Hybrid fs/ps CARS vibrational population measurements of N_2 in nonequilibrium DC plasma

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Abstract: We present N_2 vibrational population and gas temperature measurements in N_2/H_2 DC discharge using a 3-beam hybrid fs/ps coherent anti-Stokes Raman scattering system. It is found that the addition of H_2 to pure N_2 DC discharge reduces the vibrationally excited $N_2(v)$ population. These results provide insights into the roles of vibrationally excited $N_2(v)$ in plasma-assisted NH_3 synthesis.

1. Introduction

Vibrationally excited species play important roles in plasma-assisted ammonia synthesis [1]. Recent study shows that V-V and V-V' transfer of $N_2(v)$ and $H_2(v)$ provide new reaction pathways for N, H, and NH radical generation, which greatly enhance ammonia yield [2]. Time-resolved, quantitative vibrational population distribution of $N_2(v)$ and $H_2(v)$ is therefore required to understand the underlying kinetics and dominant reactions in plasma-assisted ammonia synthesis. Richards et al. performed time-resolved $N_2(v)$ measurements in ns pulsed and RF N_2/Ar/He discharges [3]. Bayer et al. measured $N_2(v)$ in an Ar/N_2/H_2 plasma using molecular beam mass spectroscopy [1]. In this work, we demonstrate a 3-beam hybrid fs/ps coherent anti-Stokes Raman scattering (CARS) system for vibrational population measurements of $N_2(v)$. In addition, the gas temperature is measured through the pure-rotational N_2 spectra. These measurements are compared with theoretical models to provide insights into the roles of vibrationally excited $N_2(v)$ in plasma-assisted NH_3 synthesis.

2. Methods

The hybrid fs/ps CARS system is consisted of a Ti:Sapphire amplifier, an optical parametric amplifier (OPA), and a second harmonic bandwidth compressor (SHBC). The amplifier outputs 800 nm pulses at 1 kHz and is used to pump the OPA and SHBC. The OPA output wavelength is set to 675 nm to target the Q-branch Raman transitions of the N_2 molecule. Both the N_2 vibrational and pure-rotational spectra are collected by a spectrometer and intensified CCD camera. The DC plasma reactor is based on a previous design [4], featuring a pin-to-pin discharge with a gap distance of 8.5 mm. The pressure is set to 75 torr with a total flow rate of 500 sccm, and the voltage is set to 2 kV. Measurements were performed at both the anode and cathode pin in pure N_2 and N_2/H_2 (80%/20%) DC plasmas. For each condition, a total of 1000 frames were acquired at 162 Hz.

3. Results and Discussion

The averaged N_2 spectra at the anode pin are shown in Fig. 1. Vibrational bands up to v=9 are observed for the pure N_2 case. It is obvious that the addition of H_2 reduces the population of vibrationally excited $N_2(v)$. This is likely due to V-V' exchange and V-T relaxation of $N_2(v)$ by H_2 [1-2]. Using the Boltzmann relationship, the first level vibrational temperature $T_{v(1,0)}$ can be calculated based on the square root intensity of the $v = 0$ and $v = 1$ bands. For the pure N_2 plasma, $T_{v(1,0)}$=2325 K, while $T_{v\,(1,0)}$ drops to 1804 K with the addition of 20% H_2. Strong vibrational non-equilibrium is observed in both cases as the second level vibrational temperature ($T_{v\,(2,1)}$) increases to 4790 K and 4621 K for the pure N_2 and N_2/H_2 mixture case, respectively.

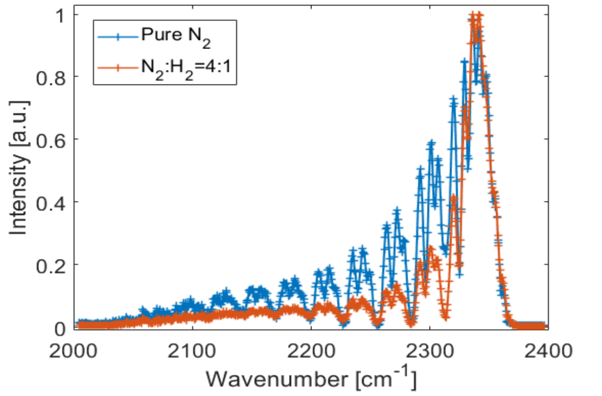

Fig. 1. Averaged N_2 vibrational CARS spectra probed at the anode pin in pure N_2 and N_2/H_2 DC plasma.

4. Conclusion

Vibrationally excited $N_2(v)$ is measured up to v=9 using hybrid fs/ps CARS. The results show that the addition of 20% H_2 in a pure N_2 DC discharge significantly lowers the population of vibrationally excited $N_2(v)$. Future work will focus on measuring the vibrationally excited $H_2(v)$ population and to understand the roles of $N_2(v)$ and $H_2(v)$ in plasma-assisted NH_3 synthesis.

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References

[1] B. Bayer et al., Plasma Sources Sci. Technol., **32**, 125005 (2023).

[2] N. Liu et al., ACS Energy Lett., **9**, 2031-2036 (2024)

[3] C. Richards et al., Plasma Sources Sci. Technol., **31**, 034001 (2022).

[4] T. Chen et al., Optics Lett. **47**, 1351-1354 (2022)