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Spatially and temporally resolved fs/ps CARS measurements of rotation-vibration non-equilibrium in a CH_4/N_2 nanosecond-pulsed discharge

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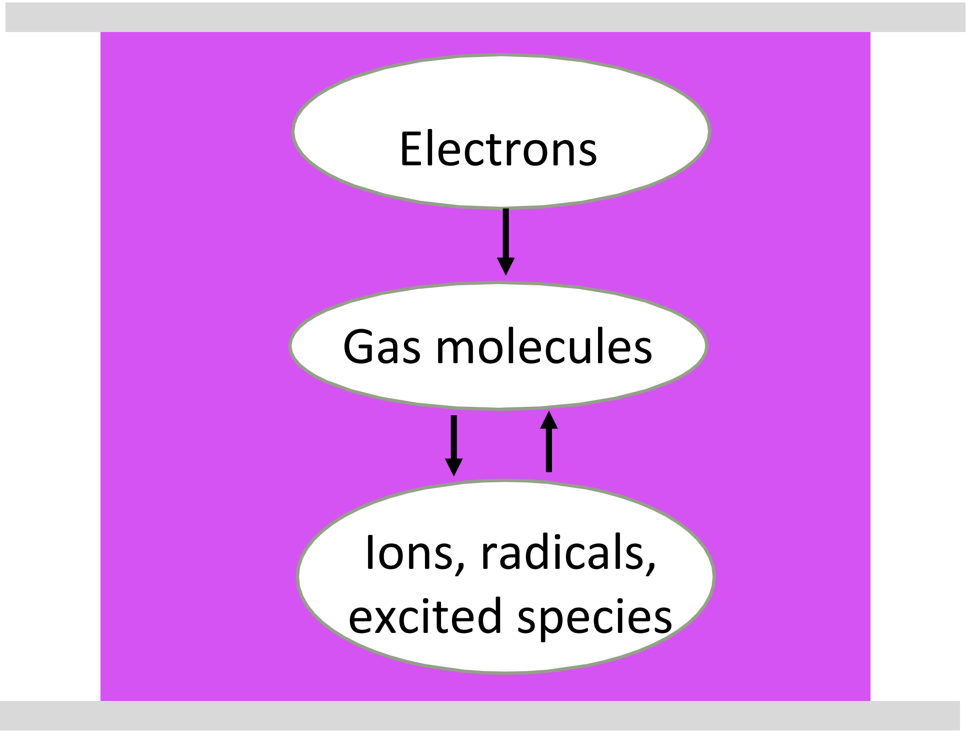
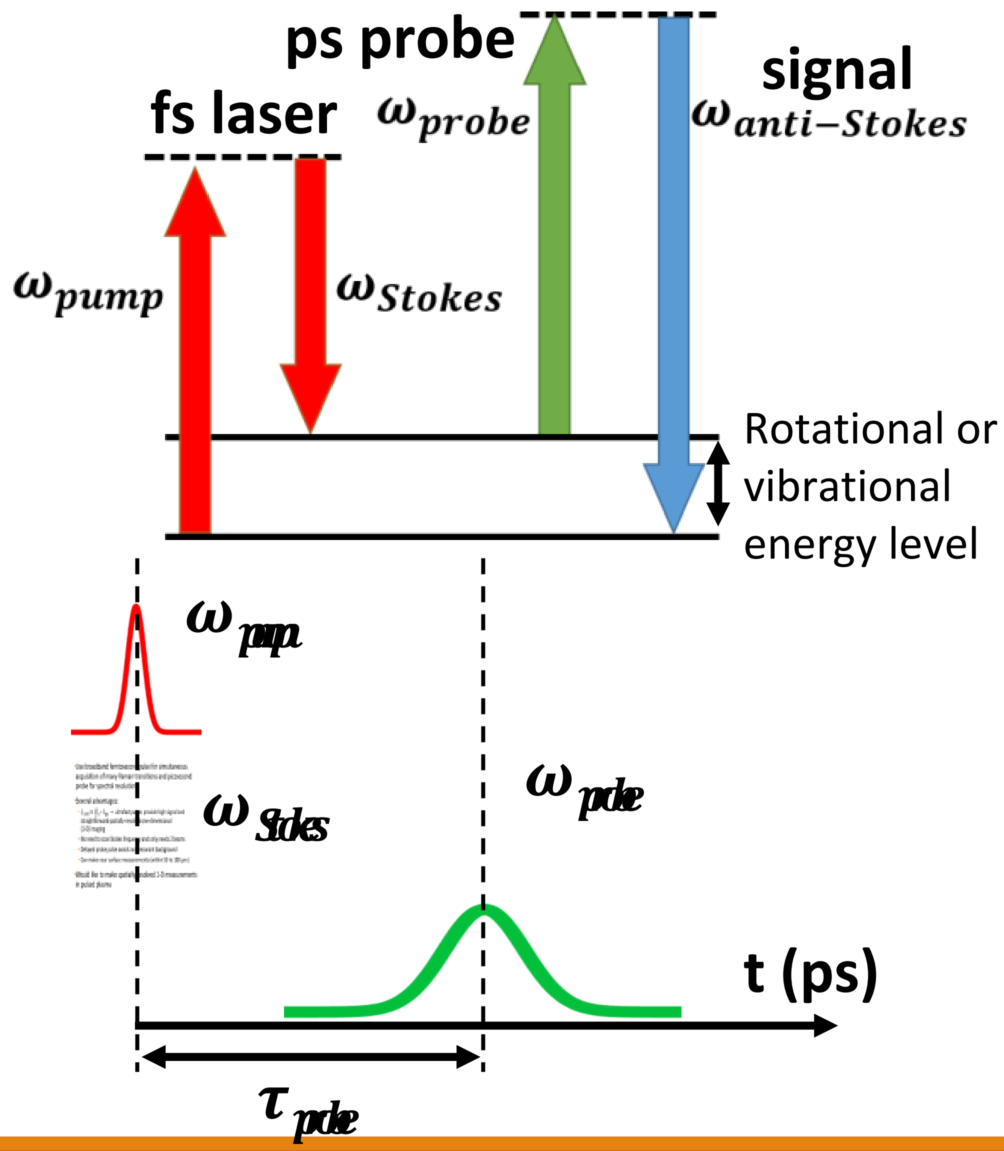
Question: How does molecular energy transfer and methane conversion evolve in space and time in plasma methane reforming?

