SAND2019-15484C

Hydrogen thermometry in aluminized propellant burns by hybrid fs/ps CARS

PRESENTED BY

Jonathan Retter, **Daniel Richardson**, and Sean Kearney

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Why study aluminized propellant burns?

- Accident scenario with propellant fires can have **extreme heat loading** on components and systems
- The heat transfer mechanisms are not currently characterized
- Current modeling efforts use simplified boundary conditions to represent these flames
- Flame characterization is very difficult:
  - Extreme temperatures (~2800 K)
  - Burning liquid metal droplets
  - Harsh chemicals
  - Optical emission
- Our group has studied these flames previously
  - Particle measurements
  - Gas phase measurements

Solid rocket motor ground test

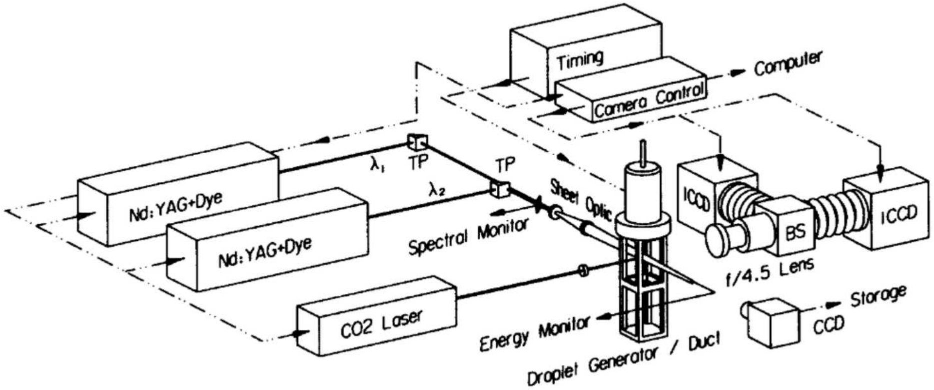
The goal of this work is to characterize the plume temperature in aluminized propellant flames.

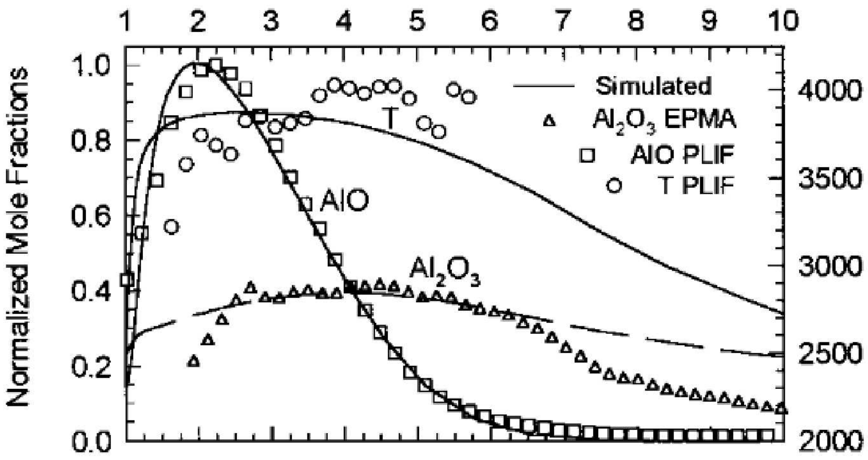
Previous work in other groups:

Bucher et al., *Symposium on Combustion*, 1998

AlO planar laser induced fluorescence (PLIF)

- Isolated aluminum particles burning in flames
- Temperature and relative AlO concentrations

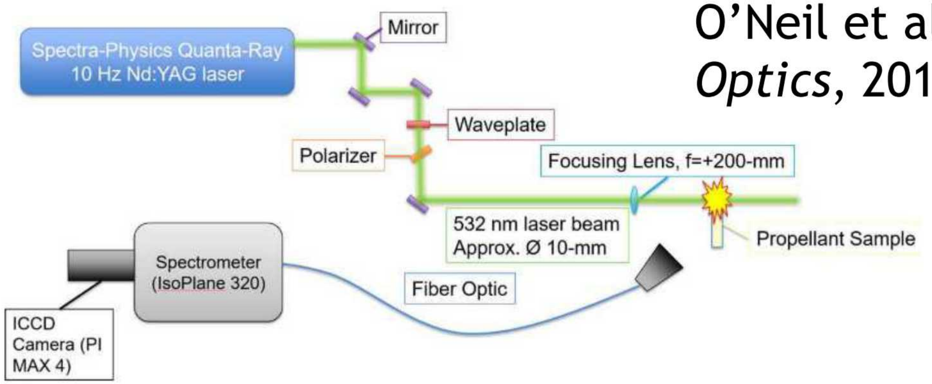


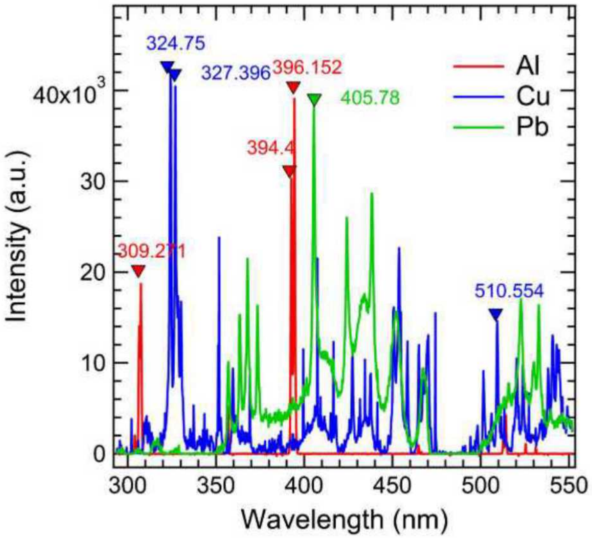


Al concentration by laser-induced-breakdown-spectroscopy (LIBS)

- Measured in actual burning propellants, but requires a calibration
- Demonstration of this technique in these challenging environments

O'Neil et al., *Applied Optics*, 2018

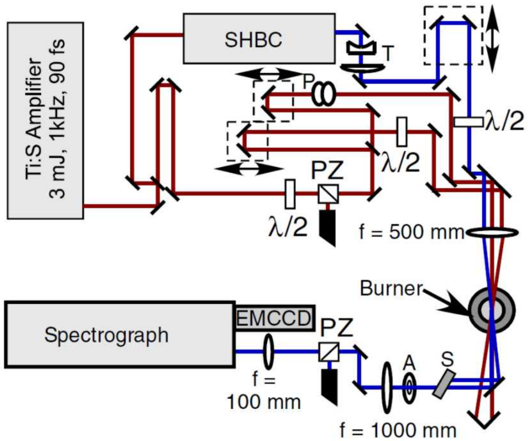


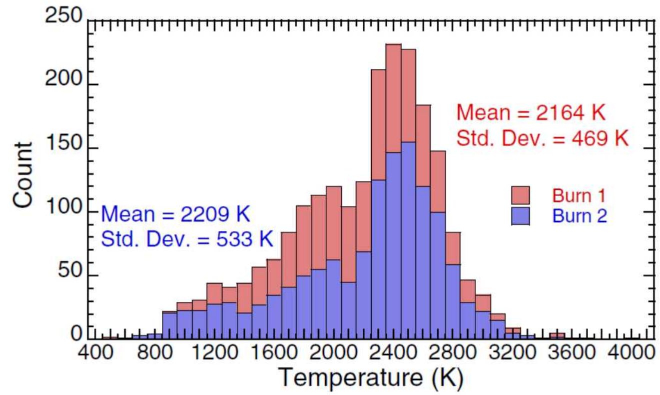


Previous work in our group:

