{N_2}$ represent the gas temperature, vibrational temperatures of O_2 and N_2 in the center region of the tube. T_g^1, T_g^2, T_g^3, T_g^4 denote the gas temperatures of the four outer regions in the radial direction. Blue dots represent gas temperatures measured by Raman scattering in the afterglow [7].

4. Conclusion

A pronounced non-thermal state is predicted in the plasma region (see Fig. 1), which favours NO_x production. However, strong vibrational relaxation processes quickly dissipate the non-thermal behaviour at the onset of the afterglow. A comparison between the model and experimental results demonstrates good agreement in both the temperature profile and the total energy cost.

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