- Want to utilize plasma to electrify CH_4 conversion technologies
- Need to understand energy transfer to and from molecules
  - How does rotation-vibrational non-equilibrium evolve in time and space? How does this influence CH_4 conversion?
- Need *in situ* measurements of rotation-vibration non-equilibrium and molecular number density → hybrid fs/ps CARS



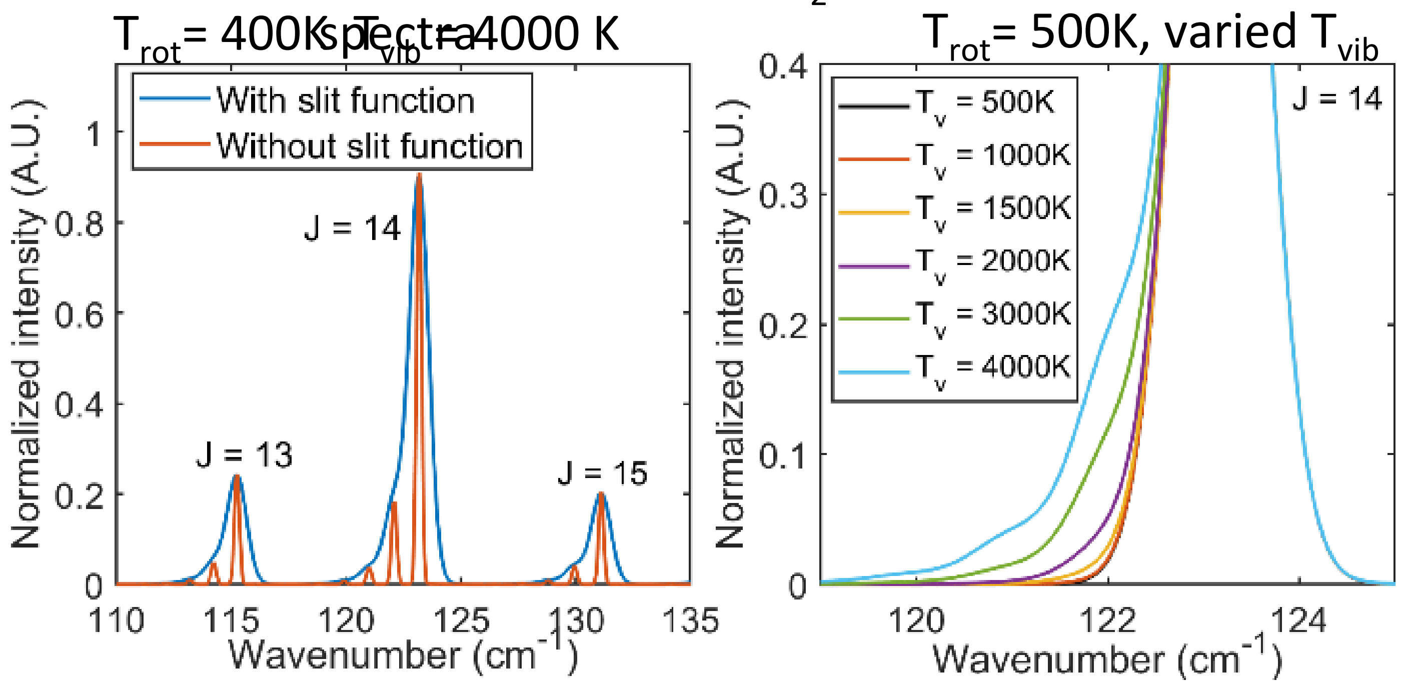
What is hybrid fs/ps CARS?

- Use broadband femtosecond pulse for simultaneous acquisition of many Raman transitions and picosecond probe for spectral resolution
- Several advantages:
  - $I_{CARS} \propto \mathrm{I}_{fs}^{2} * \mathrm{I}_{\mathrm{ps}} \rightarrow$ ultrafast pulses provide high signal and straightforward spatially-resolved one-dimensional (1-D) imaging
  - No need to scan Stokes frequency and only needs 2 beams
  - Delayed probe pulse avoids non-resonant background
  - Can make near surface measurements (within 50 to 100 μm)
- Would like to make spatially-resolved 1-D measurements in pulsed plasma



First level vibrational temperature can be measured from the pure rotational CARS spectrum

Simulated rotational N_2 CARS spectra



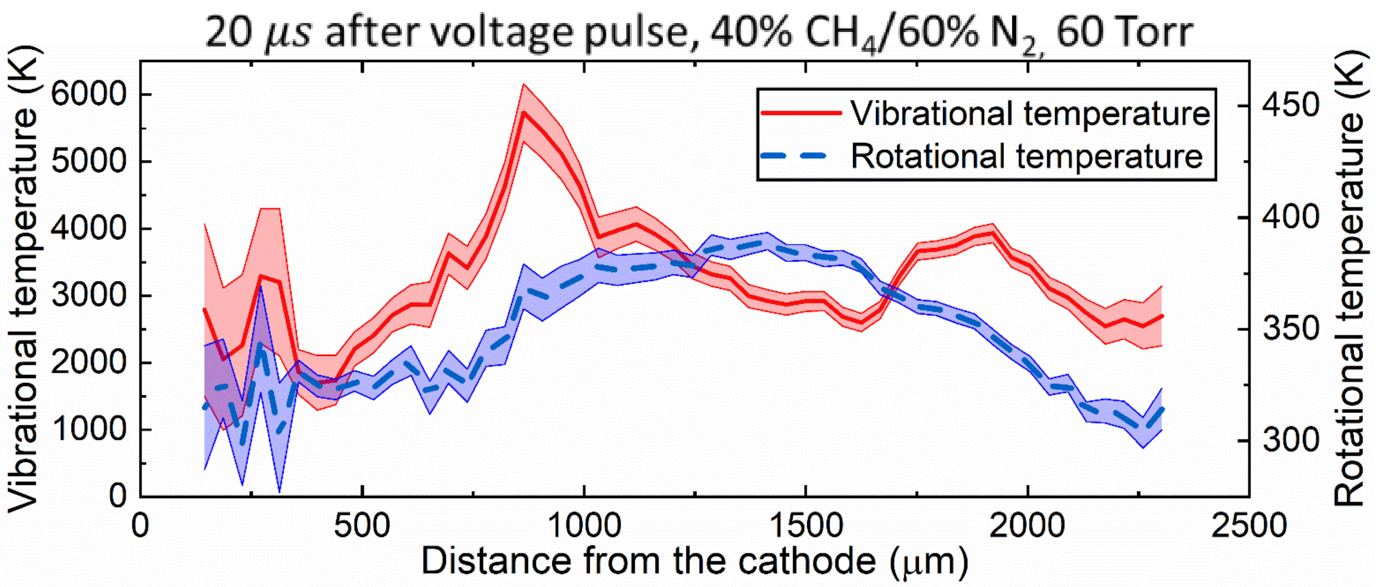
Increasing vibrational energy level red-shifts the rotational energy level F(v,J)