Nitrogen/Oxygen pure-rotational CARS

- Correlations of rotational temperature and O_2/N_2 concentration

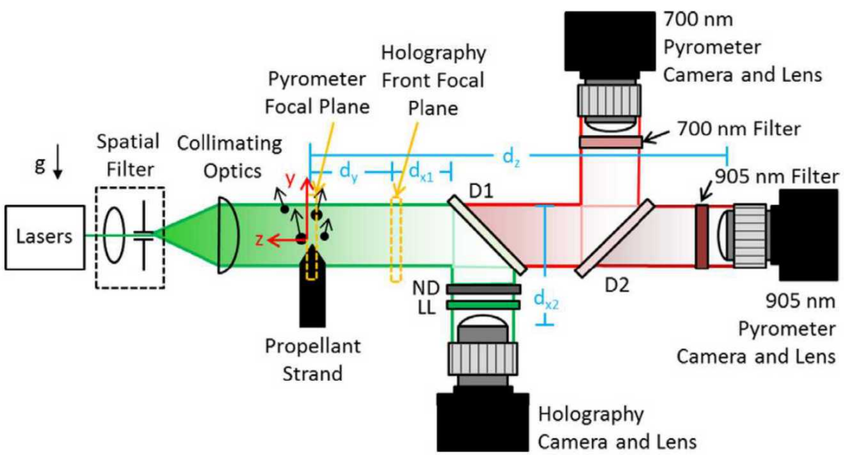


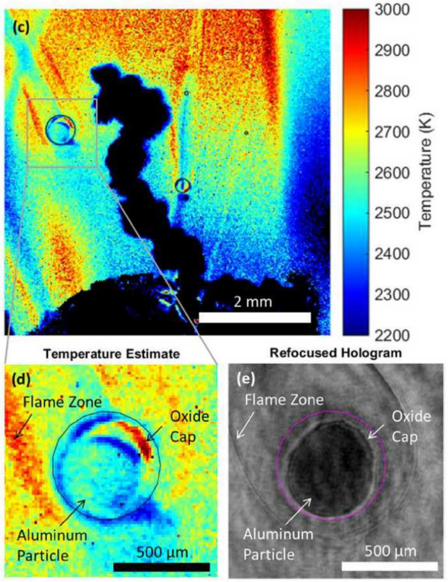


Kearney et al., *Applied Optics*, 2016

Simultaneous holography and pyrometry

- Particle size, velocity, and temperature





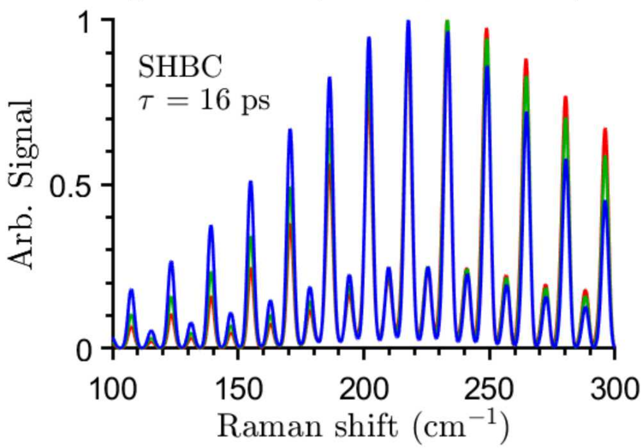
Chen et al., *Combustion and Flame*, 2017

Next step: improved thermometry

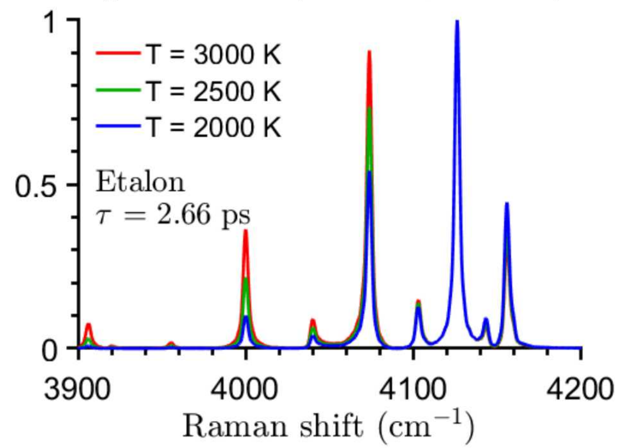
Switch to vibrational CARS

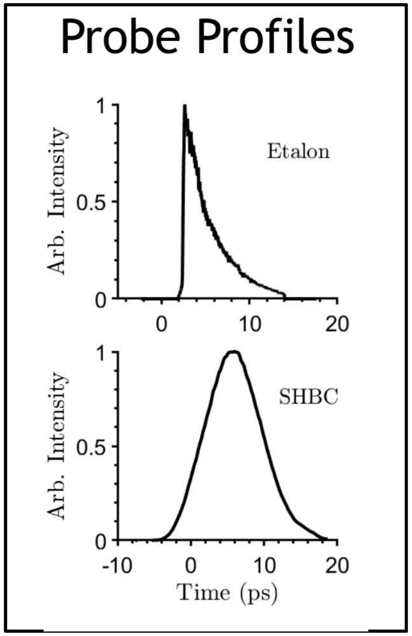
- Improved temperature sensitivity at high temperatures

N_2 S-branch (Δv = 0, ΔJ = +2)



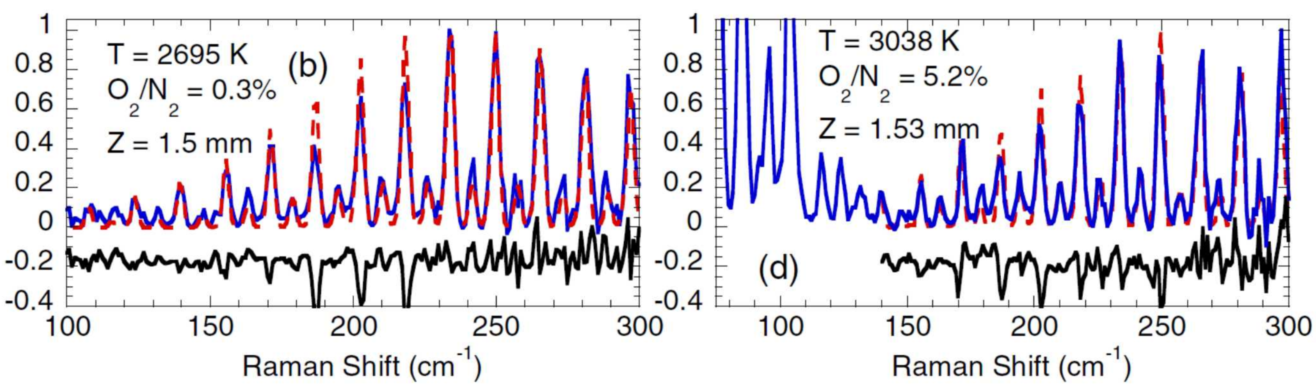
H_2 Q-branch (Δv = +1, ΔJ = 0)





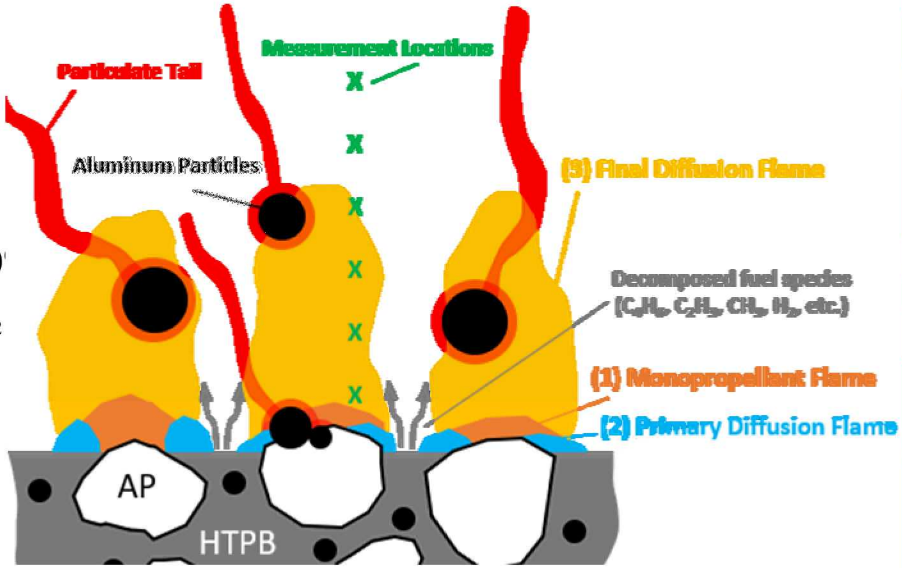
Switch from inert gas to fuel detection

- Shouldn't be plagued by spatial averaging with cold, surrounding gas
- Previous pure-rotational nitrogen, oxygen CARS:



Kearney et al., *Applied Optics*, 2016

Where does H_2 come from?



Composition of the propellant stick

- Ammonium perchlorate oxidizer (AP, 70%)
  - NH_4ClO_4, decomposes to form ammonia and oxidizer species
    - **Monopropellant flame (Flame #1)**
- Hydroxyl terminated polybutadiene binder (HTPB, 10
  - C_4H_6, bounded by OH, decomposes into hydrocarbon species and H_2
  - Decomposed hydrocarbons react with monopropellant products
    - Primary Diffusion Flame (Flame #2)
- Aluminum (20%)
  - Melts at ~933 K, forms agglomerates on the burning surface
- Final Diffusion Flame (Flame #3)
  - Combustion of any remaining reactive species

3 main sources of H_2:

- Thermal decomposition of the binder alone
  - $HTPB_{1200\ gm/mol} \rightarrow 2HTPB_{580\ gm/mol} + 3C + \mathbf{H_2}$
- As a product of decomposed binder hydrocarbons and oxidizers from the monopropellant flame
  - $HTPB_{580\ gm/mol} + 20HCLO_4 \rightarrow 8CO + 24CO_2 + 24H_2O + 20HCL + 5C_2H_2 + CH_4 + \mathbf{2H_2}$
- Recombination reactions
  - $CH_4 + H \rightarrow CH_3 + \mathbf{H_2}$

Reaction Mechanisms from Jeppson et al., AIAA 1997

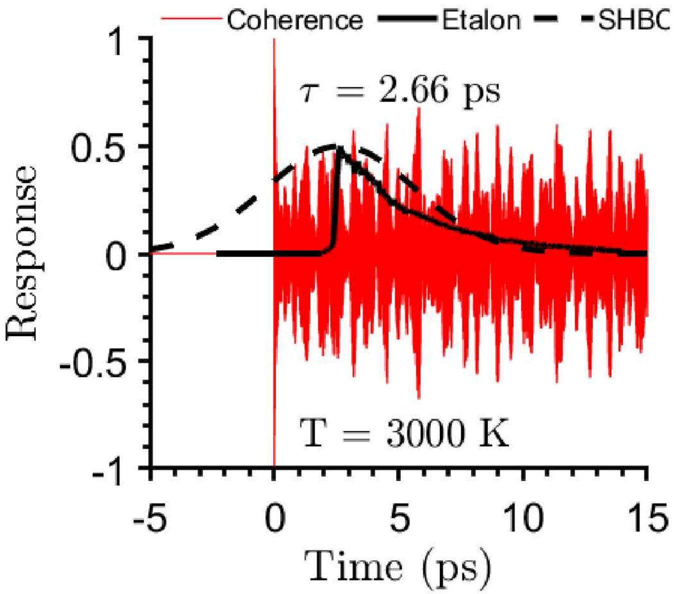
How to model H_2 CARS?

