Hybrid fs/ps CARS measurements of enhanced vibrational excitation of N_2 in ferroelectric barrier discharge

Yijie Xu[1], Ziqiao Chang[1], Tanubhav K. Srivastava[1], Yiguang Ju[1,2]
[1]*Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, USA*
[2]*Princeton Plasma Physics Laboratory, Princeton, USA*

Abstract: We report measurements of $N_2(v)$ in a ferroelectric barrier discharge by a 3-beam hybrid fs/ps coherent anti-Stokes Raman scattering system. Findings show that the high surface charge induced by ferroelectrics significantly enhances the vibrational excitation in N_2 plasma. These results provide valuable insight into the unique properties of ferroelectric barrier discharges and their potential application for ammonia synthesis.

1. Introduction

Non-equilibrium plasma has demonstrated significant potential for distributed and green chemical manufacturing across various applications. Incorporating ferroelectric materials into non-equilibrium plasma can increase surface charges and enhance the production of excited species that facilitate critical chemical reactions to reduce kinetic barriers and enable unique non-equilibrium pathways at low temperatures.[1] However, critical experimental investigations into plasma chemistry, specifically regarding vibrational excited species, are still lacking for ferroelectric barrier discharge.

Here, we use a 3-beam hybrid fs/ps coherent anti-Stokes Raman scattering system to quantitatively measure the vibrational excitation of N_2 molecules in ferroelectric barrier discharge and to understand the role of ferroelectric barriers in affecting non-equilibrium of plasma discharges.

2. Methods

The plasma reactor is designed in a plate-to-plate manner as detailed in previous work [2]. The ferroelectric barrier discharge (FBD) and normal dielectric barrier discharge (DBD) are generated with a layer of lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$, PZT) and Al_2O_3, respectively. The two electrodes are separated by a 5-mm gap and enclosed in a rectangular quartz channel. In all experiments, both FBD and DBD are operated using an AC power supply at a frequency of 20 kHz with a peak-to-peak voltage of 2.6 kV. The gas flow rates are set to maintain a residence time of 0.05 seconds at a pressure of 10 torr. Measurements are performed in both pure N_2 and N_2/H_2 (1:3) plasmas.

The hybrid fs/ps CARS system is composed of a Ti:Sapphire amplifier, an optical parametric amplifier (OPA), and a second harmonic bandwidth compressor (SHBC). The amplifier generates 800 nm pulses at 1 kHz, which are used to pump both the OPA and the SHBC. The OPA output wavelength is tuned to 675 nm to target the Q-branch N_2 Raman. The probe time delay is set to 2 ps. The spectra are collected by a spectrometer and intensified CCD camera. For each condition, 100 frames are saved on average, with 20 exposures of 300 ns per frame.

3. Results and Discussion

The N_2 vibrational CARS spectra of FBD and DBD in pure N_2 and N_2/H_2 mixture are shown in Fig. 1. The population of vibrationally excited nitrogen is greatly increased in FBD compared to DBD, which can be attributed to the higher reduced electric field in FBD [2]. In addition, this enhancement exists in both pure N_2 and N_2/H_2 mixture cases. The first level vibrational temperature $T_{v(1,0)}$ can be calculated using the Boltzmann relationship based on the relative intensity of the v=0 and v=1 bands. For the pure N_2 FBD, $T_{v(1,0)}$ = 1332 K, while $T_{v(1,0)}$ slightly drops to 1210 K with the addition of H_2.

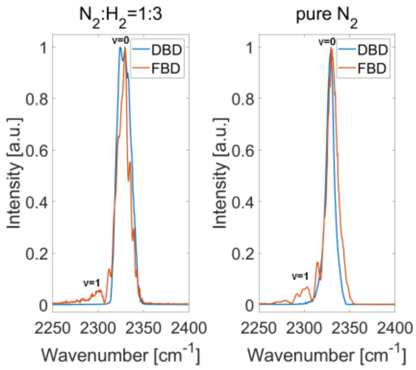

Fig. 1. Averaged N_2 vibrational CARS spectra of FBD and DBD in pure N_2 and N_2/H_2 mixture.

4. Conclusion

In this study, we investigate the formation of critical $N_2(v)$ in a non-equilibrium ferroelectric barrier plasma discharge. The preliminary results show that the introduction of ferroelectric materials enhances the vibrational excitation of nitrogen in both N_2 and N_2/H_2 discharges. Further in-situ, time-resolved research will be conducted to offer high temporal resolution, enabling precise tracking of species populations. Ultimately, the findings from this research provide valuable insight into the unique properties of ferroelectric barrier discharges.

Acknowledgment

This work is supported by the DOE Office of Science's BES EERC grant: DE-AC0209CH11466.

References

[1] A. Lele et al., Phys. Chem. Chem. Phys., **26**, 9453-9461 (2024).
[2] Y. Xu et al., Nat Commun, **15**, 3092 (2024).