$$F(v,J) = B_v\big(J(J+1)\big) - D_v\big(J^2(J+1)^2\big)$$

$$B_v = B_e - \alpha\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2, D_v = D_e + \beta_e\left(v+\frac{1}{2}\right)$$

More details available in Chen T.Y. et al. Opt. Lett. *(2020)*

Rotational CARS can easily be extended to 1-D with only two beams for time and spatially resolved measurements



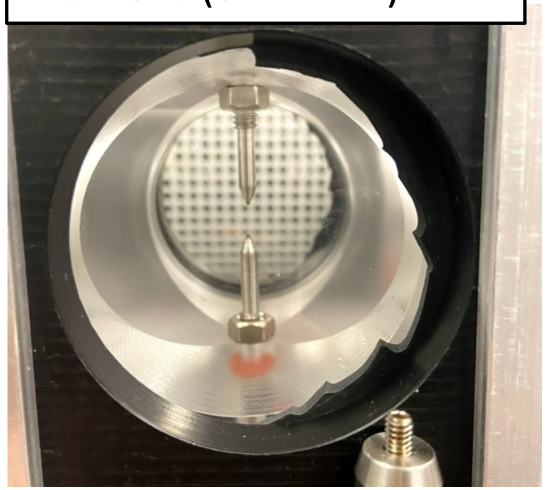
- No need for frequency-converting optics (i.e. OPA) for separate Stokes beam [1]
  - Bandwidth of 100 fs Ti:Sapphire regenerative amplifier enough to resolve rotations (<200 cm^{-1})

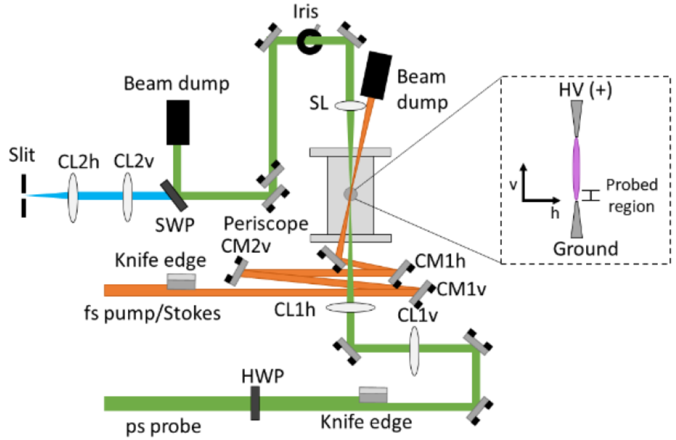
[1] Dedic, C.E. et al., *Optica*, (2017)

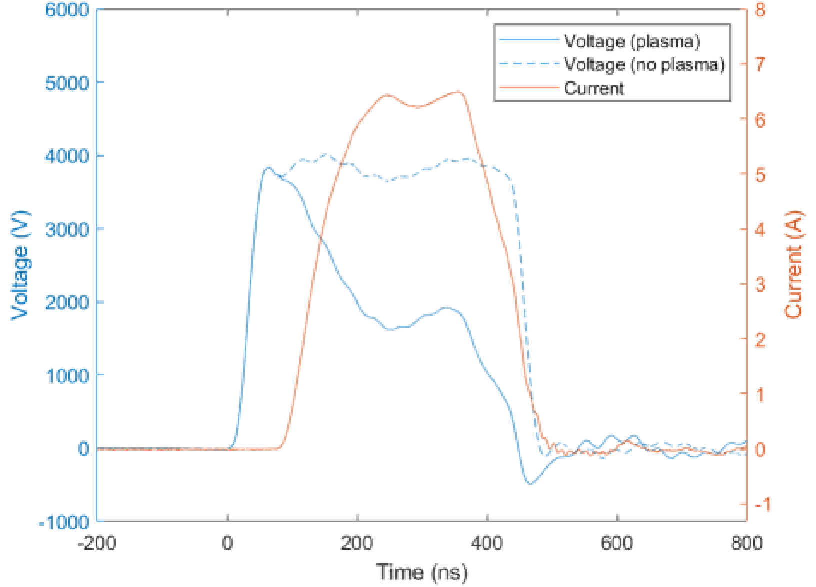
Discharge geometry and experimental setup

- 40% CH_4, 60% N_2, 60 Torr
- 4 kV, 500 ns pulse width, 20 Hz, 8 mm gap, 220 Ω resistor
- fs laser: <7 fs, 0.6 mJ (bandwidth up to CH_4 ν_1 Q-branch at 2916 cm^{-1})
- ps laser: 65 ps, 7 mJ
- Want to measure rotational N_2 CARS and vibrational CH_4 CARS
- All data is time-resolved and 1-D with 40 μm resolution starting within 150 μm of cathode

Generates stable thin filament (d ~ 1mm)