Time domain model, assuming impulsive preparation of the Raman coherence

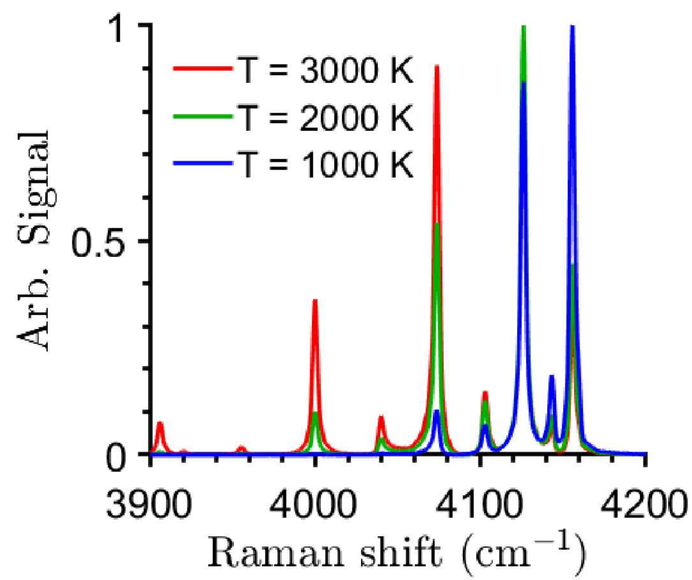
- $\chi(t)$ = induced polarization as a function of time
- $W_{v,J}$ = weight term for each rotational (*J*) and vibrational (*v*) state
- $\omega_{v,J}$ = Q-branch Raman frequencies (Morse potential? Dunham coefficients? Experimental values?)
- $H(t)$ = coherence dephasing term (collisional? Dicke? Doppler?)
- E_{probe} = electric field of the probe pulse at time delay $t = \tau$
- E_{CARS} = CARS electric field, FFT gives the frequency domain spectrum

$$\chi(t) \sim \sum_{\Delta v=1} \sum_{\Delta J=0} W_{v,J} \cos(\omega_{v,J} t) H(t), \qquad E_{CARS}(t;\tau) \sim \chi(t) E_{probe}(t-\tau)$$

Example synthetic coherence gated by an experimental probe profile:



FFT



How to model H_2 CARS?

How well do we know the energy levels of hydrogen?

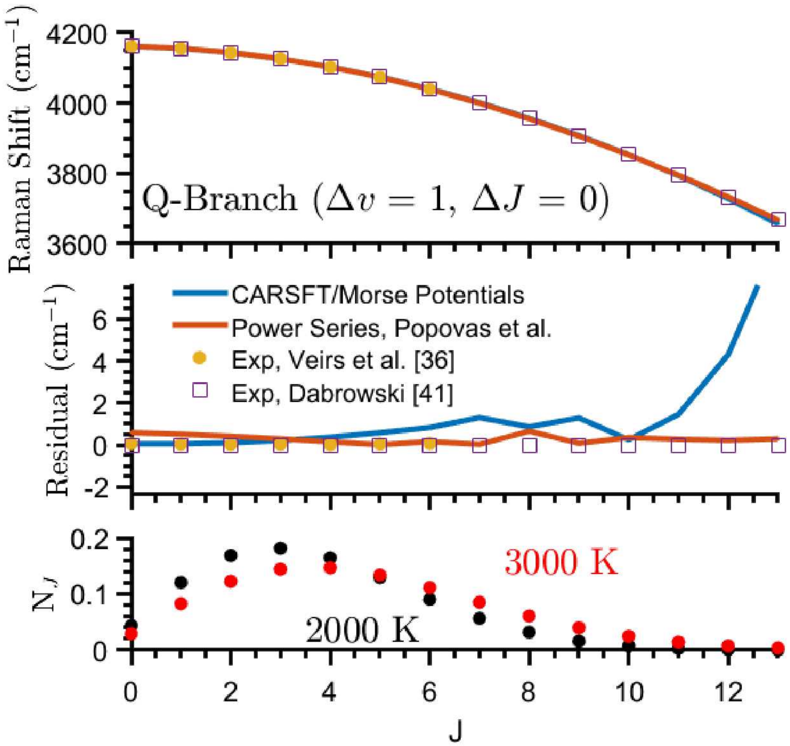
- $\omega_{v,J}$ = Q-branch Raman frequencies (Morse potentials? Dunham coefficients? Experimental values?)

$$\chi(t) \sim \sum_{\Delta v=1} \sum_{\Delta J=0} W_{v,J} \cos(\boldsymbol{\omega_{v,J}} t) H(t), \qquad E_{CARS}(t;\tau) \sim \chi(t) E_{probe}(t-\tau)$$

Not well if using Morse Potential (i.e. Sandia CARSFT)

- Energy level spacing is so large for hydrogen that using the Morse Potential to predict energy levels outside the range used to generate the diatomic constants leads to erroneous values

$$F_{rot}(v,J) = \left[B_e - \alpha_e\left(v+\tfrac{1}{2}\right) + \gamma_e\left(v+\tfrac{1}{2}\right)^2\right] J(J+1) + \ \ldots$$



Better if using Dunham coefficients

- Power series approach to rotational energy levels

$$F_{rot}(v,J) = \sum_{l,i} Y_{l,i}\left(v+\tfrac{1}{2}\right)^2 J^i (J+1)^i$$

Most $Y_{l,i}$ coefficients in literature are derived from the Dabrowski experimental dataset

Dabrowski, Can. J. Phys., Vol. 62, 1984

How to model H_2 CARS?

What about the dephasing mechanisms?

- $H(t)$ = coherence dephasing term (collisional? Dicke? Doppler?)

$$\chi(t) \sim \sum_{\Delta v=1} \sum_{\Delta J=0} W_{v,J} \cos(\omega_{v,J} t) \boldsymbol{H(t)}, \qquad E_{CARS}(t;\tau) \sim \chi(t) E_{probe}(t-\tau)$$

(1) Collisional, $H(t) = \exp(-\Gamma_{v,J} t)$, where $\Gamma_{v,J} = \gamma_{v,J}$ = HWHM linewidth ($\mathrm{cm^{-1}atm^{-1}}$)

- Dominant effect at the highest densities
- Lorentzian lineshape, exponential decay

D_o = diffusion coefficient
c = speed of light

(2) Dicke, same as collisional, now with $\Gamma_{v,J} = \dfrac{2\pi D_o \omega_{v,J}^2}{c\rho} + \gamma_{v,J}\rho$

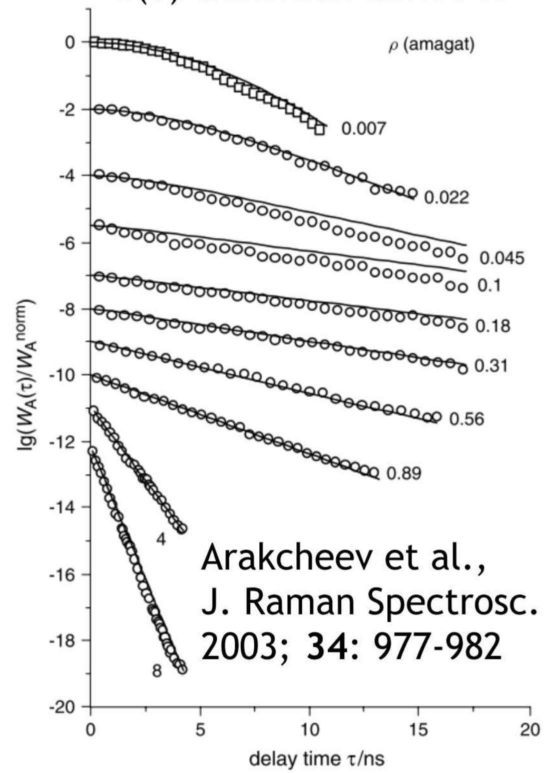
- Motional narrowing of the linewidth from velocity changing collisions
- Important when the mean free path becomes comparable to the wavelength of radiation [Murray et al., J. of Mol. Spectroscopy, 1972]
- Modeled as a Lorentzian linewidth and an exponential decay

