kinetics of N_2 vibrational excitation in a pulsed air discharge

Jun-Jie Qiao[1] , Qi Yang[1] and Qing Xiong[1]

[1] *State Key Laboratory of Power Transmission Equipment and System Security and New Technology, Chongqing University, Chongqing, PR China*

Abstract: Vibrational-excited nitrogen molecules play an essential role in plasma nitrogen fixation through the well-known Zeldovich process. In this work, efforts were devoted to discovering spark or glow, which is more energy efficient in producing vibrational-excited nitrogen molecules. A DC pulse with 70 ns rasing edge and 50 us width was applied to the pin-pin electrodes. Due to the 120 kΩ resistor cascade in the cathode, the intense spark transforms to the glow mode shortly after the breakdown. Coherent anti-stokes Raman scattering (CARS) for N_2 was established to measure the number density of N_2(v≥0), both shortly after the spark and within the glow discharge phase. On the one side, the spark discharge gives rise to a vibrational temperature higher than 3000 K while maintaining the gas temperature as low as 400 K. On the other side, both vibrational and gas temperatures rise to higher than 2000 K within the glow region. Besides, after the spark discharge, vibrational temperature descends with a lifetime of about 25 us. And from the global kinetic simulation, the inevitable and intense gas heating accelerates the vibrational-translational (V-T) energy exchange and dissipates the energy injected into the glow discharge. Generally, compared with the stable glow discharge, the transient spark discharge lead the energy to vibrational states more efficiently.

Keywords: Coherent Anti-stokes Raman Scattering, nitrogen fixation, vibrational kinetics

1. Introduction

Plasma-based nitrogen fixation has great potential for enabling carbon-free fertilizer production powered by renewable electricity. However, compared with the well-developed Haber-Bosch process, plasma-based nitrogen fixation is still trapped in research laboratories for its low energy efficiency, although its theoretical limit of energy consumption through the Zeldovich process is lower than the Haber-Bosch process[1]. As shown in equation (1-2), vibrational-excited nitrogen molecules are essential in the Zeldovich process. Spark and glow, two kinds of discharge usually used to transform air into nitrogen oxide, show their capability in reducing energy consumption, even close to the Haber-Bosch process[2,3]. Nevertheless, the production of vibrational-excited nitrogen molecules in spark and glow discharge remains limitedly understood, let alone the energy efficiency of $N_2(v)$ in these discharge.

$$N_2(v) + O \rightarrow NO + N \quad (1)$$

$$N + O_2 \rightarrow NO + O \quad (2)$$

In this work, efforts were devoted to finding out spark or glow, which is more energy efficient in producing vibrational-excited nitrogen molecules. A DC pulse with 70 ns rasing edge and 200 us width was applied to the pin-pin electrodes. Due to the 120 kΩ resistor cascade in the cathode, the intense spark transforms to the glow mode shorter after the breakdown. Coherent anti-stokes Raman scattering (CARS) for N_2 was established to measure the number density of N_2(v≥0), both shortly after the spark and within the glow discharge region. Besides, a global kinetic simulation was implemented to give deep insights into the production and loss mechanism.

2. Experimental setup and theoretical method

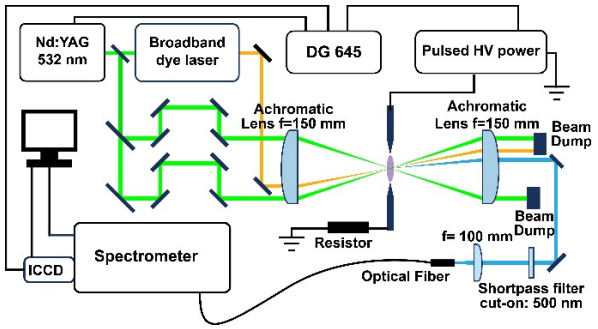

Fig. 1. CARS setup.

