Non-equilibrium vibrational kinetics and energy transfer in plasma-enhanced methane reforming

G. H. Kim[1], Z. Chang[1], B. Mei[1], Z. Shi[1], T. K. Srivastava[1], M. Adil[1], Y. Ju[1,2]
[1] *Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08540, USA*
[2] *Princeton Plasma Physics Laboratory, Princeton, NJ 08540, USA*

Abstract: This work reports measurements of translational-rotational and vibrational temperatures of vibrationally excited methane (CH_4(v)) in alternating current (AC) dielectric barrier discharge (DBD) nonequilibrium plasma. Time resolved absorption spectra are acquired to capture the rapid evolution of the CH_4(v) vibrational temperature and further investigate the CH_4 vibrational energy transfer process.

1.Introduction

Non-equilibrium (NE) plasma-assisted low-temperature reforming of CH_4 offers a promising approach to overcome the challenges in conventional dry methane reforming. Recent studies indicate that vibration-to-vibration (V-V') energy transfer of CH_4(v) with other species generated in NE plasmas can enhance reaction efficiency in plasma-driven chemical reforming [1]. In this study, we employed infrared laser absorption spectroscopy (IR-LAS) to measure the translational-rotational (T_{rot}) and vibrational temperatures (T_{vib}) of CH_4(v) in plasma.

2. Methods

The CH_4 asymmetric bending mode (**ν_4**) is targeted in a plane-to-plane double dielectric barrier discharge (DBD) plasma reactor with an alternating current (AC) power supply. Details of the reactor setup can be found in Lefkowitz et al. [2]. The plasma is produced in a CH_4/He (40%/60%) mixture at a flow rate of 300 sccm, a pressure of 18 torr, and peak-to-peak voltage of 3.8 kV, with a discharge current of 20 mA, and a frequency of 22 kHz. A continuous-wave external-cavity quantum cascade laser (Daylight Solutions 21074-MHF) is scanned at 100 Hz with a sinusoidal waveform sent from an arbitrary function generator to the controller for the piezo-electric actuator in the laser cavity. Two absorption lines from the first excited vibrational level, located at 1320.40 cm^{-1} and 1320.49 cm^{-1}, are used to measure T_{rot} and T_{vib} of CH_4(v) following the methodologies of Farooq *et al* [3] and Jelloian *et al* [4].

3. Results and Discussion

T_{rot} and T_{vib} were measured through scanned wavelength direct absorption spectroscopy (DAS) at 100 Hz. The measurements show thermal equilibrium is established at approximately 320 K. This observed equilibrium is likely due to the rapid vibrational-translational (V-T) relaxation of CH_4(v), occurring on a timescale of 50 µs at a pressure of 18 torr [5]. To further resolve the vibrational non-equilibrium and the rapid V-V' energy transfer of CH_4(v), sub-microsecond time-resolved, broad scanning range measurements are required. To resolve this, we will apply a step-scan technique [6], acquiring absorption data at sub-microsecond scale with the laser frequency fixed at a specific wavelength. The absorption spectrum will be constructed by scanning the laser frequency with a step size of 0.01 cm^{-1} and repeat the experiments.

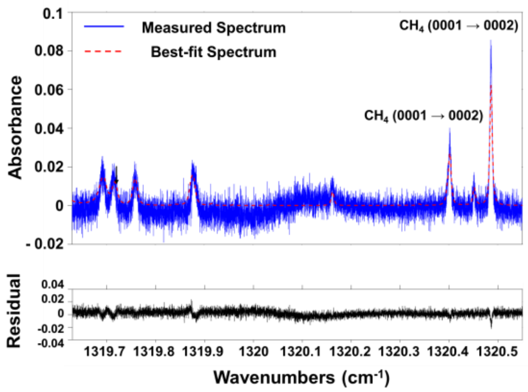

Fig. 1. Comparison of the experimental and simulated (HITRAN) CH_4 absorption spectra in AC DBD plasma containing 40% methane in helium at 18 Torr.

4. Conclusion

This work provides insights into the rovibrational characteristics of CH_4(v) in AC DBD plasma. The DAS measured T_{vib} and T_{rot} confirm rapid V-T relaxation, resulting in thermal equilibrium at approximately 320K. Time-resolved measurements of CH_4(v) T_{rot} and T_{vib} will be acquired to further reveal the rapid vibrational kinetics and V-V' energy transfer process in NE plasma.

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