Advancing Sustainable Ammonia Synthesis through Plasma-Assisted Catalysis

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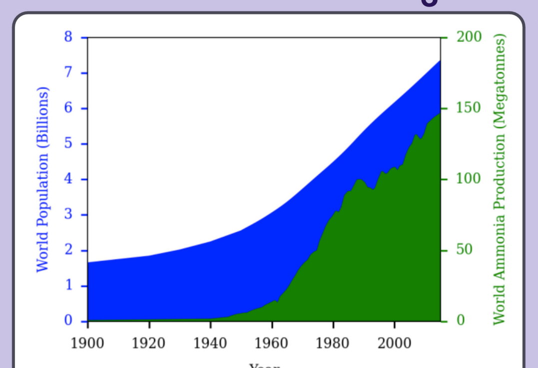
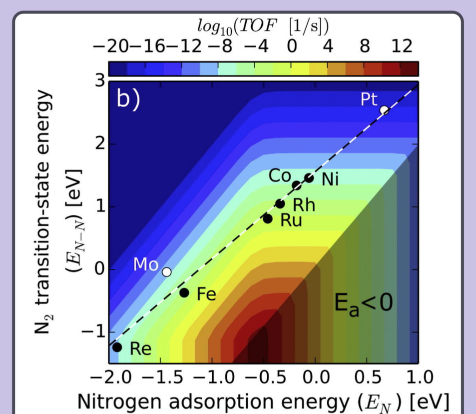
Introduction

Can we make a low pressure, low temperature NH_3 synthesis process?



50% of the nitrogen in the human body was once on an Haber-Bosch catalyst

(*DOE Roundtable Report, 2016*)

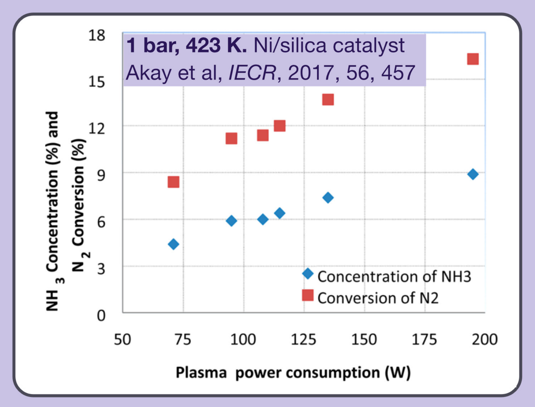


Medford *et al*, J. Catal., 2015, 328, 36

Haber-Bosch conditions:

- 100-150 bar
- 700-800 K

Limited by scaling relations: Materials that easily dissociate N_2 bind NH_x too strongly

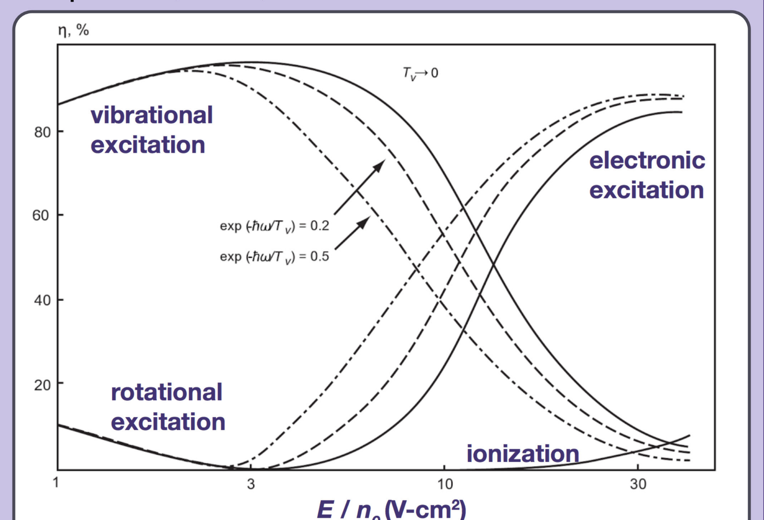


Near ambient synthesis possible with plasma-catalysis

Mechanisms; roles of plasma and catalyst unknown

Plasma: a non-thermal, non-photo means of putting energy into a system

- Gas ionized by an electric discharge
- Comprised of reactive intermediates: electronically and vibrationally excited species, ions, radicals