(3) Doppler, $H(t) = \exp\{-k_o^2 \tau_v^2 \sigma_v^2 [{}^{t}/_{\tau_v} - 1 + \exp({}^{-t}/_{\tau_v})]\}$

- Gaussian decay of the coherence
- Collection angle dependent
- Important at low densities

k_o = transition wavenumber
τ_v = velocity correlation time
σ_v = dispersion of thermal velocities

S(0) transition at 296 K



Arakcheev et al., J. Raman Spectrosc. 2003; **34**: 977-982

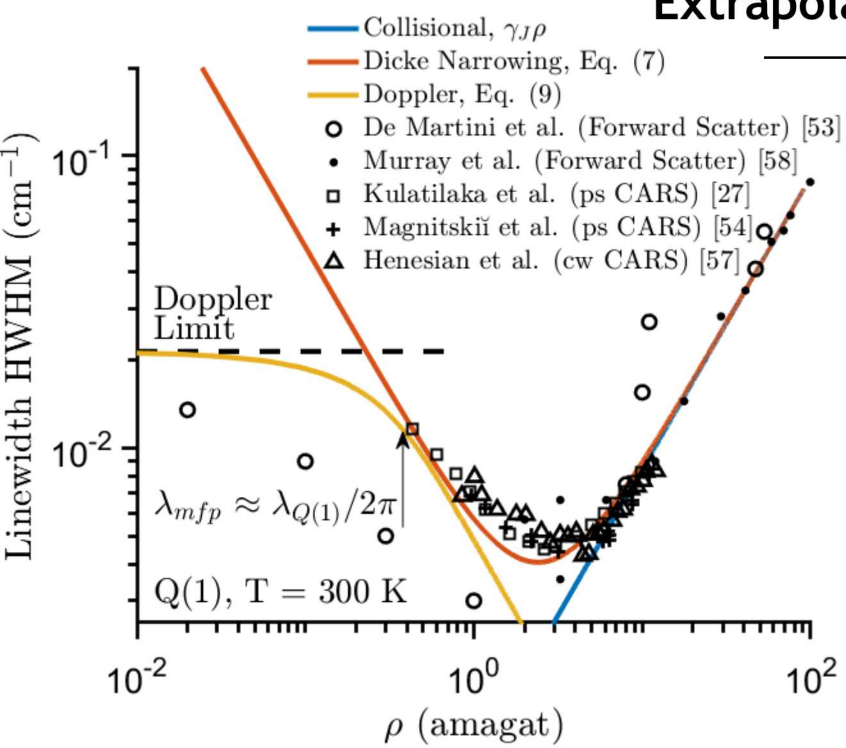
How to model H_2 CARS?

Now plotting these relations in comparison to our regime in the propellant fires

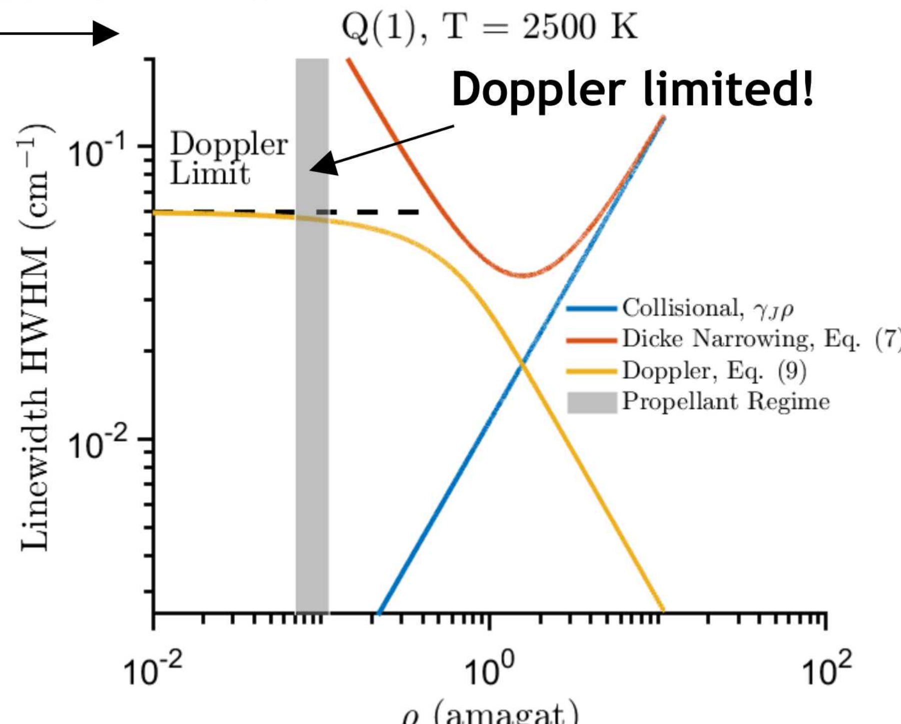
(1) Collisional, $H(t) = \exp(-\Gamma_{v,J} t)$, where $\Gamma_{v,J} = \gamma_{v,J}$ = HWHM linewidth ($cm^{-1}atm^{-1}$)

(2) Dicke, same as collisional, now with $\Gamma_{v,J} = \frac{2\pi D_o \omega_{v,J}^2}{c\rho} + \gamma_{v,J}\rho$

(3) Doppler, $H(t) = \exp\{-k_o^2 \tau_v^2 \sigma_v^2 [t/\tau_v - 1 + \exp(-t/\tau_v)]\}$



Extrapolate to our domain…



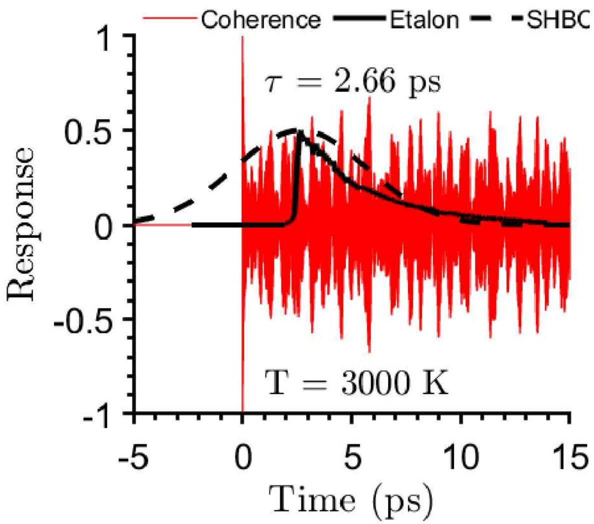
Mitigation effort: etalon probe pulse

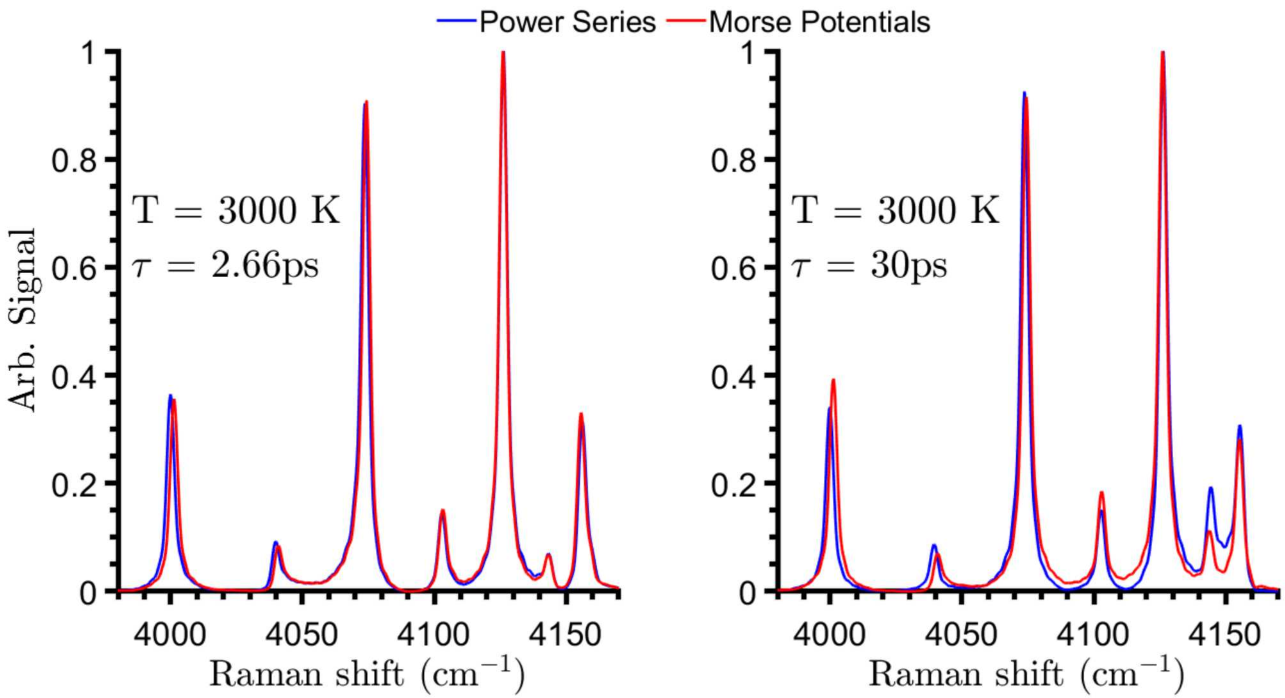
Uncertainties in Raman frequencies and dephasing mechanisms nearly eliminated with a short probe pulse at a short delay

$$\chi(t) \sim \sum_{\Delta v=1} \sum_{\Delta J=0} W_{v,J} \cos\left(\boldsymbol{\omega_{v,J}} t\right) \boldsymbol{H(t)}, \qquad E_{CARS}(t;\tau) \sim \chi(t) E_{probe}(t-\tau)$$

