Sandia National Laboratories

*Exceptional service in the national interest*

# SPECTRALLY INTEGRATED RAMAN SCATTERING IMAGING FOR QUANTITATIVE MIXING MEASUREMENTS IN METHANOL SPRAYS UNDER ELEVATED PRESSURE AND TEMPERATURE


Julien Manin & Junghwa Yi, Lyle Pickett

*Sandia National Laboratories*


Laser Safety Workshop

Livermore, CA
20 May 2026

Julien Manin (JManin@sandia.gov)

Lyle Pickett (LMPicke@sandia.gov)



Acknowledgements:
Gurpreet Singh & Kevin Stork (DOE VTO)

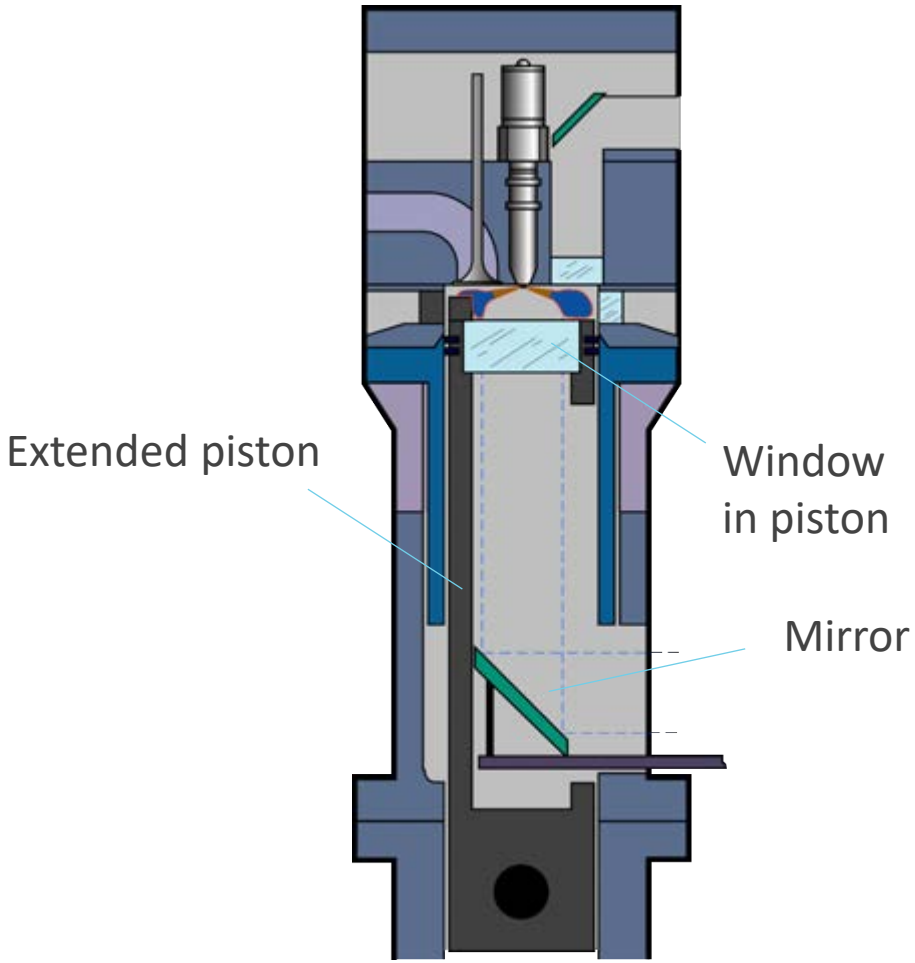


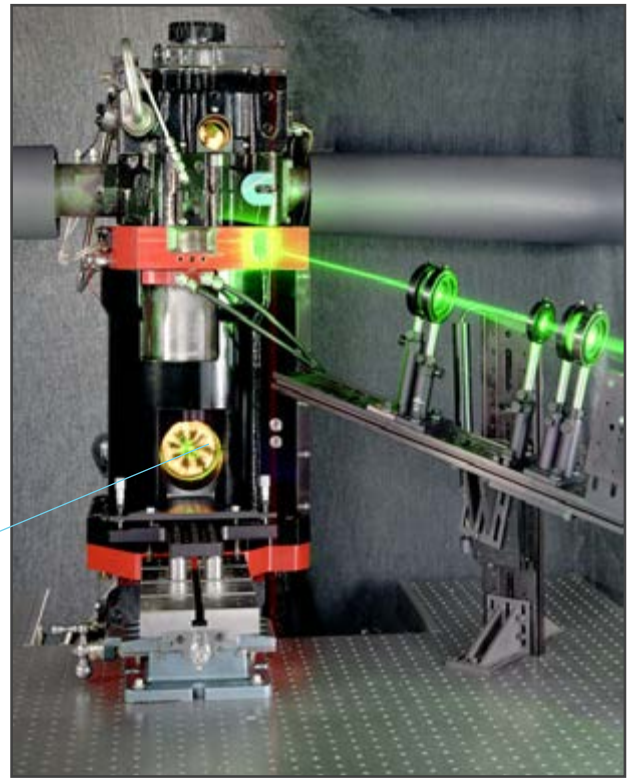
U.S. DEPARTMENT of ENERGY | NNSA National Nuclear Security Administration

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

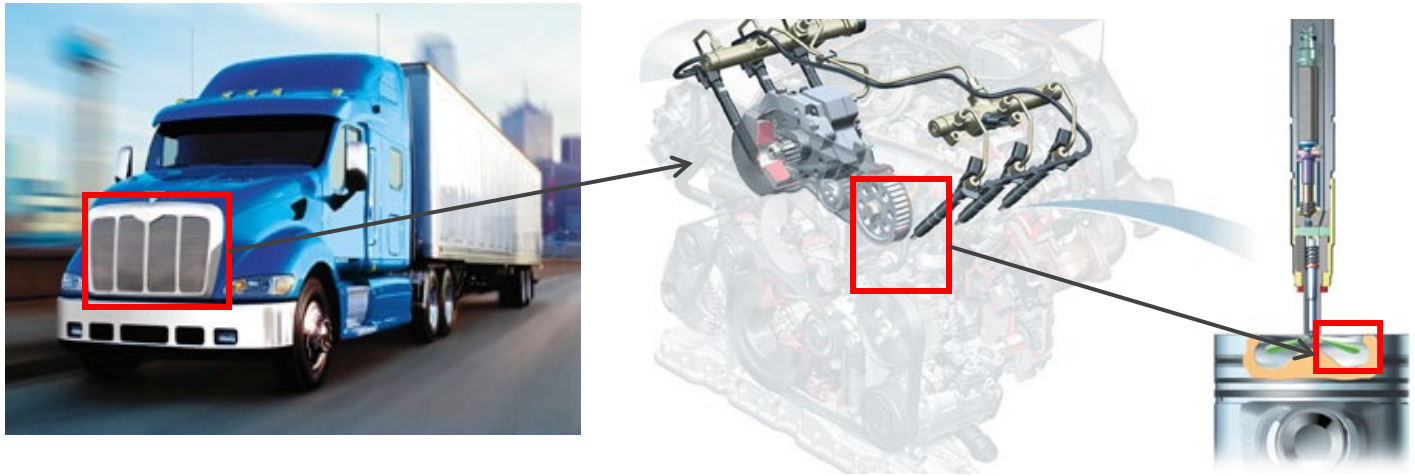
# Use of “optical” engine at Sandia Combustion Research Facility

