$CH_4(v)$ and $H_2(v)$ Kinetics in Nanosecond-Pulsed Discharge Generated in a Preheated Methane Mixture

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Abstract: We report on the role of vibrationally excited CH_4 and H_2 in a nanosecond pulsed $He/CH_4/H_2$ discharge generated in a preheated gas using CHEMKIN. Our modelling suggests that while $CH_4(v)$ contribution towards H_2 formation is low, the vibrational population is significantly underpredicted, and that $H_2(v)$ can contribute towards product selectivity.

1. Introduction

Plasma reforming of methane has attracted a lot of interest due to its ability to drive otherwise kinetically difficult chemistry at lower temperatures [1]. However, the kinetics of plasma-produced species in the context of ns-pulsed discharge, especially that of vibrationally excited species, are not well understood.

Here we use CHEMKIN model for a ns-pulsed discharge kinetics with preheated gas (~ 600 K). Initial findings suggest that (a) the vibrational populations, especially that of $CH_4(v_{24})$ are significantly underpredicted and (b) $H_2(v)$ can affect the decay of atomic carbon, affecting the yield and selectivity of carbon products produced.

2. Methods

A 0-D Plasma PSR transient model was used to simulate the nanosecond pulsed discharge in a preheated 95% He/2.5% CH_4/2.5% H_2 mixture (T = 600 K, P = 250 Torr, ~ 200 sccm flow, V = 2 cm^3, 2 kW plasma input power, 500 ns pulse, 1 kHz frequency). The reaction mechanism and thermodynamic data used were the same as [2], with the electron-impact collision rate coefficients being approximated as equivalent Arrhenius form dependent on electron temperature obtained from fitting the rate coefficients as a function of electron temperature for a given reaction threshold energy calculated from BOLSIG+ [3] for 2 eV ≤ T_e ≤ 7 eV range. $R^2 \geq 0.8$ were obtained for the equivalent Arrhenius fitting for all reactions except for C_3H_8 dissociation reactions, which is a minor species in this case. The electron temperatures predicted by the simulation during the plasma pulse ranged between 2 and 6 eV, justifying the assumed range for the fitting.

3. Results and Discussion

Comparing the total rate of production of H_2 the contribution of vibrationally excited methane was found to be up to ~ 0.8% in the afterglow. On the other hand, > 90% of C consumption during the early afterglow was predicted to be due to $H_2(v)$ ($C + H_2(v) \rightarrow CH + H$), which can affect the selectivity of carbon products. It was observed that the gas temperature can reach up to ~ 930 K at quasi-steady state. Fig 1 shows the mole fraction variation of total vibrational excitation of the ν_{13} and ν_{24} modes of $CH_4(v)$ and v = 1-3 levels of $H_2(v)$ along a quasi-steady state pulse and compares with the mole fractions assuming Boltzmann Vibrational Distribution at $T_{vib} = T_g$ calculated from the respective vibrational partition functions [4]. We observe that the methane vibrational populations are massively underpredicted and even though H_2 exhibits vibrational excitation, relaxation is overpredicted. This suggests that the current model underpredicts vibrational kinetics and therefore experimental investigation is necessary, which would be discussed in detail during the presentation.

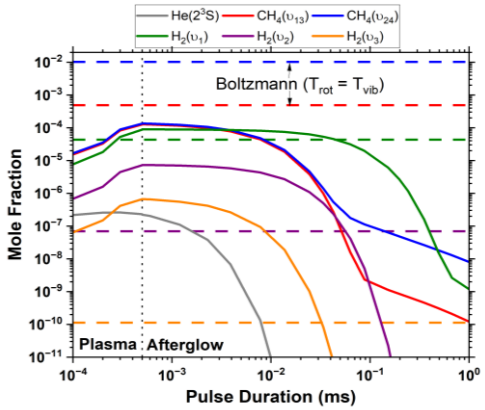

Fig. 1. Mole fraction of $CH_4(v)$ and $H_2(v)$ over the duration of a quasi-steady state pulse (dashed line represents Boltzmann distribution at $T_{vib} = T_g$)

4. Conclusion

The modeling predictions suggest a possible underprediction of the role of vibrationally excited species, especially CH_4 while vibrationally excited hydrogen can affect the yield and selectivity of carbon products produced, therefore demanding further experimental evidence to be discussed.

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