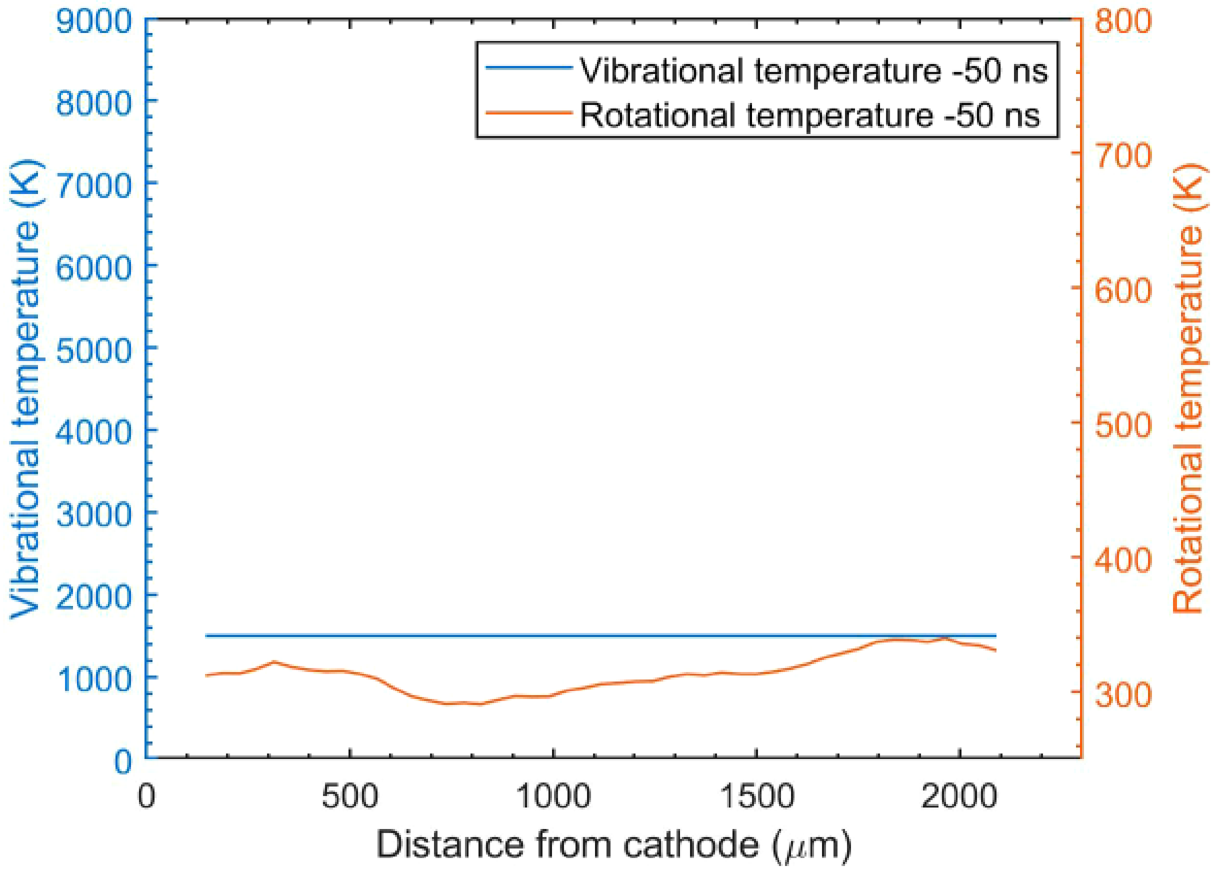




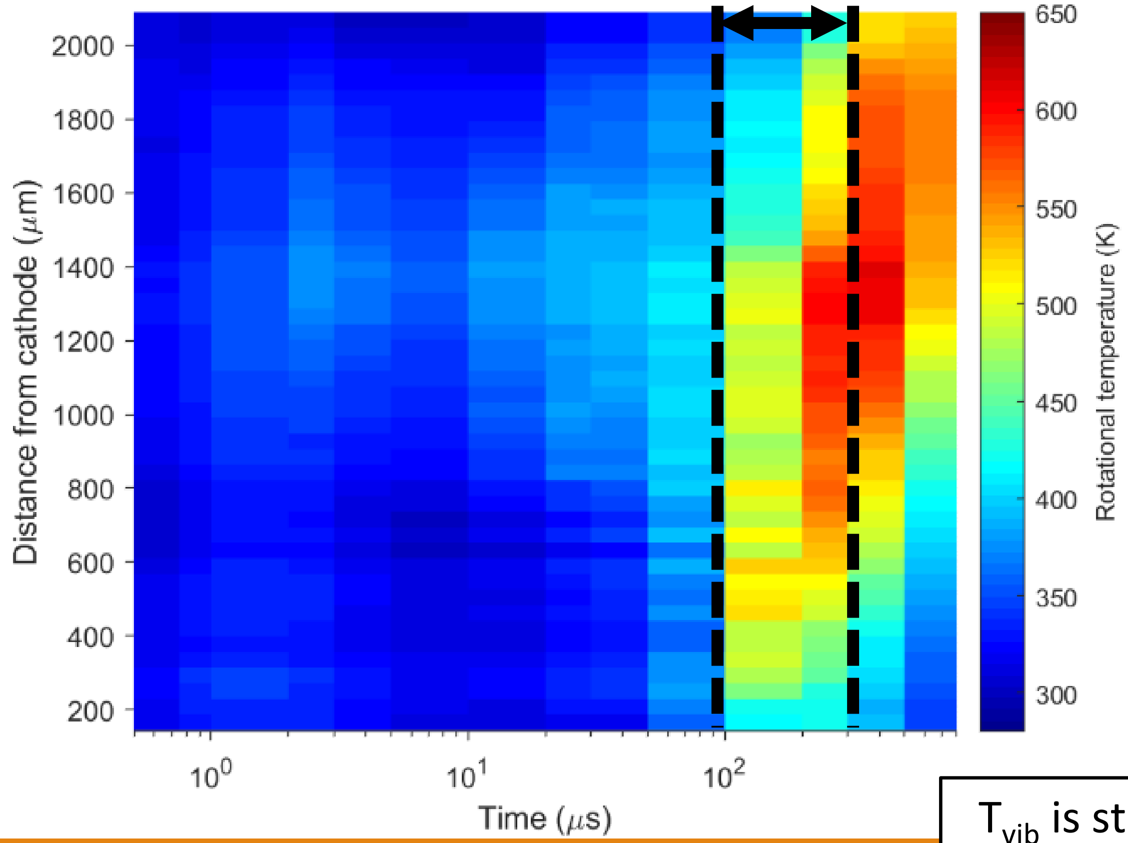


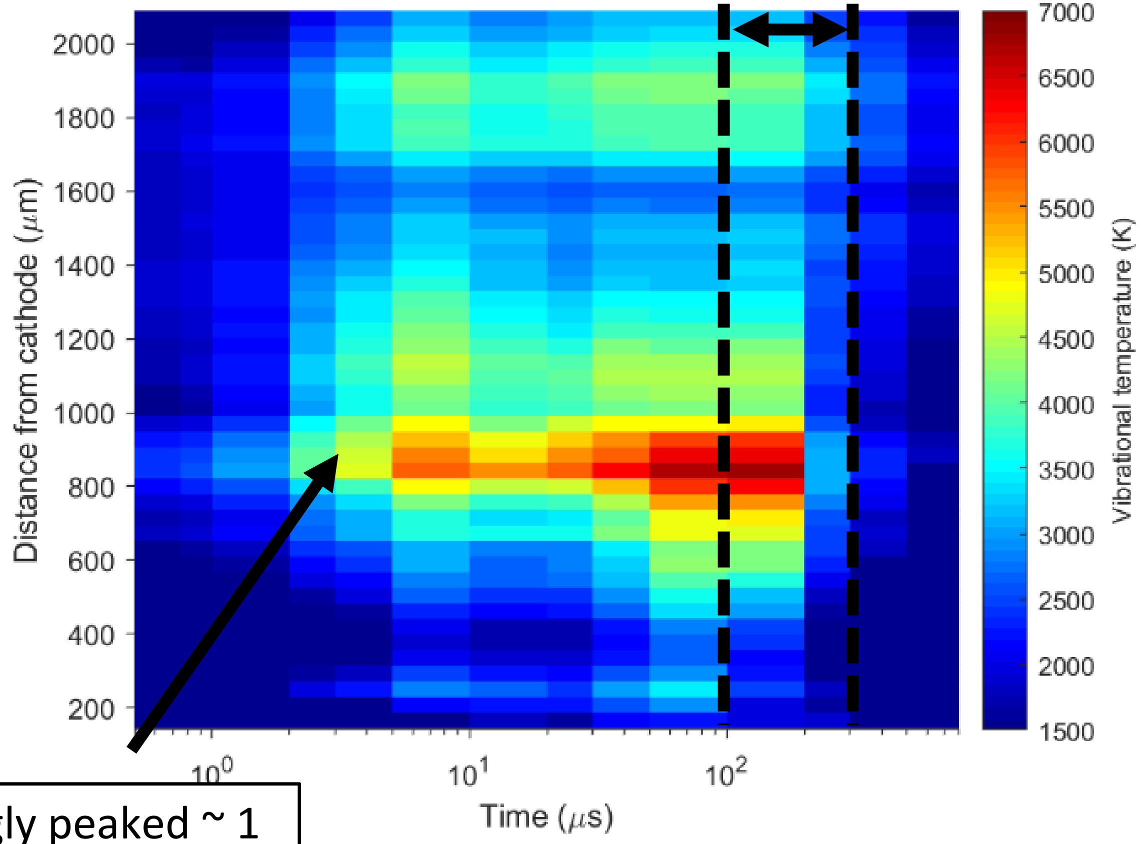
Significant spatial gradients in vibrational temperature of N_2 were detected as a function of time