- Use lasers and optical diagnostics to provide scientific understanding in working engines and high-pressure chambers

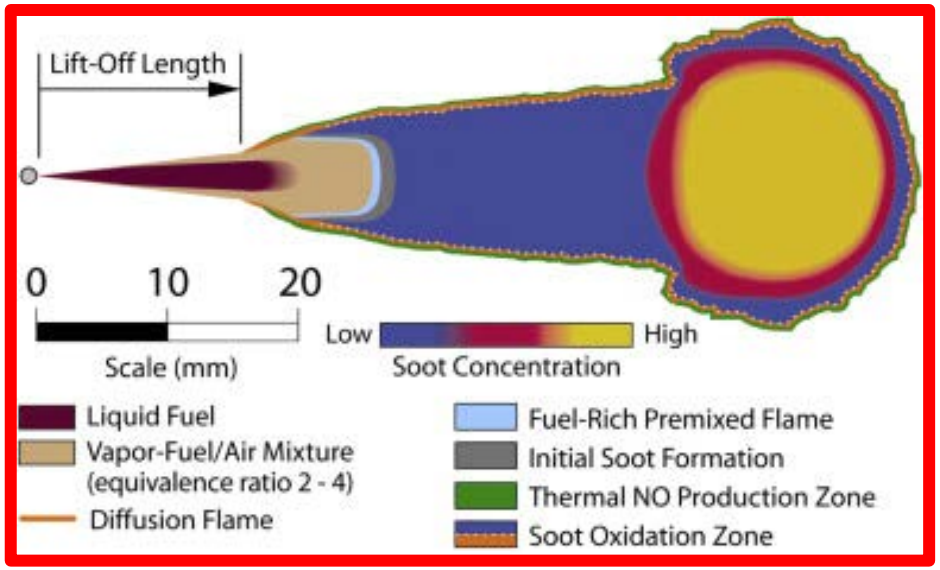


# What happens inside a diesel engine?



John Dec, Sandia
*Conceptual model of diesel combustion*

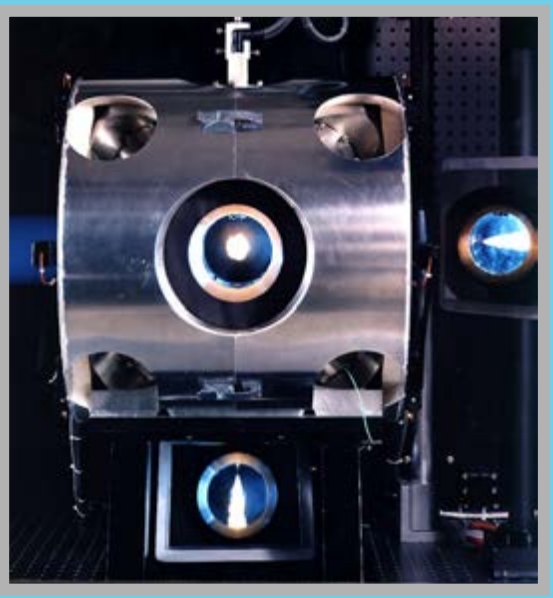


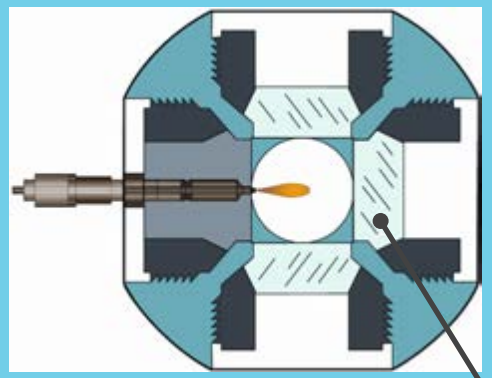



Mark Musculus
*High-speed imaging of diesel combustion*

# Spray combustion chambers to emulate engine conditions

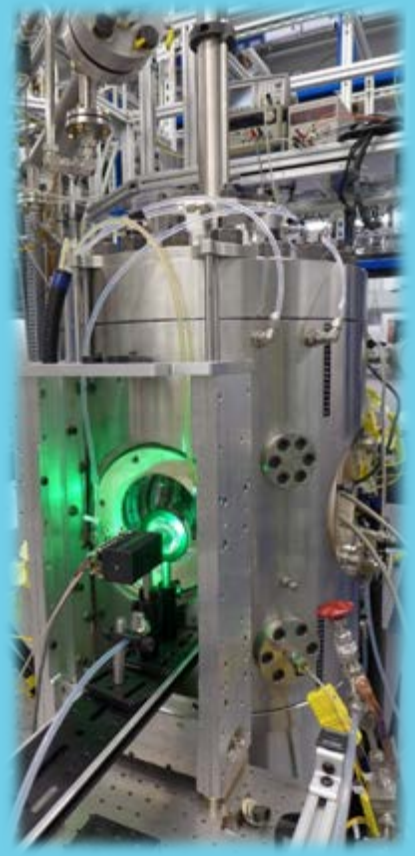
Constant-volume spray chamber

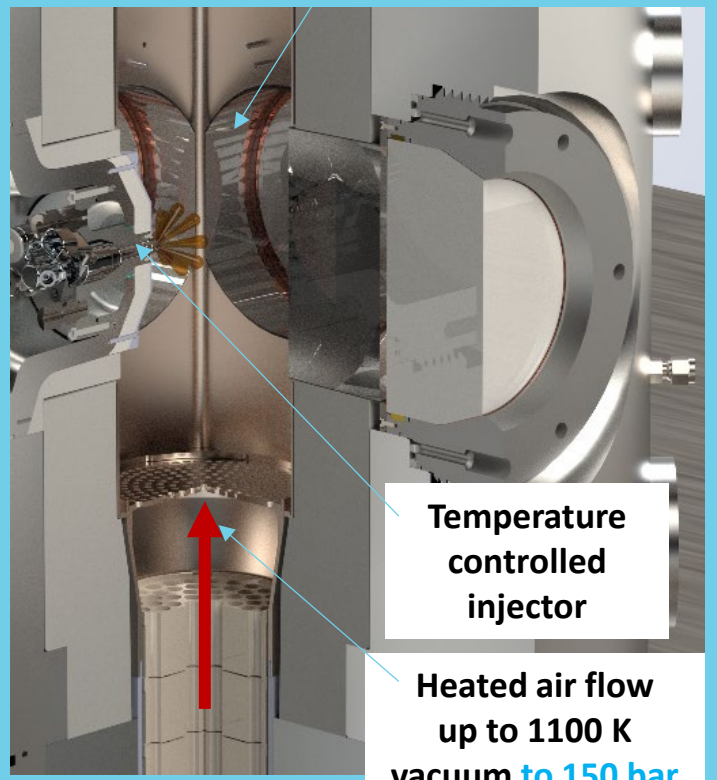




Sapphire 48 mm thick, conical seat to minimize tensile stresses **to 350 bar**

Continuous-flow spray vessel





**Thermally isolated optically accessible spray test section**

**Temperature controlled injector**

**Heated air flow up to 1100 K vacuum to 150 bar**

- **Well-defined ambient conditions**
  - 300 to 1800 K (1100 K, continuous-flow)
  - up to 350 bar (150 bar)
  - **0-21% $O_2$** EGR ($O_2/N_2$)
- Fuel injection systems
  - single- or multi-hole injectors
  - gaseous injection (hydrogen, methane)
  - High-pressure syringe pump up to 2000 bar
  - Tolerant to a wide range of alternative fuels and gases
- Full optical access
  - From deep UV to IR diagnostics
  - 100+ mm on a side
- **Accurate boundary conditions for CFD model development and validation**
  - Better control than an engine
  - Easier to grid