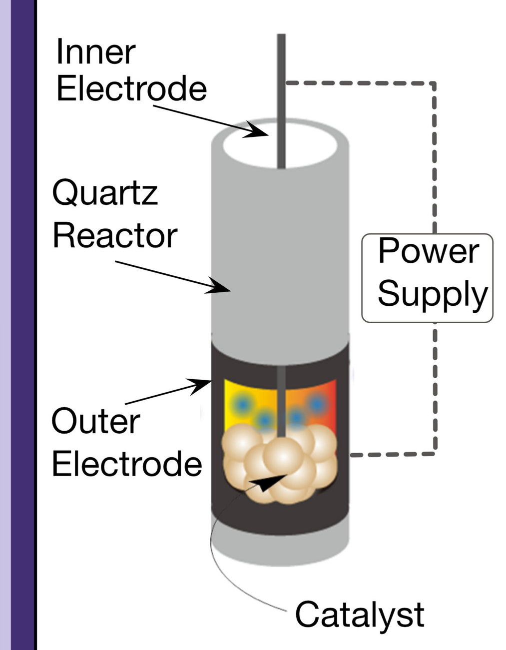


Electron energy distribution between different excitation channels in nitrogen (Fridman, *Plasma Chemistry*, 2008)

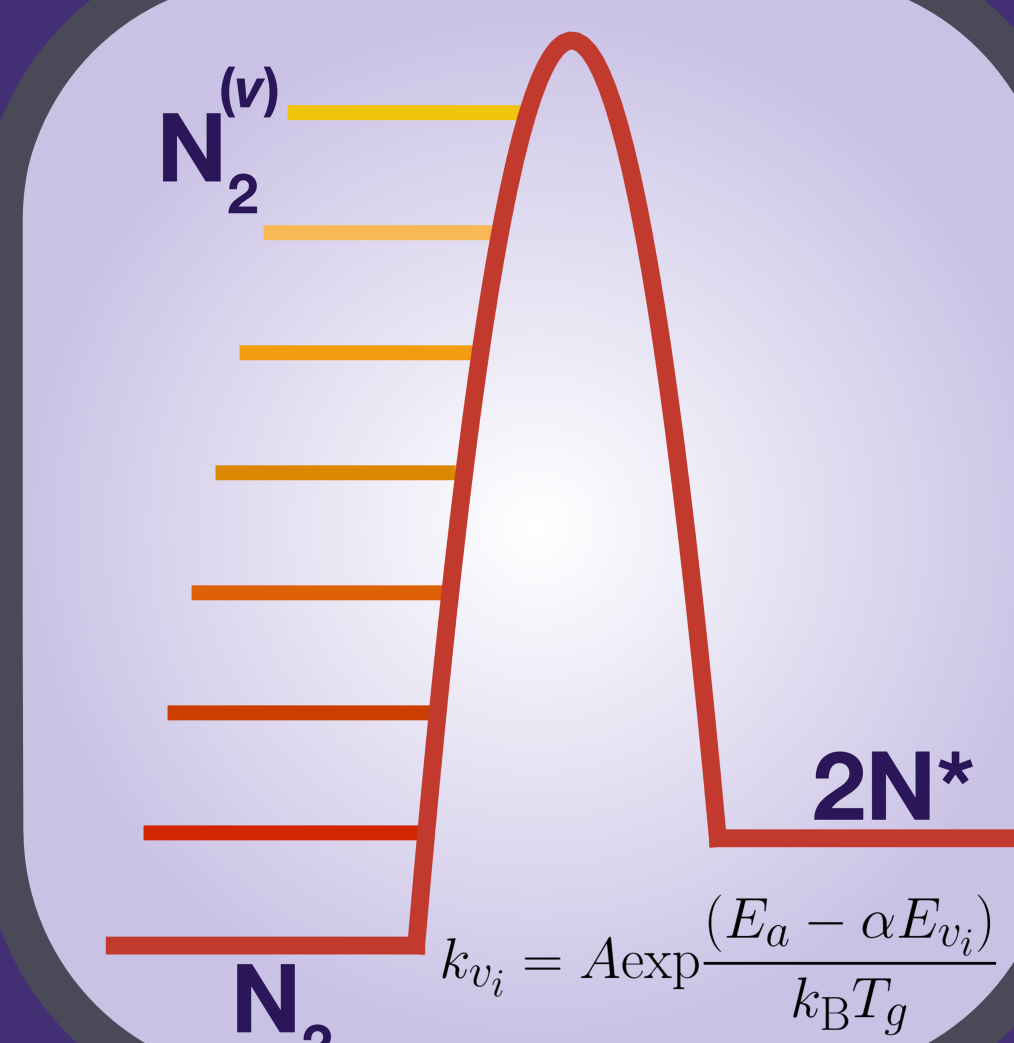
Dielectric Barrier Discharge

- Non thermal plasma: $T_{elect} > T_{vib} > T_{rot} \cong T_{trans}$
- Atmospheric pressure