1500 K set as detection limit for evaluation of T_{vib}



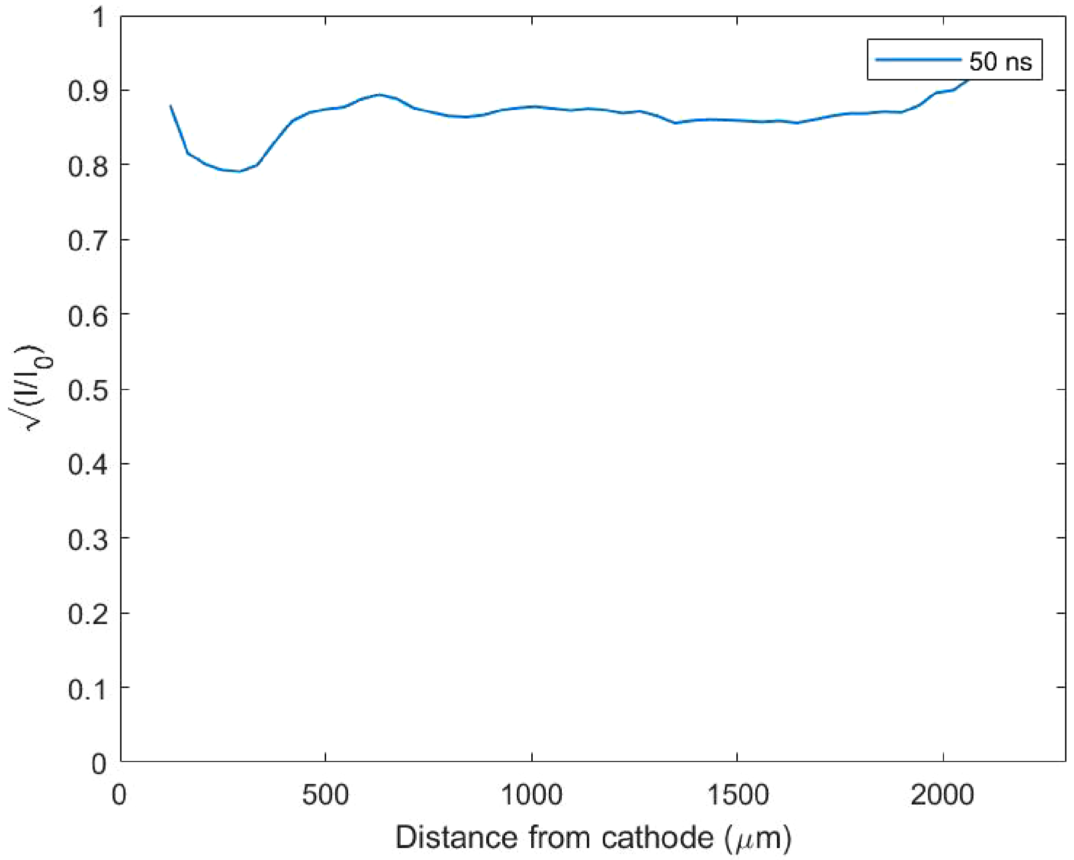
V-T relaxation and peaks in T_{vib} are immediately obvious from time evolutions of T_{vib} and T_{rot}