# Diagnostics in engine fuel sprays

**Diesel single-hole**
**Spray A**
**1500 bar**
**90° C**

**900 K**
**60 bar**

Liquid

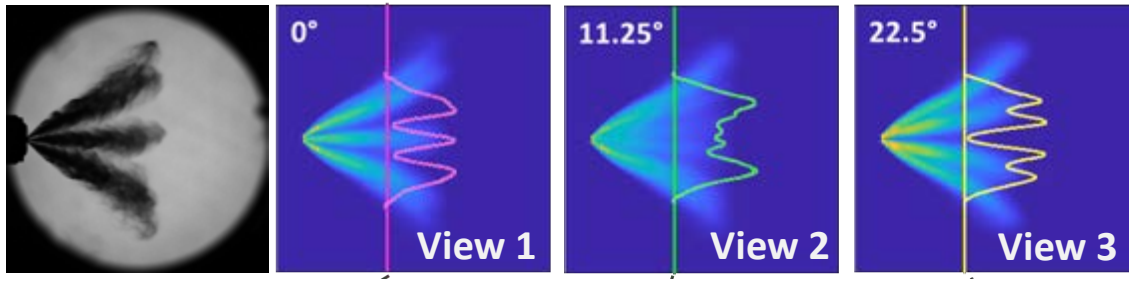
Fuel vapor

Soot

Argonne
APS

Raw data

Ensemble-average (many injections)




Tomographic reconstruction

liquid volume fraction
for 8-hole injector

**Spray G gasoline**

# The Engine Combustion Network

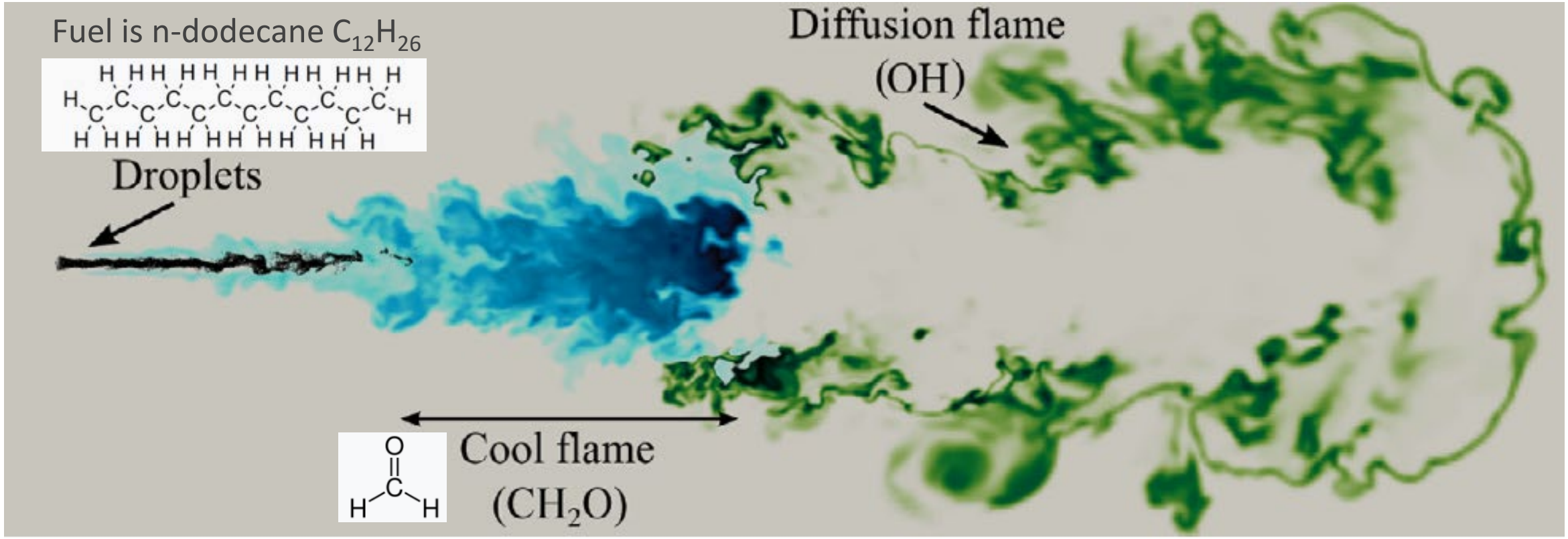
## https://ecn.sandia.gov

ENGINE COMBUSTION NETWORK

- Online archive with data specifically tailored for computational simulations
- ECN target conditions to emphasize modeling shortcomings
  - Spray A,B,C,D,G,M, H2 injector
  - >75 measurements at targets
  - >30 institutions contribute modeling submissions
  - Includes massive fuel database >30 fuels
- U.S. industry vehicle OEMs use ECN archive to improve their own computer modeling tools –> improved engines
- AI is applied to understand data and accelerate model improvement

...

# Example LES predictions of formaldehyde ($CH_2O$) distribution for Spray A

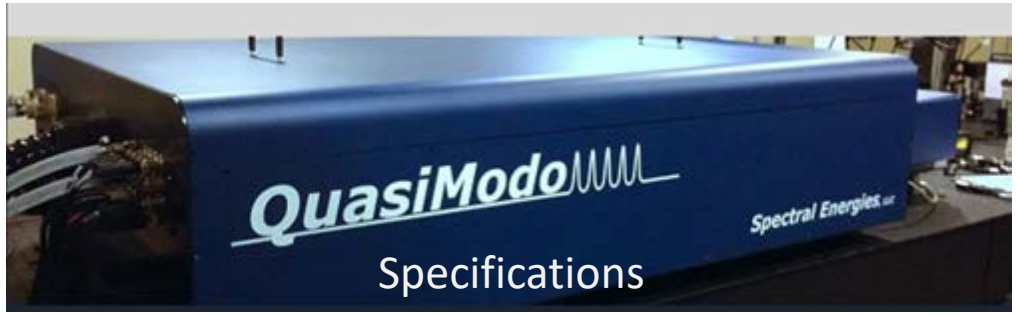



*Kahila et al. Combust. Flame 2018*

flamelet generated manifold chemistry: Ranzi et al. Int. J. Chem. Kinet. 2014
130 species and 2395 reactions