Density range approaching 0.07 amagat at 3000 K, dephasing is negligible at early times

At 2.66 ps, the difference in the gated response in negligible (delay used in the experiment)
At 30 ps, the difference is significant

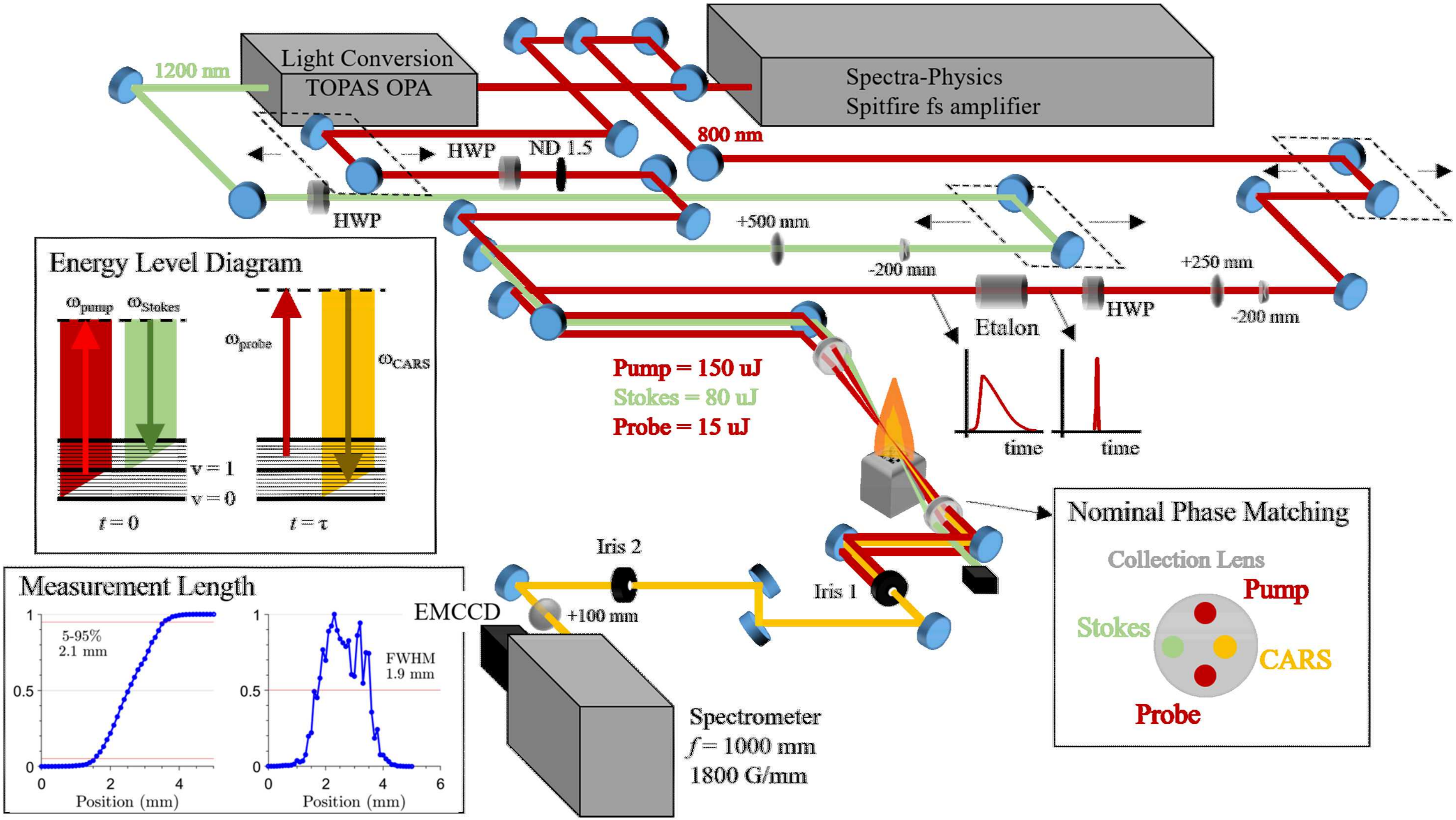




Experimental Setup

3-beam vibrational hydrogen CARS

- Nominally 50 fs preparation beams



Experimental Setup

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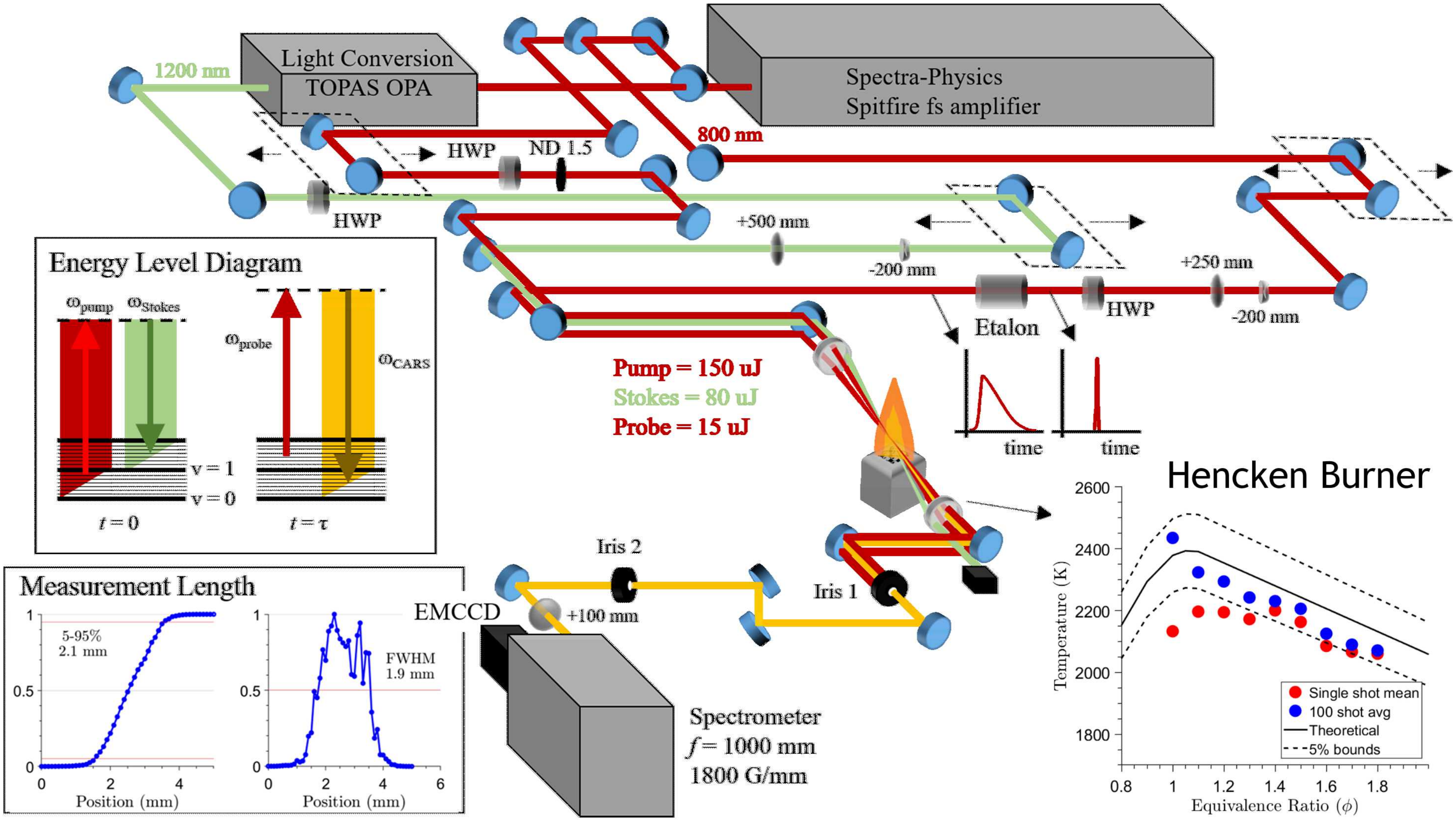
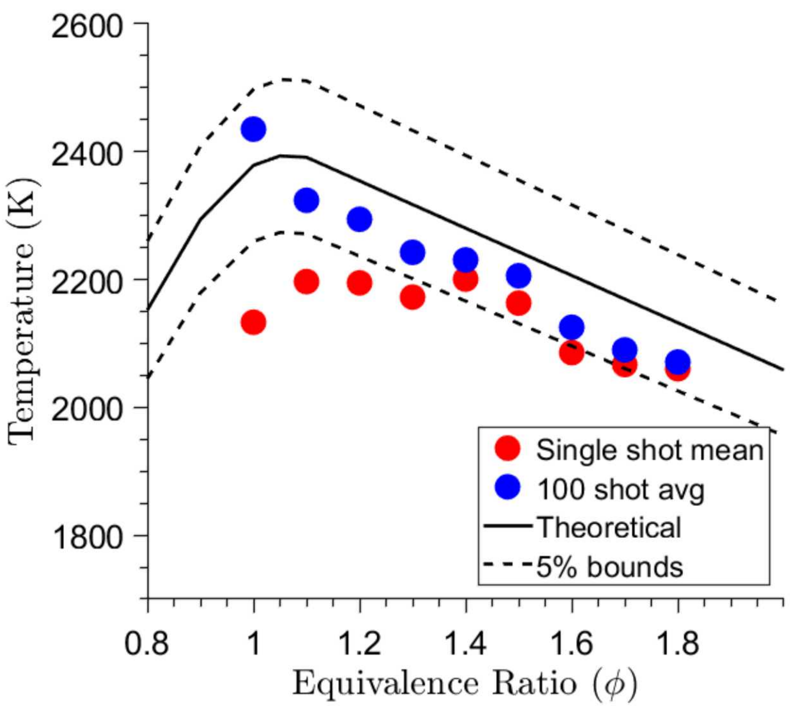