The second harmonic of an Nd:YAG laser (532 nm, Spectra-Physics, 8 ns FWHM, 10 Hz repetition rate) is used both as the pump for the homemade broadband dye laser and pump/probe beams for the CARS process. A three-dimensional folded BOXCARS phase-matching geometry is adopted to achieve a spatial resolution along the beam path of 0.6 mm. The anti-stokes signal was first collimated, then passed through a shortpass filter to reduce stray light from the lasers, and finally guided to the spectrometer (Andor, SR750, 1200 lines mm^{-1}) equipped with an intensified camera (Andor, DH340T).

The measured CARS spectroscopy was first corrected with the profile of stokes laser and then fitted following the algorithm from Jan Kehfeld et al [4]. From the fitting procedure, rotational (which usually equals gas temperature at atmospheric), first-level vibrational, and vibrational temperature of N_2 were determined. The total number density of N_2 was determined by ideal gas law, and then the number density for every vibrational state was determined. Besides, with the help of ZDPlaskin [5], a

global model was implemented to investigate the vibrational kinetics.

As the discharge setup, pin-pin electrodes made by tungsten were fixed with a distance of 2 mm, and a pulsed positive high voltage, with 70 ns rising edge and 50 us width, was applied on the anode at the repetition rate of 10 Hz. The high voltage power was homemade with fast high voltage solid-state switching modules in MOSFET. The experiment used dry air with a flow rate of 1.5 L/min. Discharge voltage and current were monitored by high voltage probe (Tektronix P6015A) and a current probe (Tektronix TCP0020).

3. Results and discussion

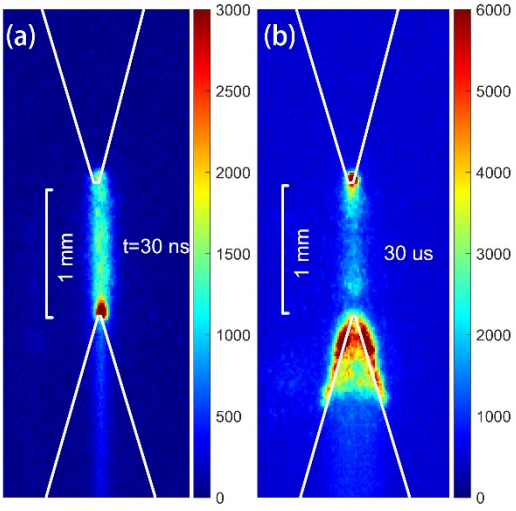

Fig. 2. (a): ICCD image of spark phase (gate with=2 ns), and (b): glow phase (gate width=2 us).

As shown in Fig. 2, due to the 120 kΩ resistor in the cathode, the discharge presents two phases: intense spark and mild glow. These separated discharge phases are also evident in the voltage and current waveform shown in Fig .3.

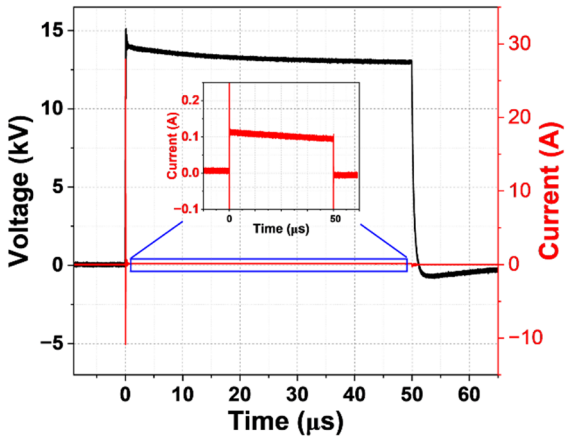

Fig. 3. Waveforms of discharge voltage and current.