# Experimental setup for pulse-burst planar imaging @ 50 kHz with 355-nm excitation (fluorescence of $CH_2O$)

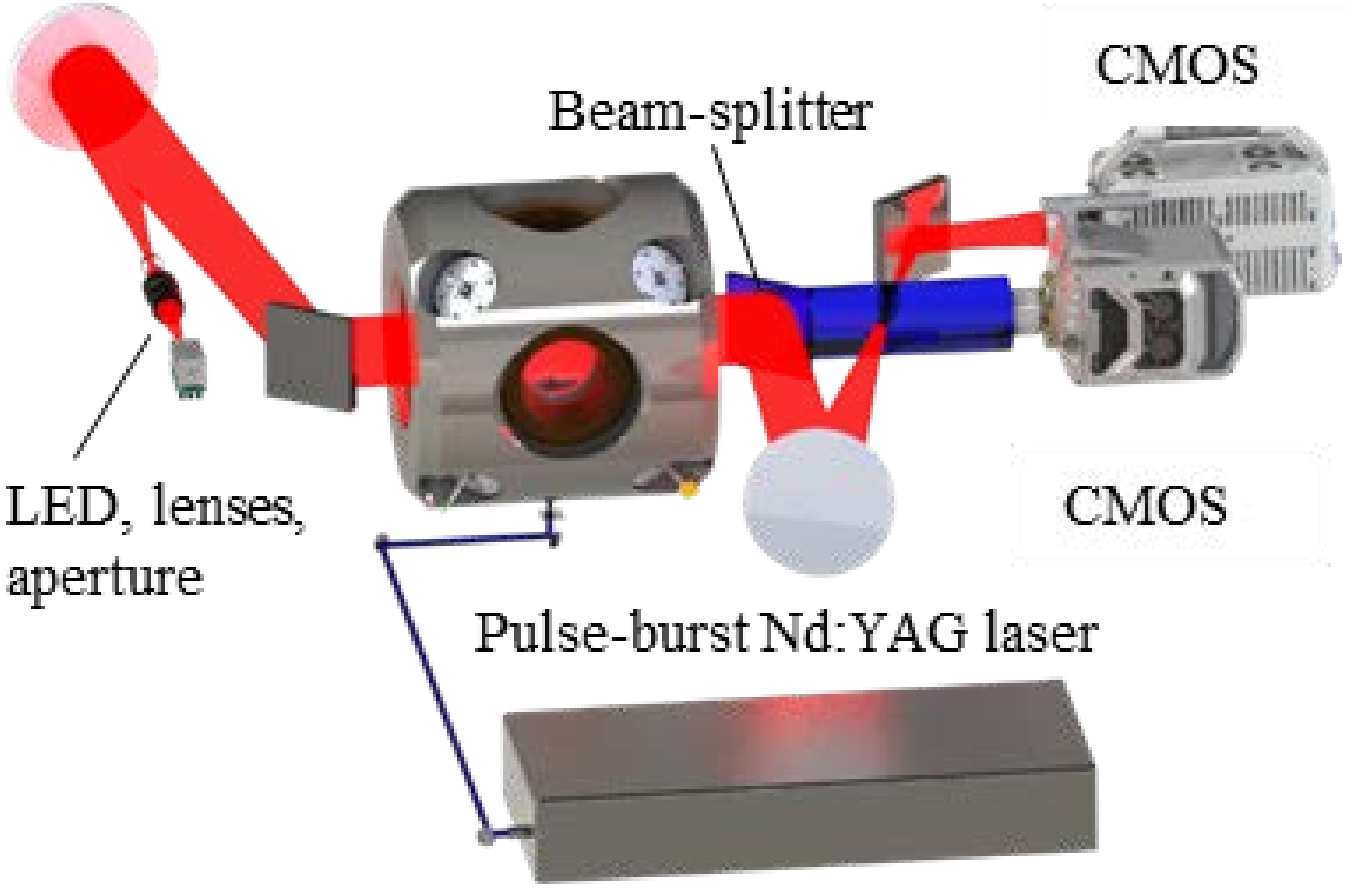
- Pulse burst-mode 355-nm Nd:YAG laser
  - Spectral Energies QuasiModo
  - **50 kHz & 6.0 ms period**
  - 300 sequential **70-mJ** laser pulses (**21 J** total)
  - 55 mm x 0.5 mm laser sheet




Specifications

| Wavelength (nm) | Pulse Energy @ 10 kHz (mJ/pulse) | Total Energy (J) |
|---|---|---|
| 1064 | 1000 | 100 |
| 532 | 600 | 60 |
| 355 | 300 | 30 |
| 266 | 100 | 10 |
| # pulses in 10 ms | 100 | |

Planar AND line-of-sight imaging



# Spray A Condition: 100 kHz schlieren and planar imaging ($CH_2O$ and soot precursors, polycyclic aromatic hyrocarbons)

https://ecn.sandia.gov/pub-links/hss001/pulse-burst-formaldehyde/

# High-speed LIF measurement compared to large-eddy simulation

- See Tagliante et al PROCI 2022

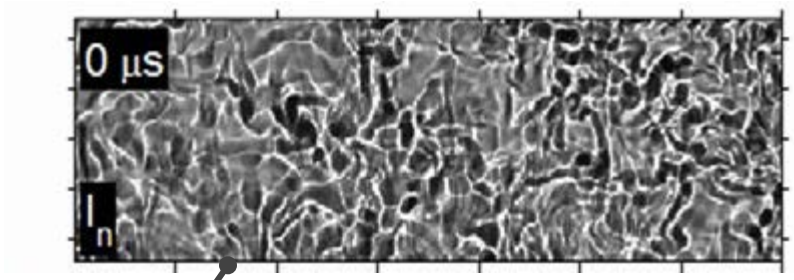
https://ecn.sandia.gov/pub-links/ft001/high-speed-oh-formaldehyde/

- Spray A-3, 60 bar 900 K
- 50 kHz LIF at 355 nm
  - on central plane
  - formaldehyde upstream
  - PAH downstream
- OH* chemiluminescence
  - Line-of-sight
  - simultaneous to LIF
  - high-speed lift-off