DBD Reactor



Kim, Abbot, Go, Hicks, *ACS Energy Lett*, 2016, 1, 94
Kim, Go, Hicks, *PCCP*, 2017, 19, 13010



$$k_{v_i} = A\exp\frac{(E_a - \alpha E_{v_i})}{k_B T_g}$$

Reaction Kinetics

Experimental conditions

1 atm, no external heating (T ~ 400 K), 10 W, 20 ml/min

Computational details

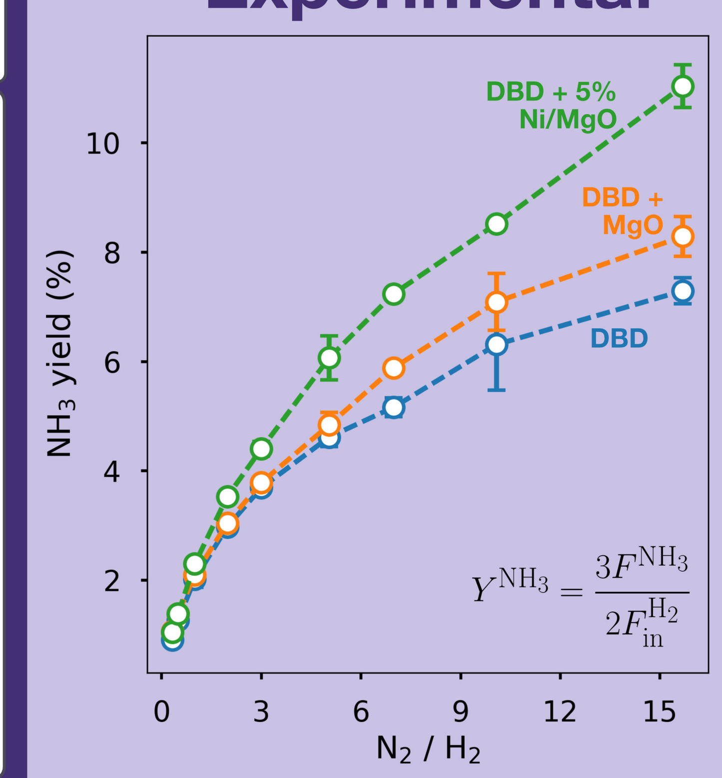
1: $N_2(g) + 2^* \rightarrow 2N^*$
2: $H_2(g) + 2^* \rightarrow 2H^*$
3: $N^* + H^* \rightarrow NH^* + ^*$
4: $NH^* + H^* \rightarrow NH_2^* + ^*$
5: $NH_2^* + H^* \rightarrow NH_3^* + ^*$
6: $NH_3^* \rightarrow NH_3(g) + ^*$