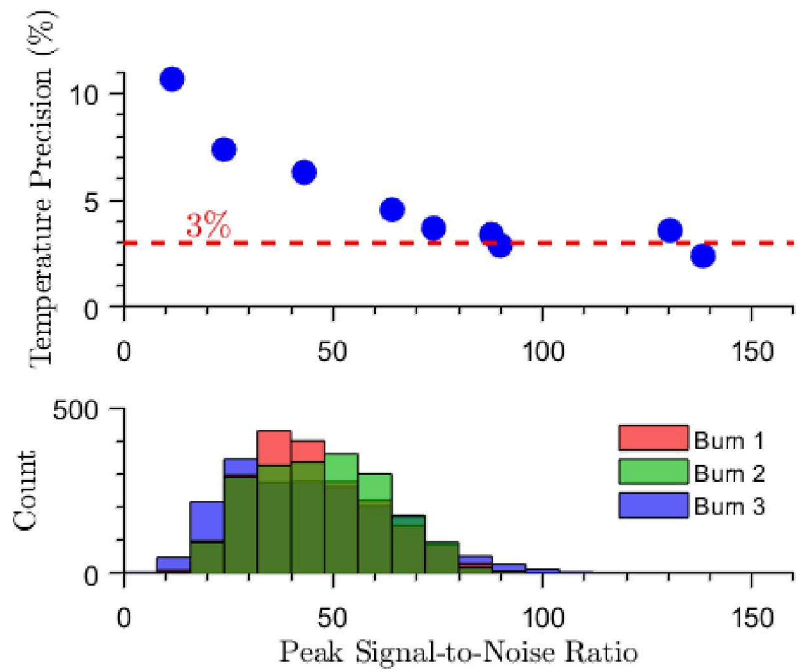
Hencken Burner Measurements

Average fitted temperature from single shots and 100 shot means
- Instrument accuracy and precision as a function of signal-to-noise ratio (SNR)
- Results converge for higher equivalence ratio (higher signal-to-noise)

Systematically low fitted temperature
- Likely from the burner deviating from the adiabatic assumption

Instrument precision approaches 3% (~6-7% for SNRs in the propellant burns)
- Limited by the use of a Stokes pulse originating from an OPA

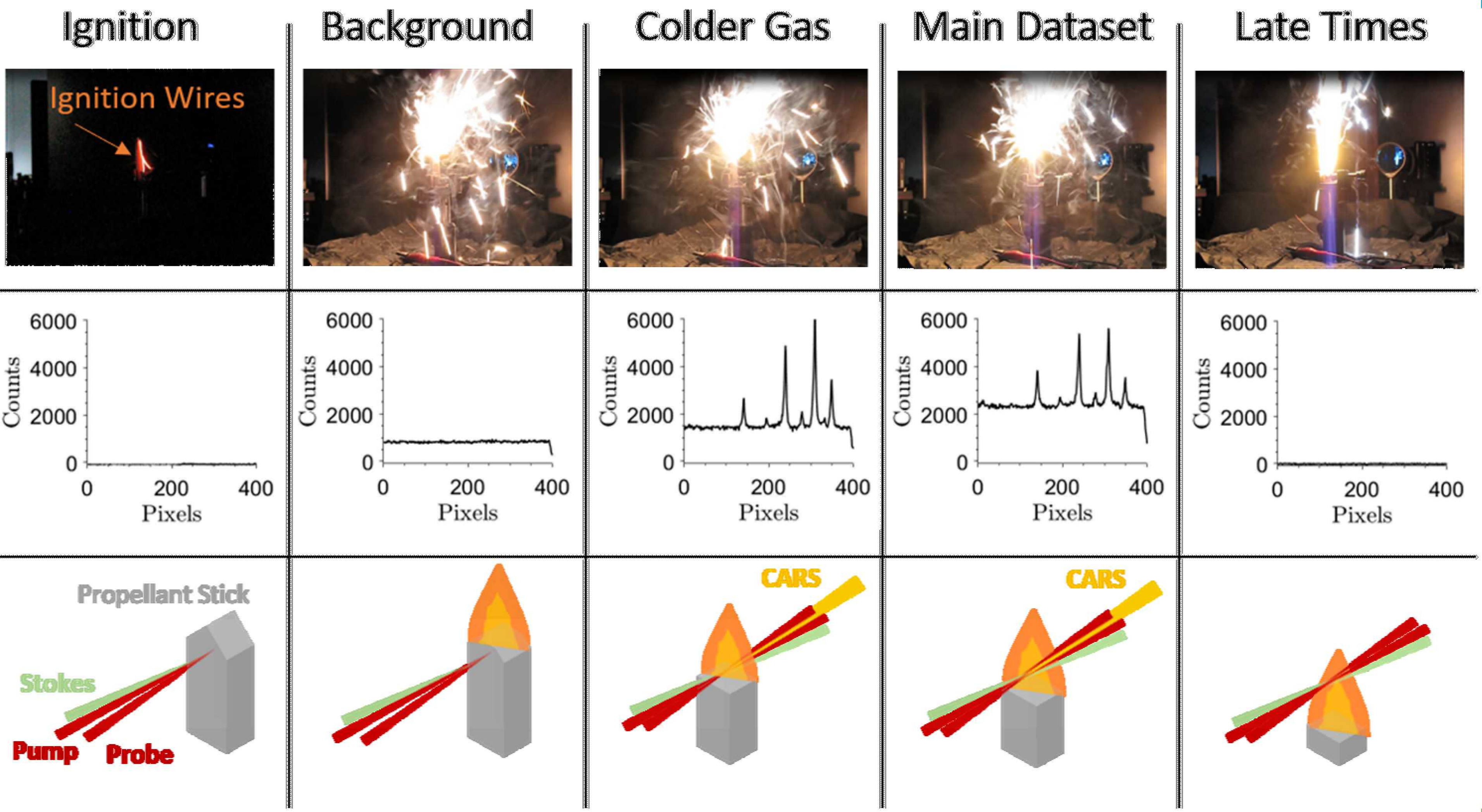




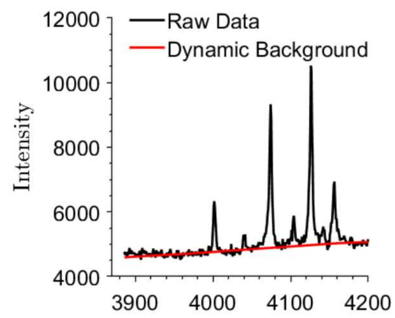
Propellant Burn Timeline

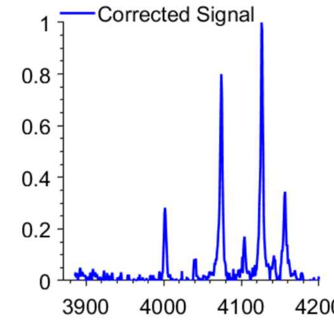
Photographs, detector images, and cartoons of the measurement timeline

- Results converge for higher equivalence ratio (higher signal-to-noise)