# Challenges for diagnostics at engine conditions:

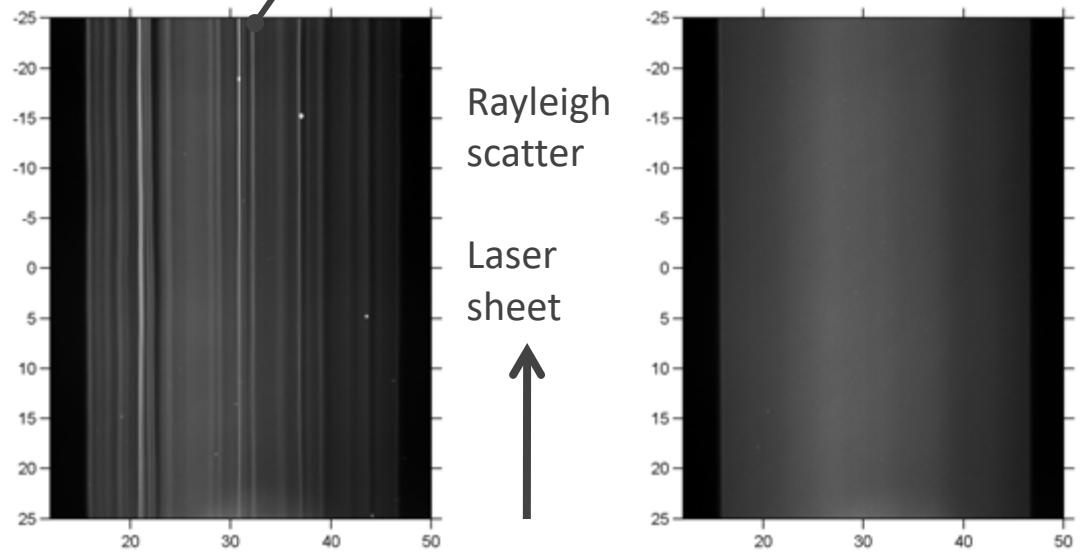
Schlieren image with no spray:

light/dark zones indicate gradients in refractive index



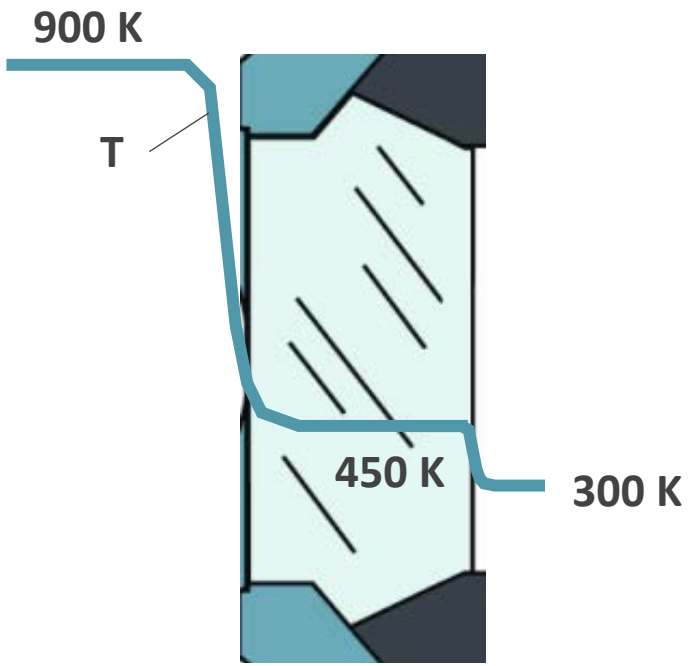

900 K, 60 bar

440 K, same density



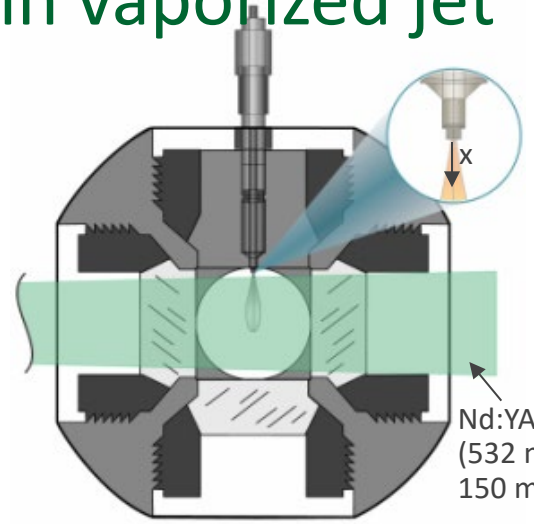

Rayleigh scatter

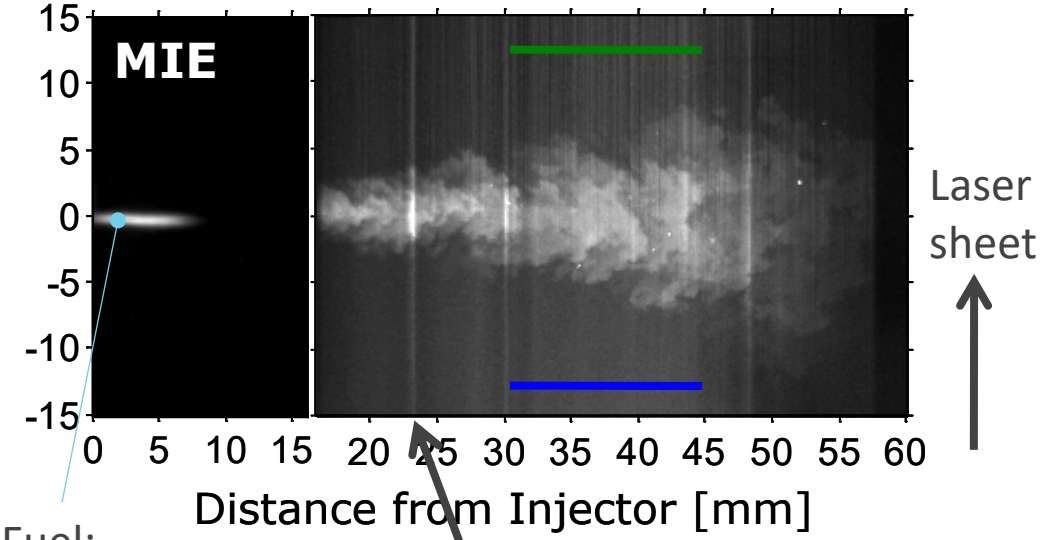
Laser sheet

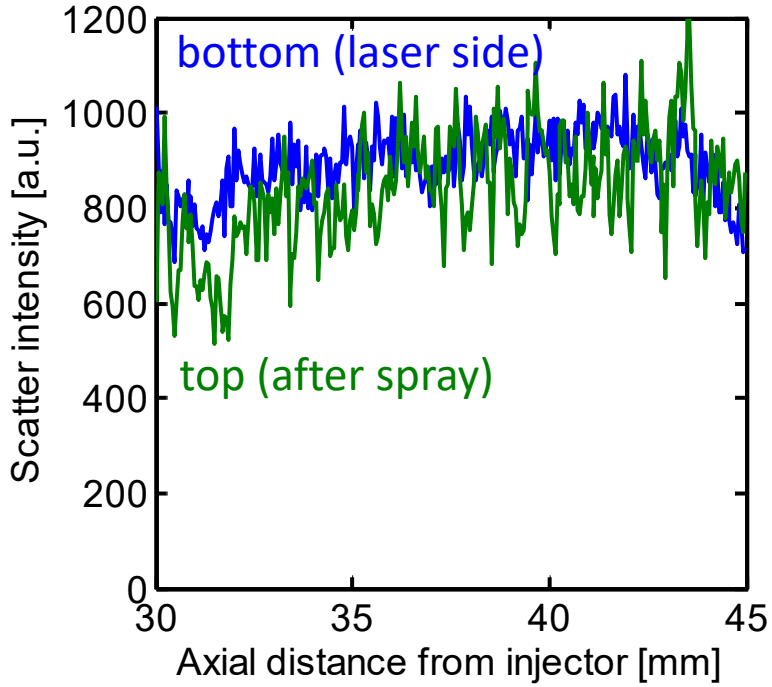



Thermal boundary layer clearly causes beam-steering

# Implement Rayleigh scattering for quantitative mixture fraction measurement in vaporized jet



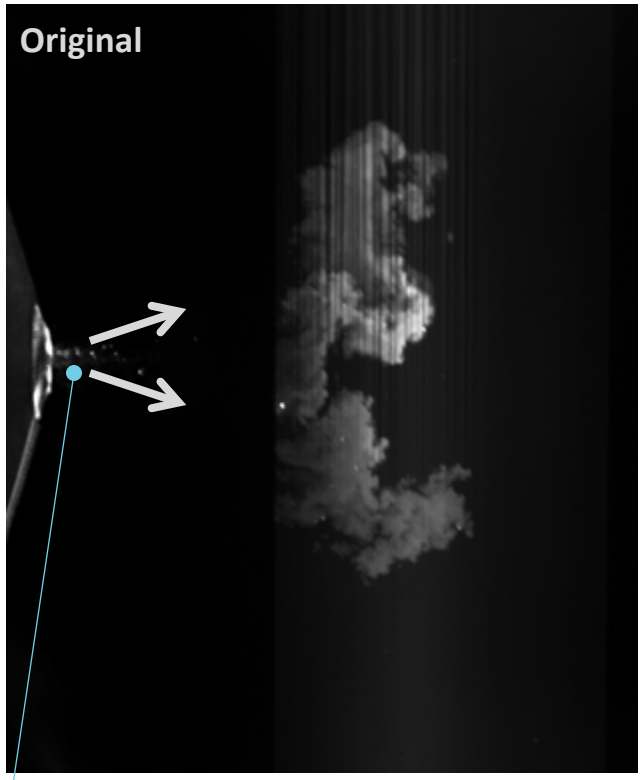



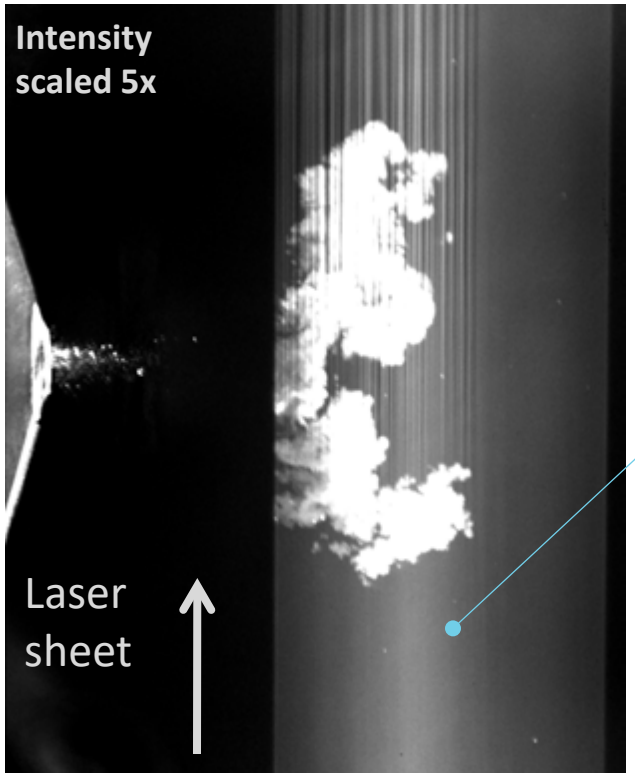




Fuel:
n-heptane,
373 K

Hot spot in laser intensity caused by thermal boundary layer at window

# Beam-steering problem is more severe with multi-plume injector



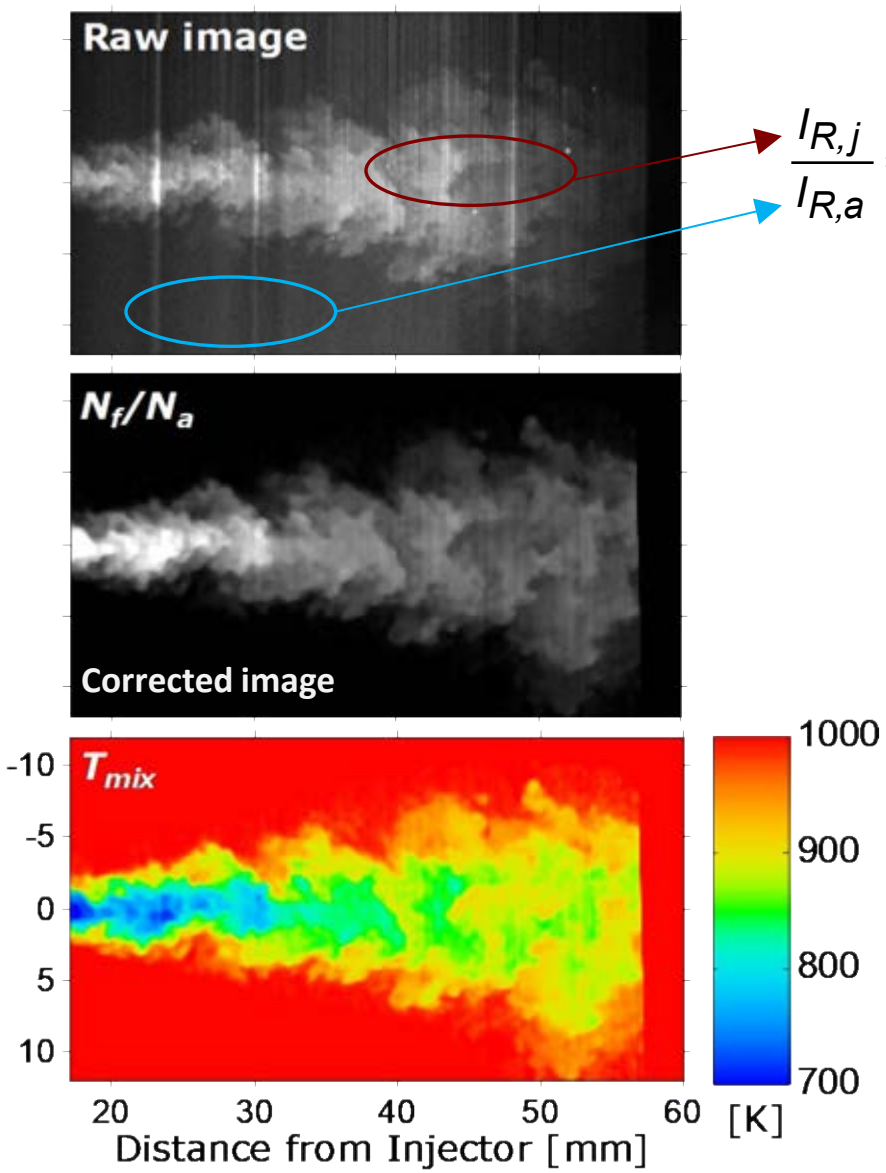

Problematic exit laser intensity distribution

Ambient gas:
16 bar, 900 K

Multi-plume injector 8-hole GDI

- Fewer hot spots in laser intensity distribution because of lower ambient pressure (16 bar).