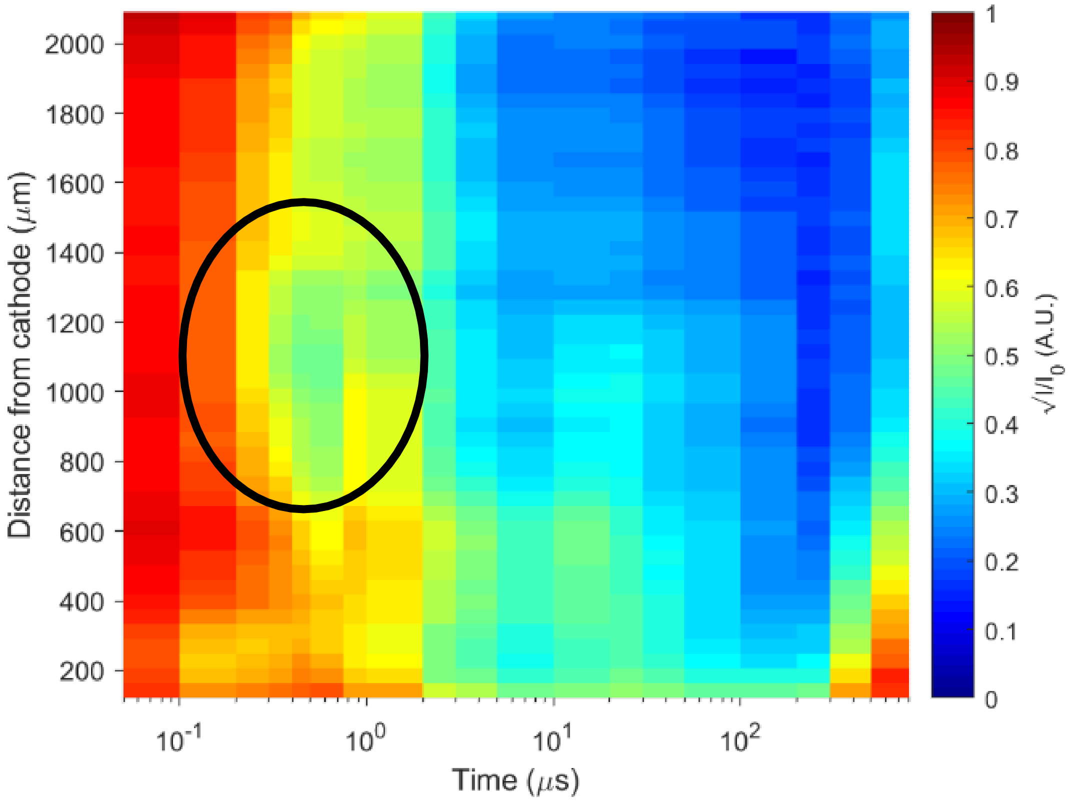
T_{vib} is strongly peaked ~ 1 mm from the cathode

There is some spatial structure to the CH_4 profile but smoother than N_2 T_{vib} and T_{rot}



$I_{CARS} \propto N^2$ so $\sqrt{\frac{I}{I_0}}$ is a measure of N or number density

There is some spatial structure to the CH_4 profile but smoother than N_2 T_{vib} and T_{rot}



- Around 1 mm there is a local dip in CH_4 number density where peak in T_{vib} was observed
- How does this correlate with temperature? ($T \propto \sim 1/N$ for constant pressure ideal gas)