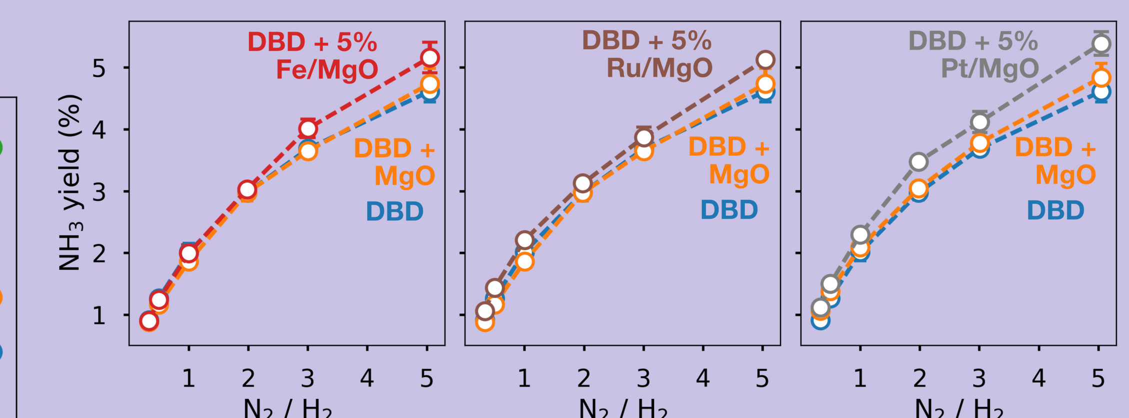
DFT energies from CatApp

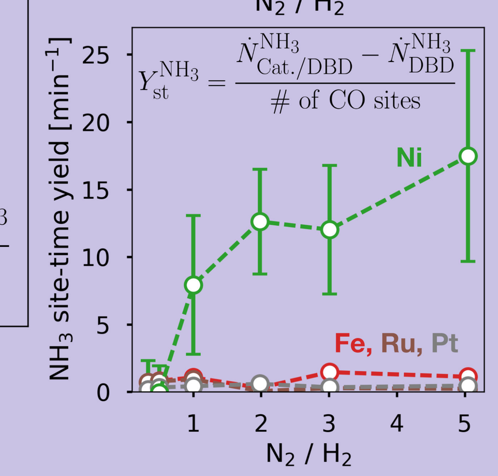
No rds assumption; ODEs integrated to steady state

Excitation lowers E_{act} for R1 (Fridman α model)