# Correct for instantaneous beam-steering/laser intensity variation by using $I_{R,a}$




$$\frac{I_{R,j}}{I_{R,a}} = \left( \frac{\sigma_f/\sigma_a + N_a/N_f}{1 + N_a/N_f} \right) \frac{T_a}{T_{mix}} \qquad T_{mix} = f(N_a/N_f)$$

- Measure both $I_{R,a}$, $I_{R,j}$
  - Use in-situ calibration for shot-to-shot $I_{R,a}$ variation in laser sheet intensity because of laser or beam-steering
  - Utilizes one *benefit* of the high P environment—high number density
  - Linear interpolation algorithm improved to include local jet gradients
- Measurement provides
  - Fuel mixture fraction (mass fraction)
  - Mixture temperature (indirectly)

# Changing diesel engines to operate on green methanol

- Methanol is a commodity found in every port
- Can be made from biomass or power-to-liquid processes
- Maersk, Orsted and Liquidwind have ordered 1 million tons of methanol needed for 19 vessels [1,2]

Maersk container ship operating on methanol and 5% diesel

- How should methanol be injected in the engine?
  - Use 5% renewable diesel as a pilot fuel to ignite methanol
  - Must inject about twice as much methanol as diesel to deliver the same energy
  - Larger nozzles can splash liquid into the cylinder liner and oil
- How does the spray vaporization of methanol compare to diesel?

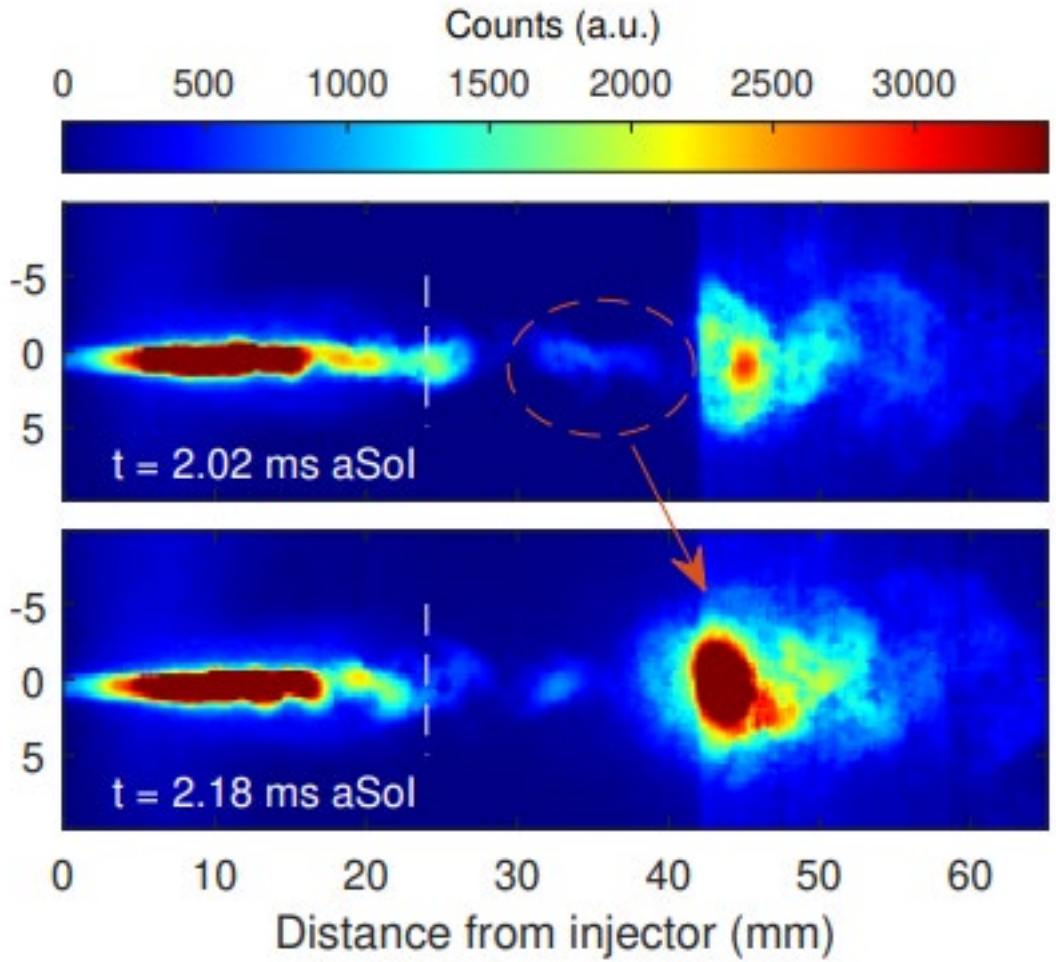
| Fuel Property | Methanol ($CH_3OH$) | n-Dodecane |
|---|---|---|
| Boiling Point Temperature | 64.5 °C (148.1 °F) | 216.3 °C (421.3 °F) |
| Cetane Number | < 5 | 74 – 87 |
| Latent Heat of Vaporization | ~1100 kJ/kg | ~256 kJ/kg |

[1] https://www.globalmaritimeforum.org/news/methanol-as-a-scalable-zero-emission-fuel
[2] https://www.liquidwind.se/emethanol