Spectral Fitting



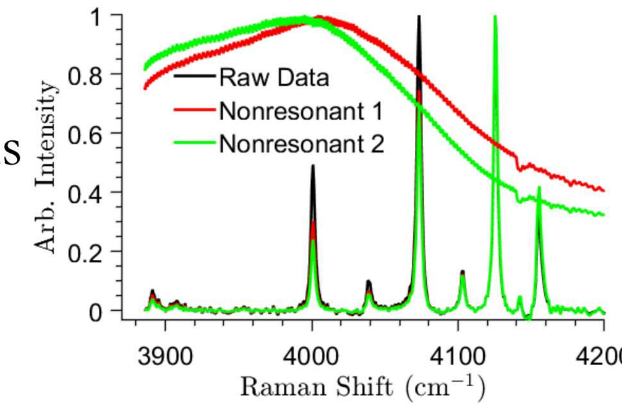


Dynamic background fitting

- Required to avoid broadband emission
- Linear fits to background pixels

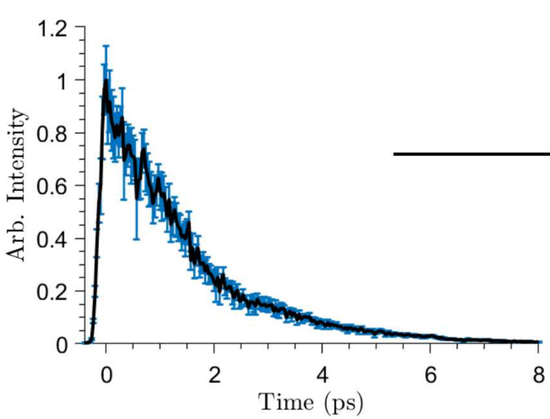
Normalize by nonresonant spectrum

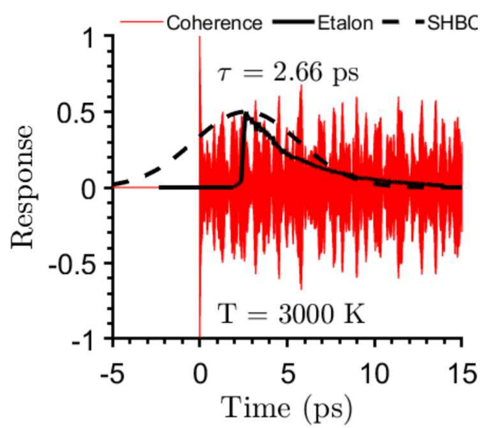
- Drifting nonresonant spectrum created problems
- Lack of consistency from the OPA Stokes pulse

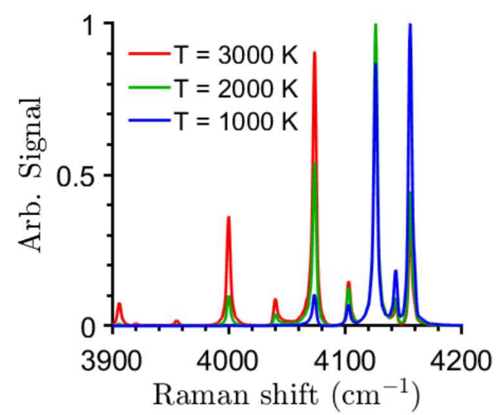


Generate synthetic CARS libraries

- 1D temperature library for a fixed probe delay
- Use experimentally determined probe profile to gate the coherence



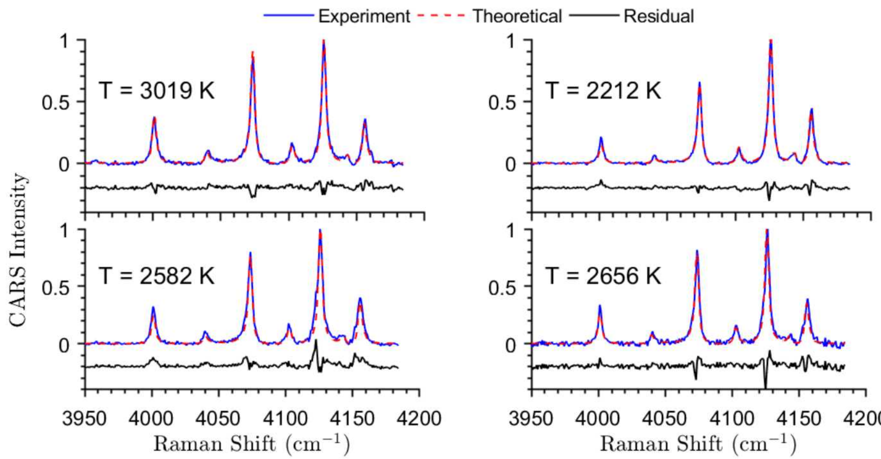


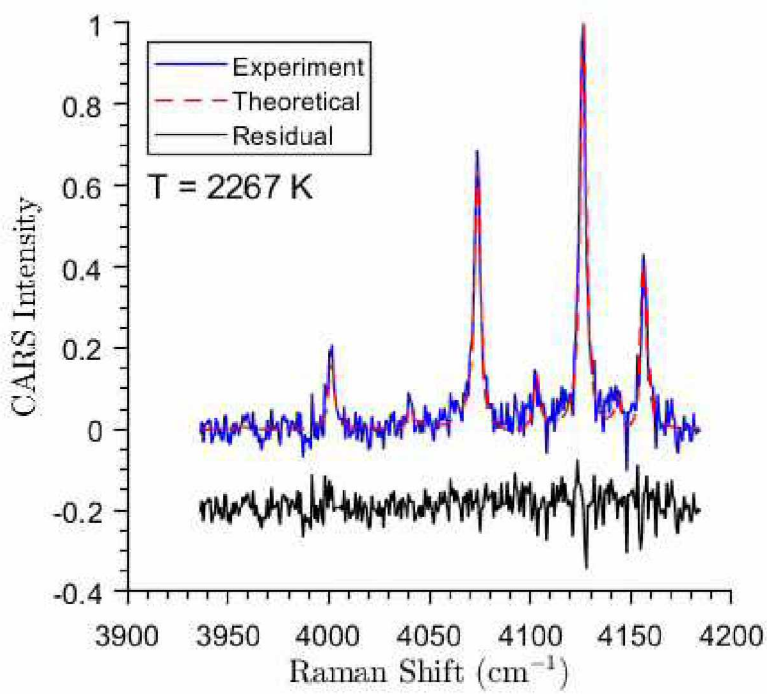


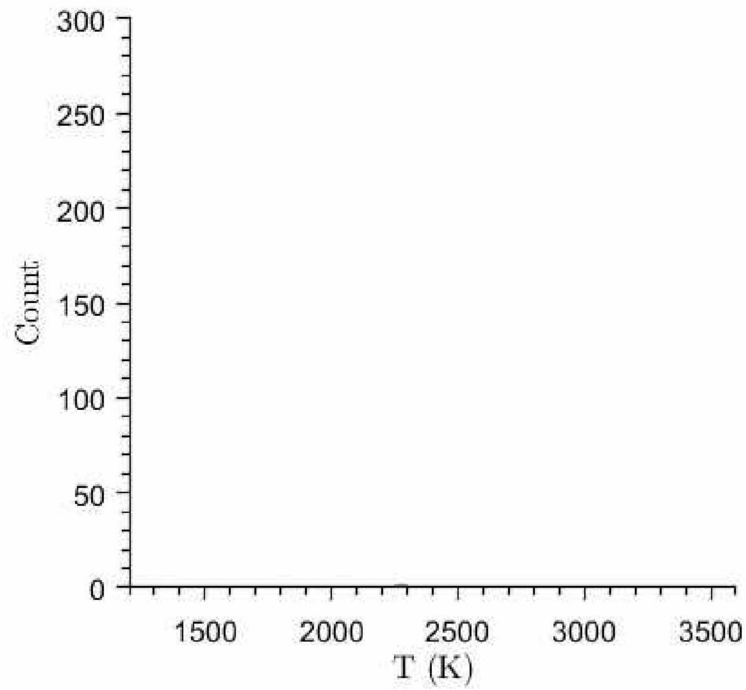
Spectral Fitting

Fit experimental spectra to library

- Linearly interpolate over the temperatures
- Least-squares fitting to minimize the residual
- Examples of the best fits
- Video of all the fits