The voltage was detected from the anode, and the current was detected from the cathode. At the spark phase, a peak current up to 28 A was detected; at the glow phase, the current was only about 0.1 A for the restriction of current by the 120 kΩ resistor. Shorter after the breakdown, the resistor prevents the discharge development from spark to arc and finally restricts the current at 0.1 A,

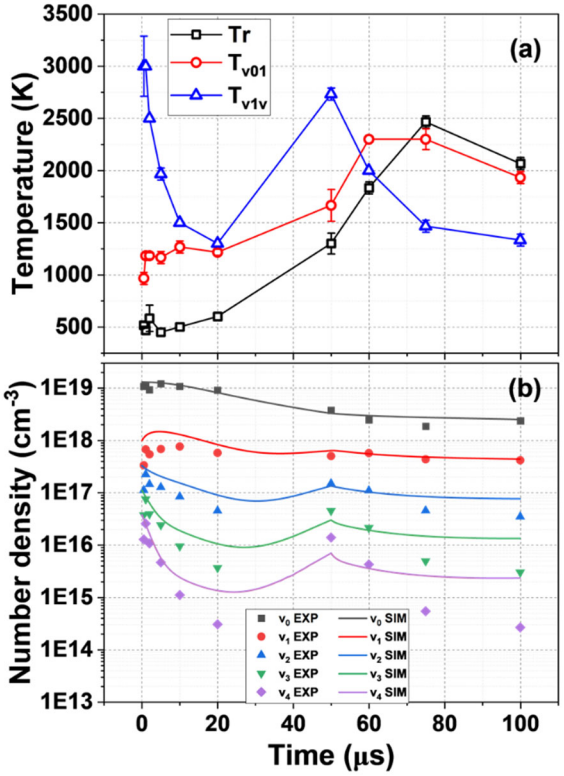

Fig 4. (a): temperature evolution; (b): measured (scatter) and simulated (line) number density of vibrational state N_2(v=0-4).

By the procedure described in section 2, rotational, first-level vibrational, and vibrational temperature were shown in Fig.4. (a). Evidently, the transient intense spark discharge excited a considerable amount of vibrational-excited nitrogen molecules with little gas heating. After the spark, the vibrational-excited nitrogen molecules dropped quickly through the vibrational-translational (V-T) energy exchange, as shown in equation (3).

$$N_2(v > 0) + O \rightarrow N_2(v - 1) + O \qquad (3)$$

Under the effect of V-T energy exchange and glow heating, the gas temperature gradually increases to higher than 2000 K, inducing the increase of reduced electric field (E/N). Higher E/N leads more energy to vibrational states and eventually results in a vibrational temperature of about 2500 K. Because of the inevitable gas heating in the glow phase, energy efficiency for vibrational-excited states exciting is obviously lower than that of the spark phase. After the whole voltage pulse, the vibrational temperature decreased quickly through the V-T energy exchange while the rotational temperature decrease slowly within 100 us.

4. Conclusions

CARS spectroscopy was established to diagnose a pulsed pin-pin discharge in air, giving the density of vibrational-excited nitrogen molecules. Due to the restriction of discharge current by the resistor, two discharge phases were observed, spark and glow. By the measurement of CARS and the global model simulation, due to the inevitable V-T energy exchange and its result in gas heating at the glow phase, spark discharge shows better energy efficiency in exciting vibrational states of N_2. This result will be significant and instructive for nitrogen fixation by air discharge plasma.

5. References

[1] Brandenburg R, Bogaerts A, Bongers W, Fridman A, Fridman G, Locke B R, Miller V, Reuter S, Schiorlin M, Verreycken T and Ostrikov K (Ken), *Plasma Process Polym* **16** 1700238 (2019)

[2] Pei X, Gidon D, Yang Y-J, Xiong Z and Graves D B, *Chemical Engineering Journal* **362** 217–28 (2019)

[3] Britun N, Gamaleev V and Hori M, *Plasma Sources Sci. Technol.* **30** 08LT02 (2021)

[4] Kuhfeld J, Lepikhin N D, Luggenhölscher D and Czarnetzki U, *J. Phys. D: Appl. Phys.* **54** 305204 (2021)

[5] S. Pancheshnyi, B. Eismann, G.J.M. Hagelaar, L.C. Pitchford, Computer code ZDPlasKin, http://www.zdplaskin.laplace.univ-tlse.fr (University of Toulouse, LAPLACE, CNRS-UPS-INP, Toulouse, France, (2008).