Experimental

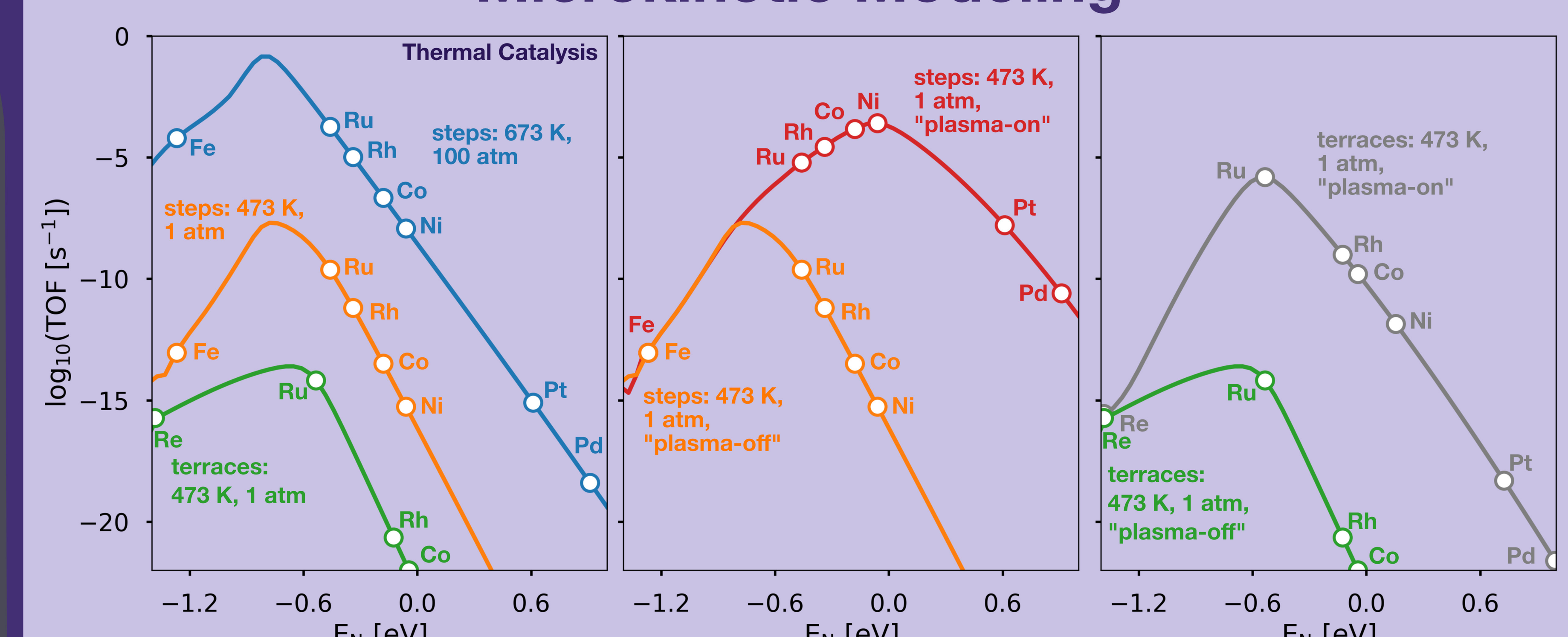






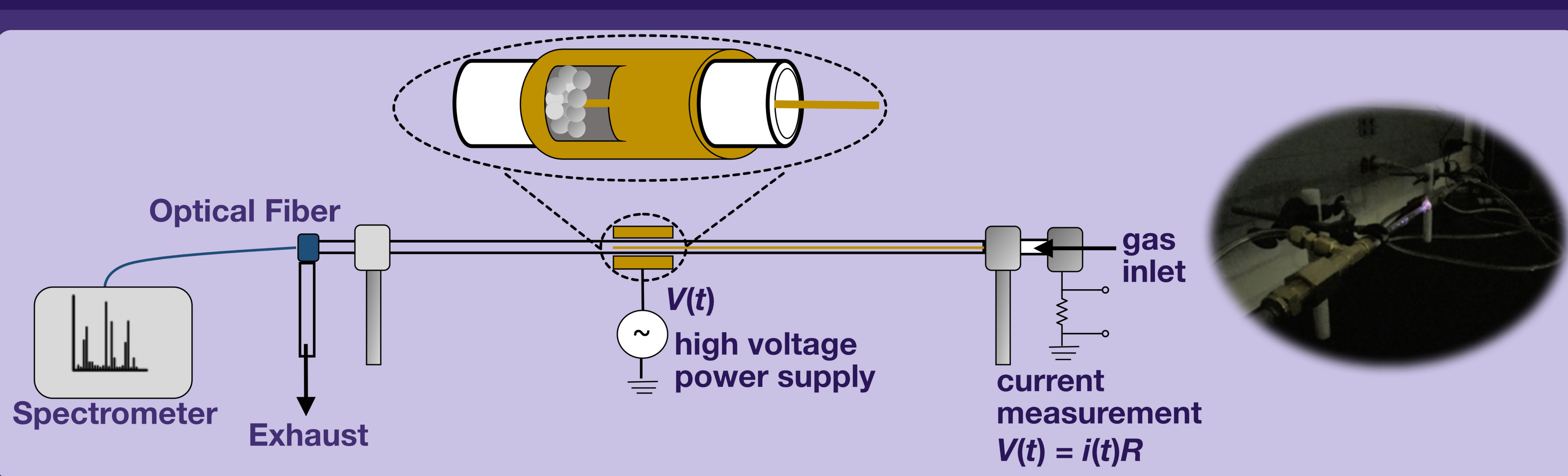
- Ammonia yields obtained under plasma only conditions; enhanced by metal catalysts
- Yields increase with increasing N_2 concentration
- No ammonia detected with thermal catalysis in the absence of plasma
- Ni outperforms other metals under plasma conditions