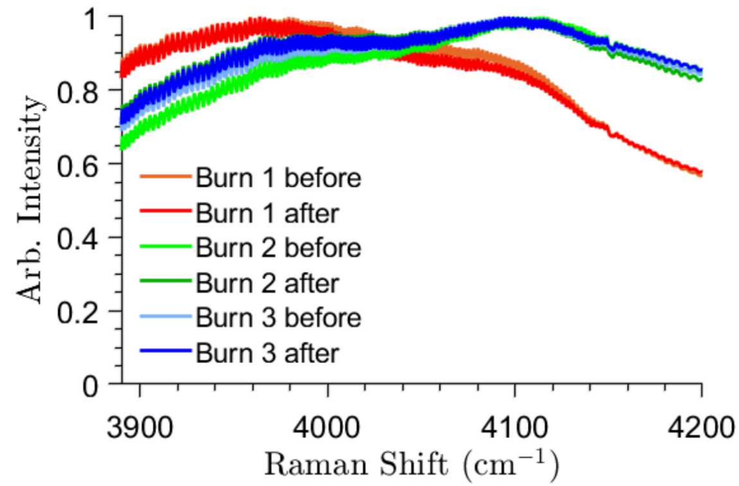




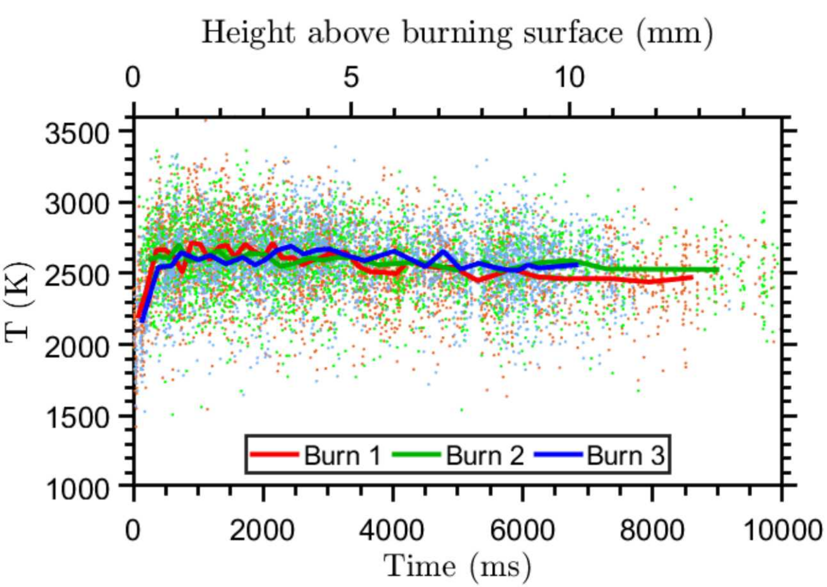
Results

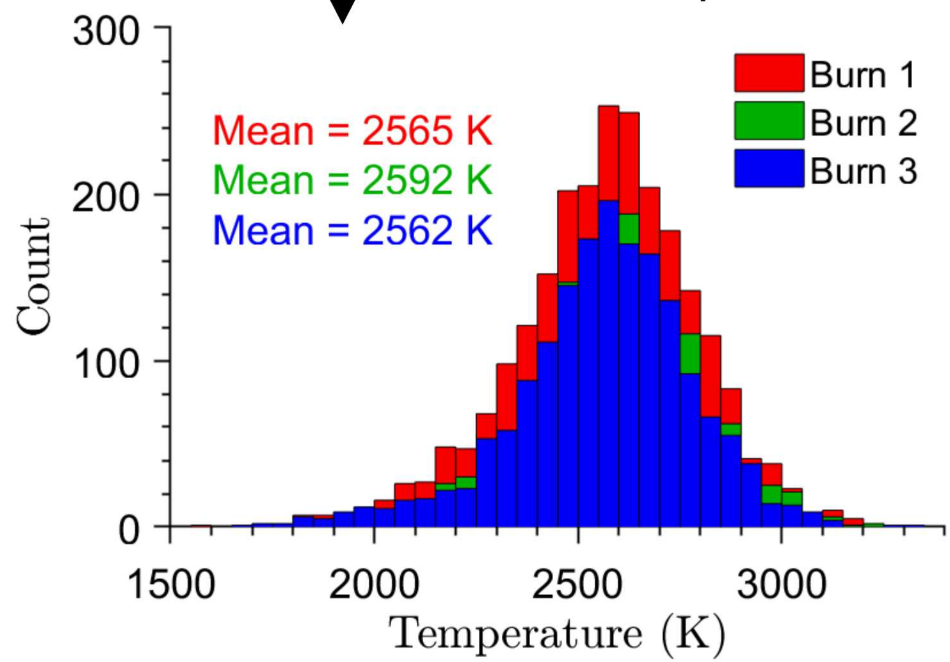
3 Burns

- Mean values within 30 K
  - Even with different nonresonant corrections
- Overall mean of 2574 K
- Temperature rise in the first 200 ms
  - Near the surface… monopropellant flame?
  - Colder, decomposed binder?



Each burn bounded by a nonresonant spectrum





Comparison to previous work

Nitrogen and oxygen CARS, fuel CARS, and particle pyrometry

Kearney et al., *Applied Optics*, 2016

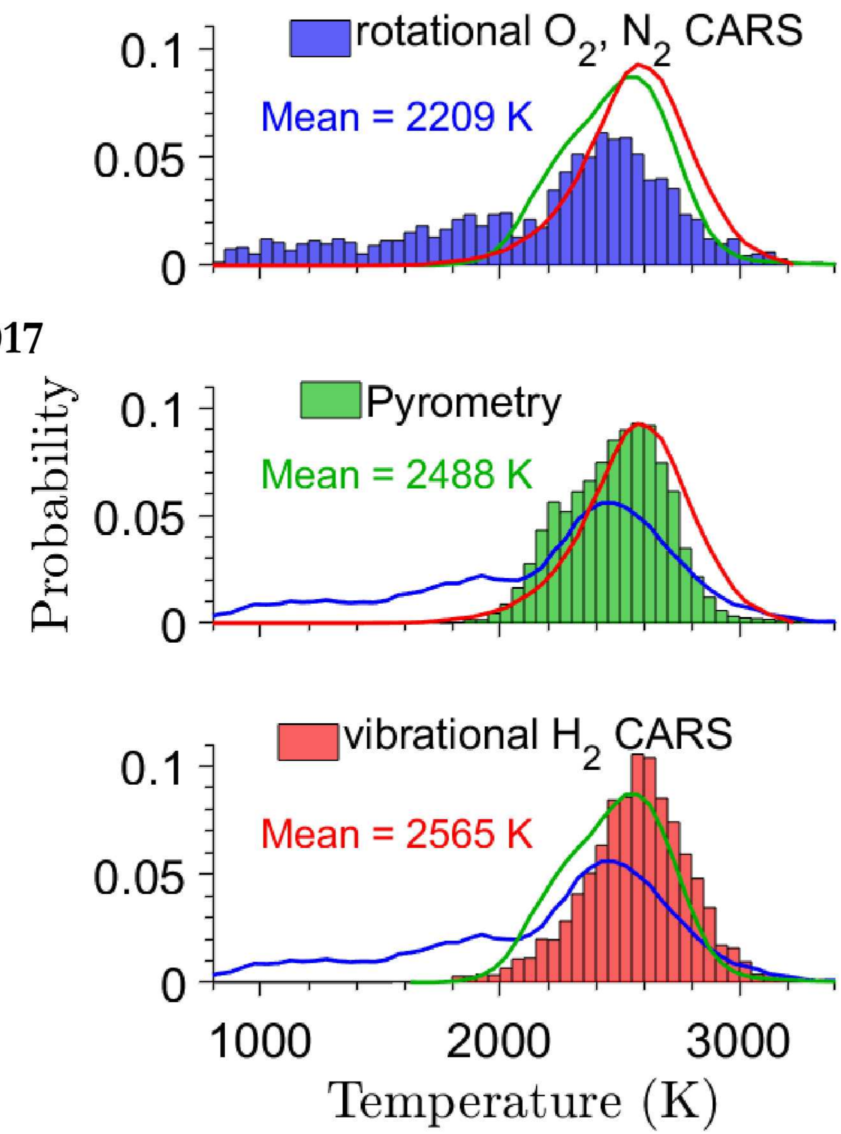
- Rotational temperatures from nitrogen and oxygen
- Temperature, O_2/N_2 correlations
- Low-temperature wing not seen in the H_2 CARS or particle temperatures

Chen et al., similar to *Combustion and Flame*, 2017

- 2-color pyrometry of aluminum particles
- Particulate temperature is comparable to the gas phase
- Peak in histogram in between the O_2, N_2 and H_2 CARS

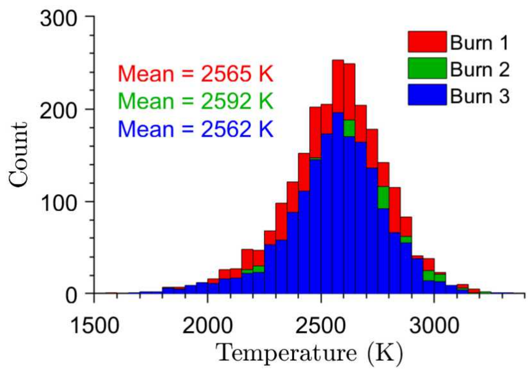
This work

- Rotational temperatures from hydrogen
- Highest mean temperature from all three techniques
- **Improved understanding of the gas-phase burning environment of the aluminum particles**



Summary and Conclusions

1) Developed a vibrational CARS instrument to probe hydrogen
2) Discussed some discrepancies in the literature with H_2 CARS modeling
3) (Once again) demonstrated the effectiveness of probe delayed hybrid CARS in these extreme scattering environments
4) Measured rotational temperatures in the plume of a burning propellant



5) Future work could involve parametric studies to examine if these temperatures scale with physical size of the propellant

Special thanks to Howard L. Stauffer, Sam M. Reardon, and Glen White for their assistance with the propellant burns. Thanks to Yi Chen and Daniel Guildenbecher for providing the aluminum pyrometry data.

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Thank you! Questions?