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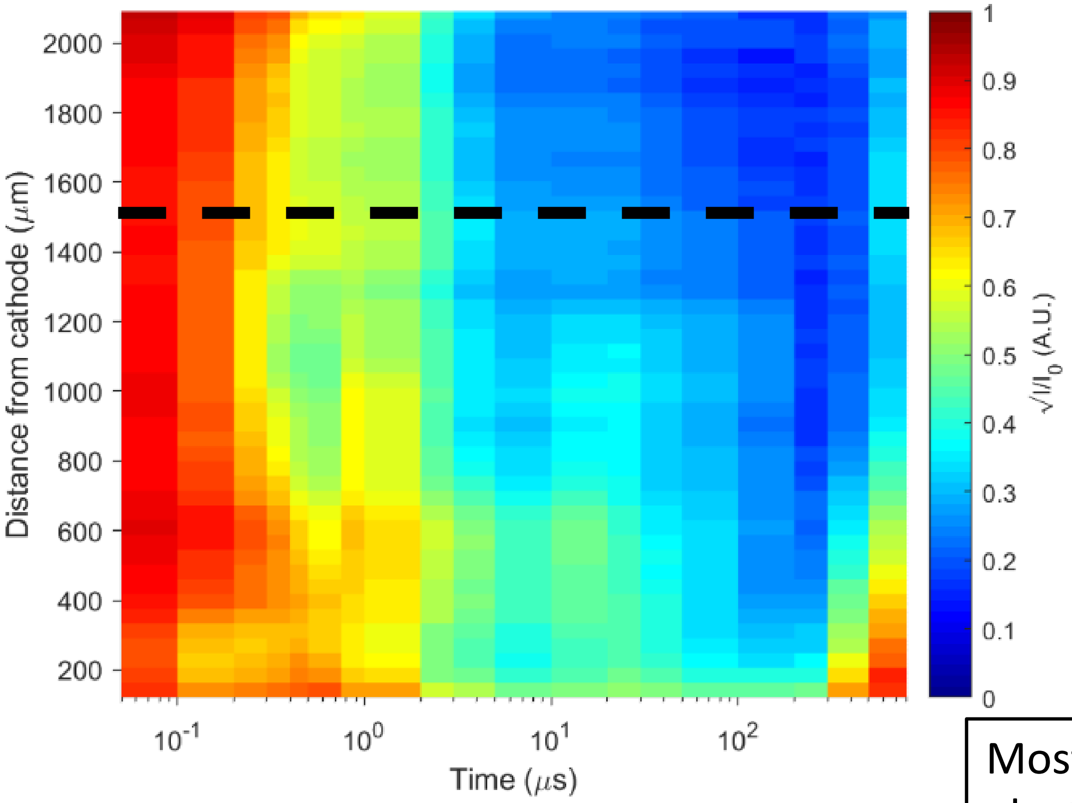
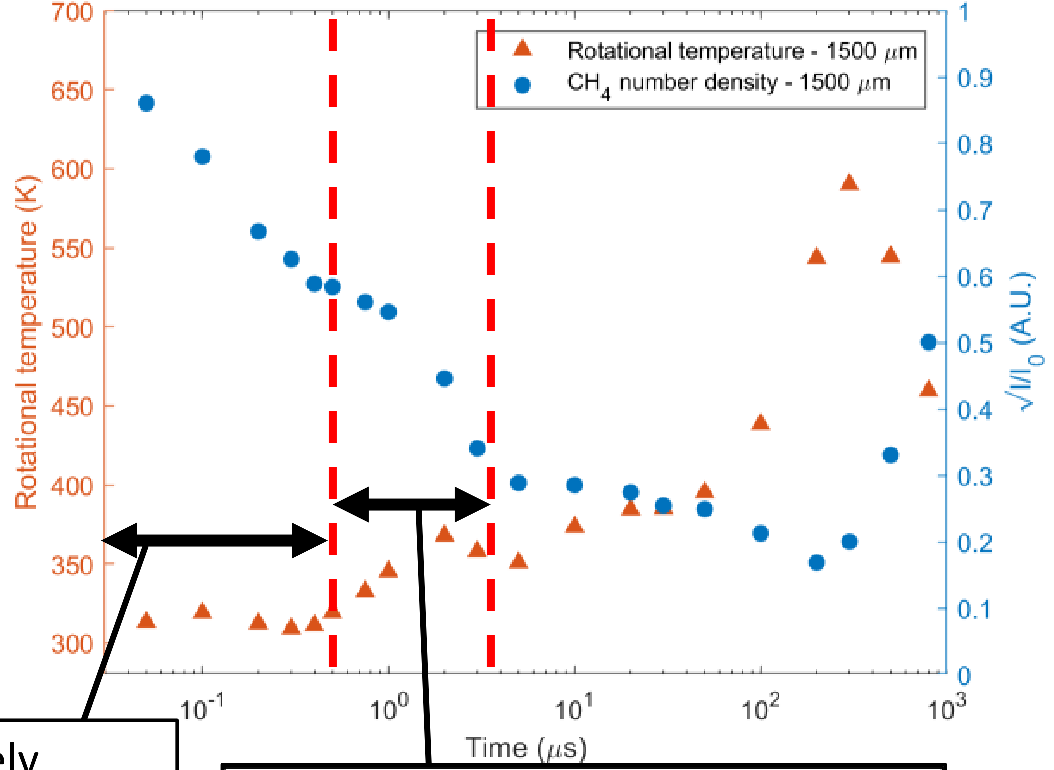
Time evolution shows significant number density drop unrelated to temperature (high CH_4 conversion)