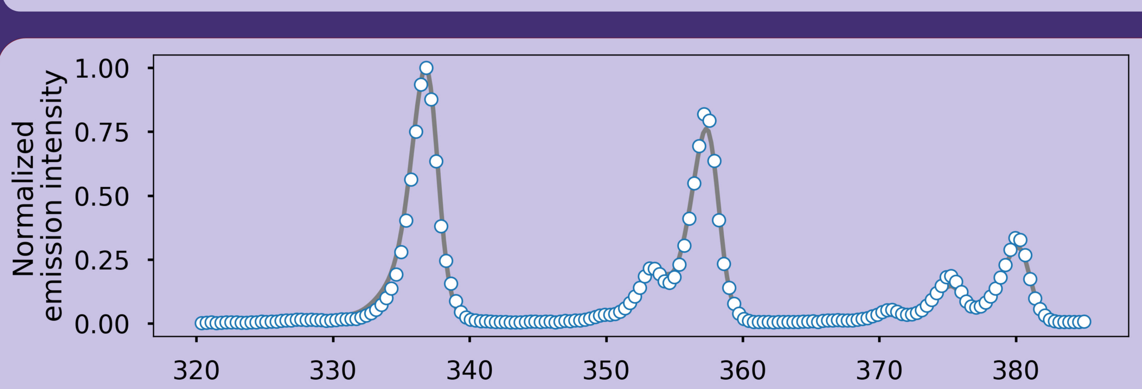
Microkinetic Modeling



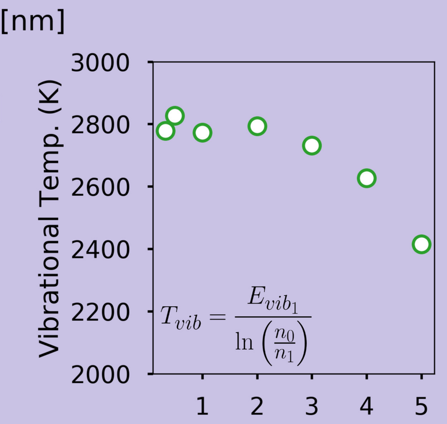
- NH_3 synthesis rates may increase by many orders of magnitude by vibrational excitation of N_2
- Rates can increase until limited by a hydrogenation step (hydrogenation barriers larger on left of volcano)
- Top of volcano shifts right on steps: Ni most active
- Plasma-catalysis rates of optimal catalyst comparable to Haber-Bosch rates

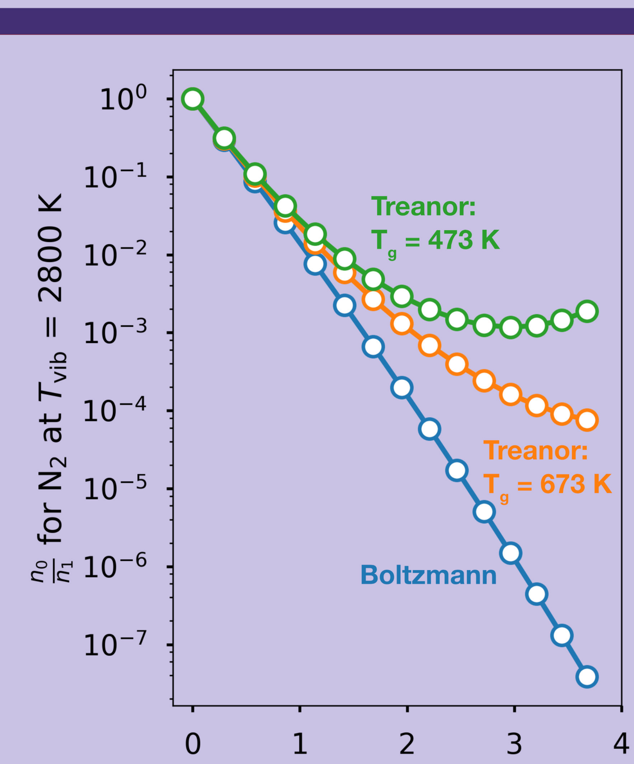
Plasma Characterization





- Optical emission spectroscopy (OES) used to extract vibrational and rotational temperatures at different N_2:H_2 ratios and input power
- N_2 vibrational temperatures tend to decrease at higher N_2 concentrations
- Boltzmann and Treanor vibrational distributions fit to T_{vib} for input into microkinetic models





Non-equilibrium vibrational kinetics

- First few vibrational levels populated by collisions with free electrons (e-V process)

$$e + N_2(v{=}0) \rightleftharpoons N_2^- \rightleftharpoons e + N_2(v{=}1)$$

- Higher levels populated by V-V energy exchange (anharmonicity important)

$$N_2(v) + N_2(w) \rightleftharpoons N_2(v+1) + N_2(w-1)$$

- Higher levels depopulated by V-T relaxation (heats gas)

$$N_2(v) + N_2 \longrightarrow N_2(v-1) + N_2$$

- Treanor distribution:

$$f(v, T_g, T_v) = B\exp\left(-\frac{\hbar\omega v}{T_v} + \frac{x_e \hbar\omega v^2}{T_g}\right)$$

Summary

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- **NH_3 was synthesized using plasma-catalysis at 1 atm and 400 K**
- **Plasma characterization and computational efforts focused towards understanding rate enhancements by vibrationally excited nitrogen**
- **Best catalysts for thermal catalysis may not be optimal under plasma conditions:** rate measurements and microkinetic model indicate Ni as the best catalyst for plasma-catalytic ammonia synthesis