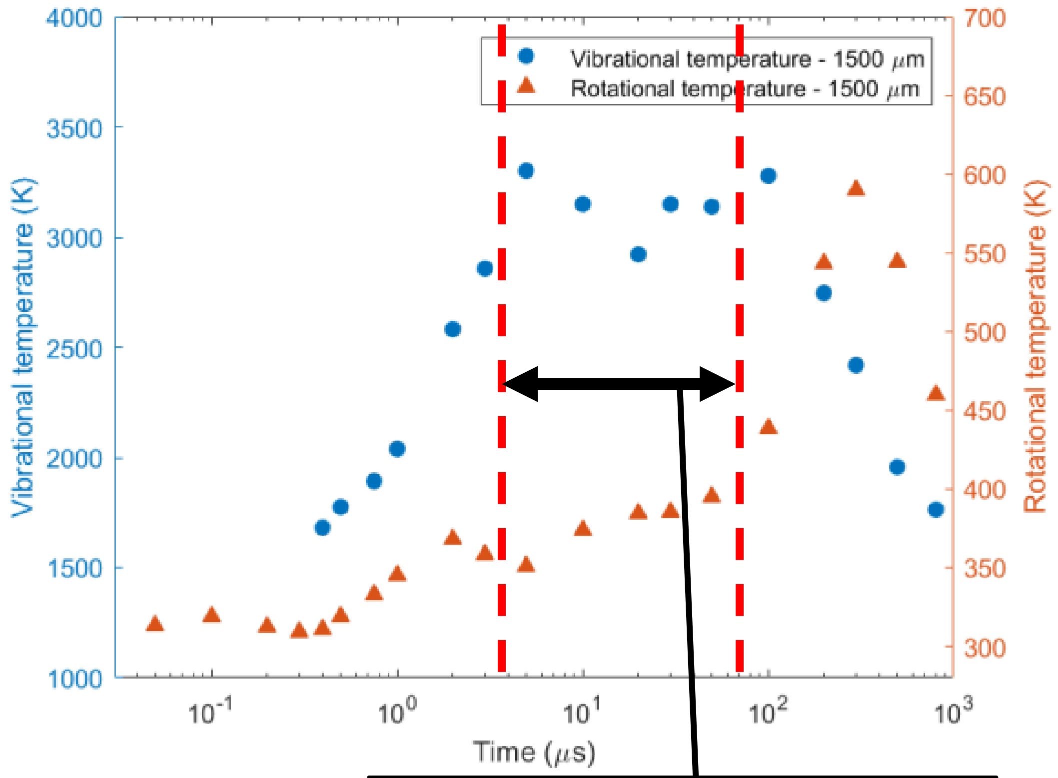




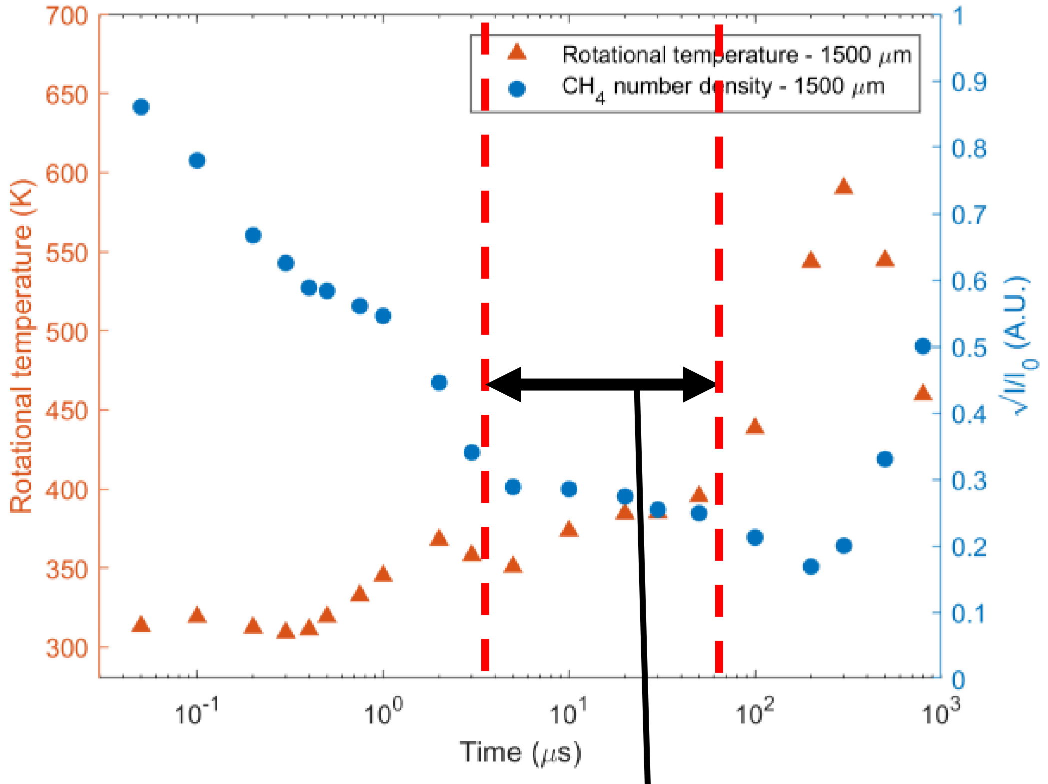
Most likely electron impact dissociation

Likely dissociation by N_2 electronic state quenching (μs lifetime, A. Montello et al. JPhysD 2013)

CH_4 number density appears to be insensitive to high N_2 T_{vib}



Time interval with high T_{vib}



CH_4 number density is almost flat with near constant T_{rot}

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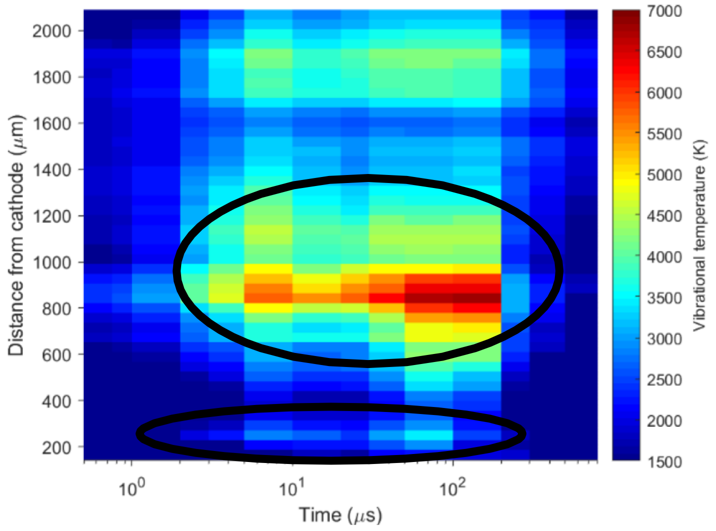
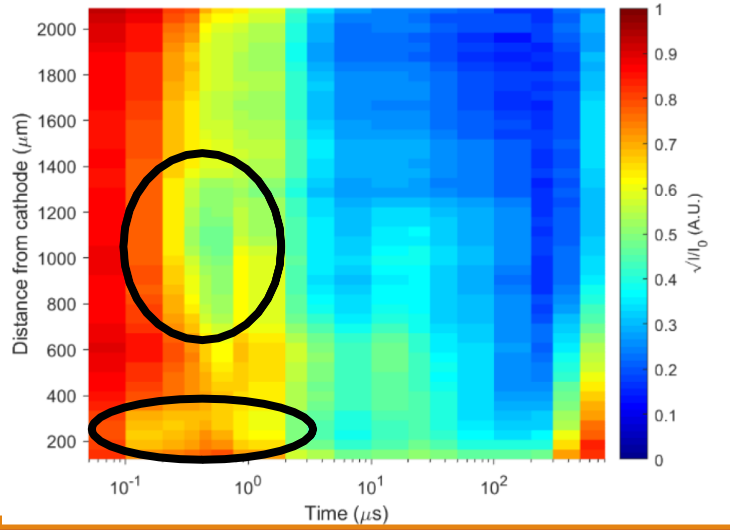
Some remaining questions

- Why is there this highly peaked structure in T_{vib}?
  - Possible indication of transition or formation of a pulsed spark and local non-uniformities in electron density
- Why is the peaked structure not more pronounced in the CH_4 number density figure?





Conclusions and future work

- Measured T_{vib}/T_{rot} and CH_4 number density in a 40%/60% CH_4/N_2 pin-to-pin pulsed discharge with time and spatially-resolved broadband fs/ps CARS
- Spatial structure of T_{vib} has a large peak and is non-uniform
- Majority of CH_4 consumption likely due to electron-impact and electronically excited N_2 quenching
- Peak in T_{vib} found to correlate with a dip in CH_4 number density
- 2-D modeling of the discharge formation is underway to try to understand the spatial structure in T_{vib} and CH_4 number density

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Questions?

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