# Rayleigh scattering measurement shows very long clusters of liquid when using methanol

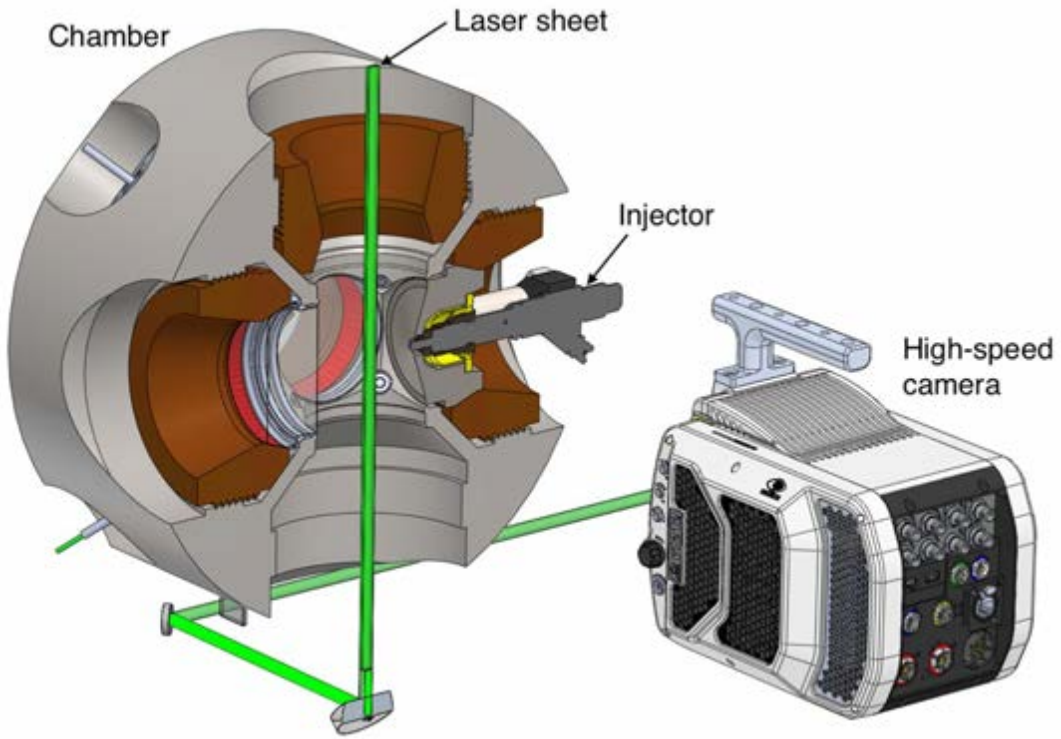
- Laser sheet positioned downstream of 40 mm, even though ECN-defined liquid length is < 30 mm
- 100 kHz planar imaging shows sequence of upstream structure (visible because of reflection) that reaches the laser sheet and scatters strongly
- Recall the $d^6$ dependency for Rayleigh scattering—even 1 μm droplets can saturate imaging sensor!
- We do not see this same effect with other fuels (n-C12, ethanol)

**Methanol Spray D 1500 bar and 363 K mixing with 1000 K, 67 bar gases**




Wan, Kevin, Junghwa Yi, Lyle Pickett, and Julien Manin. "Mixing and combustion of methanol and ethanol high-pressure sprays." *Experimental Thermal and Fluid Science* (2026): 111704.

# RAMAN IMAGING EXPERIMENTAL SETUP




- High-speed pulsed burst-mode laser set to 532-nm
  - 10 kHz operation, 2.5 ms burst duration
  - 200 mJ per pulse energy (25 pulses for 5 J)
  - Laser sheet: 6.3 mm wide by 160 μm thickness
  - Pulses stretched to 100 ns to avoid laser-induced breakdown of the ambient gases
- Raman signals collected with a high-speed CMOS camera
  - Synchronized with laser
  - 580-nm long-pass filter (OD 6+ at 532 nm)
- Raman signals recorded for the following species:
  - Nitrogen stretch (~607 nm)
  - OH stretches (~640–660 nm) from water and methanol
  - CH-stretch methanol (~630 nm)

# SPECTRALLY-INTEGRATED RAMAN SCATTER IMAGING

- Raman scattering is an inelastic light-scattering process in which incident photons interact with the vibrational modes of molecules
  - This results in a frequency shift in the scattered light that is specific to the molecular species

$$I_R = I_0 \times N \times \left(\frac{\partial \sigma_R}{\partial \Omega}\right) \times \Omega \times L_{opt} \times \eta_{opt}$$

- The spectrally-integrated approach compares the Raman signal from the fuel–ambient mixture to that of the ambient alone
  - This comparison eliminates many experimental constants and enables the estimation of mixture fraction through a relative intensity ratio
  - We relate mixture temperature and mixture fraction by applying an adiabatic mixing model

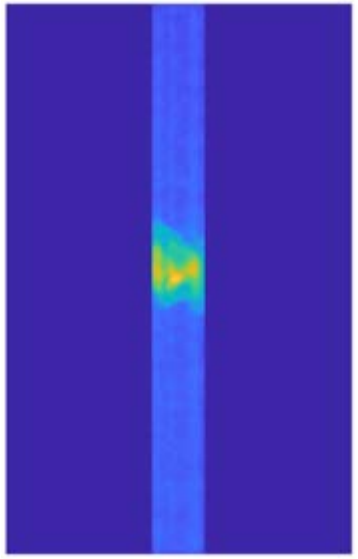
$$\frac{I_{mix}}{I_{amb}} = \frac{\frac{\sigma_{fuel}}{\sigma_{amb}} + \frac{N_{amb}}{N_{fuel}}}{\frac{N_{amb}}{N_{fuel}} + 1} \times \frac{T_{amb}}{T_{mix}} \times \frac{\eta_{mix}}{\eta_{amb}}$$

Calibration

$$\frac{I_{mix}}{I_{amb}} = \frac{\frac{\sigma'_{fuel}}{\sigma'_{amb}} + \frac{N_{amb}}{N_{fuel}}}{\frac{N_{amb}}{N_{fuel}} + 1} \times \frac{T_{amb}}{T_{mix}}$$

- The intensity comparison enables terms such as laser intensity, optical path length and collection solid angle to cancel out in this formulation
  - However, further calibration is needed due to species-dependent Raman shifts to obtain a system-specific cross-section ratio: $\sigma_{fuel}/\sigma_{amb}$

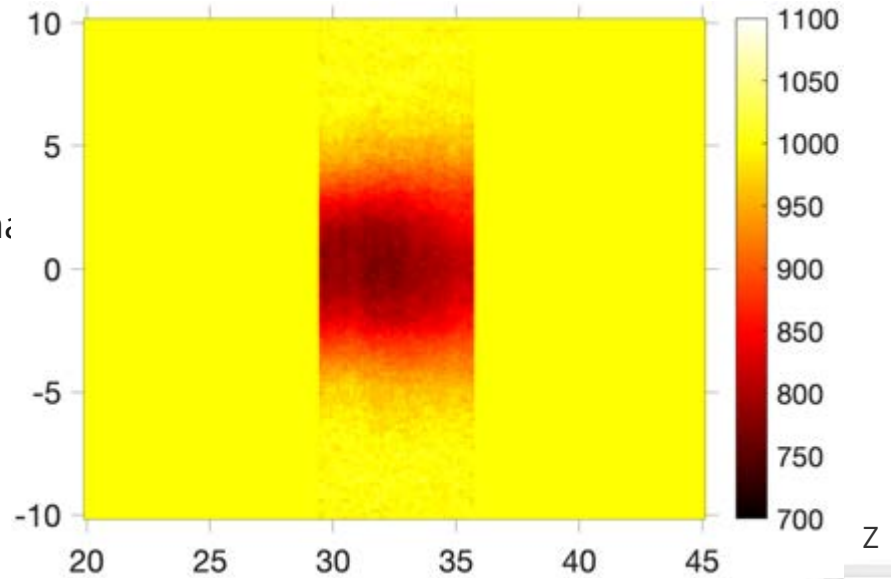
# MIXING MEASUREMENTS IN METHANOL SPRAYS



- Both the ambient and the fuel-ambient mixture is captured with the spectrally-integrated Raman scatter imaging technique
  - Note: Images are particle and background corrected only
- Single-shot high-speed videos reveal significant variations in signal intensity
  - Richer mixtures are observed near the centerline, with leaner mixtures appearing toward the jet periphery
  - Ensemble averaging performed
  - Time-averaging performed during quasi-steady period

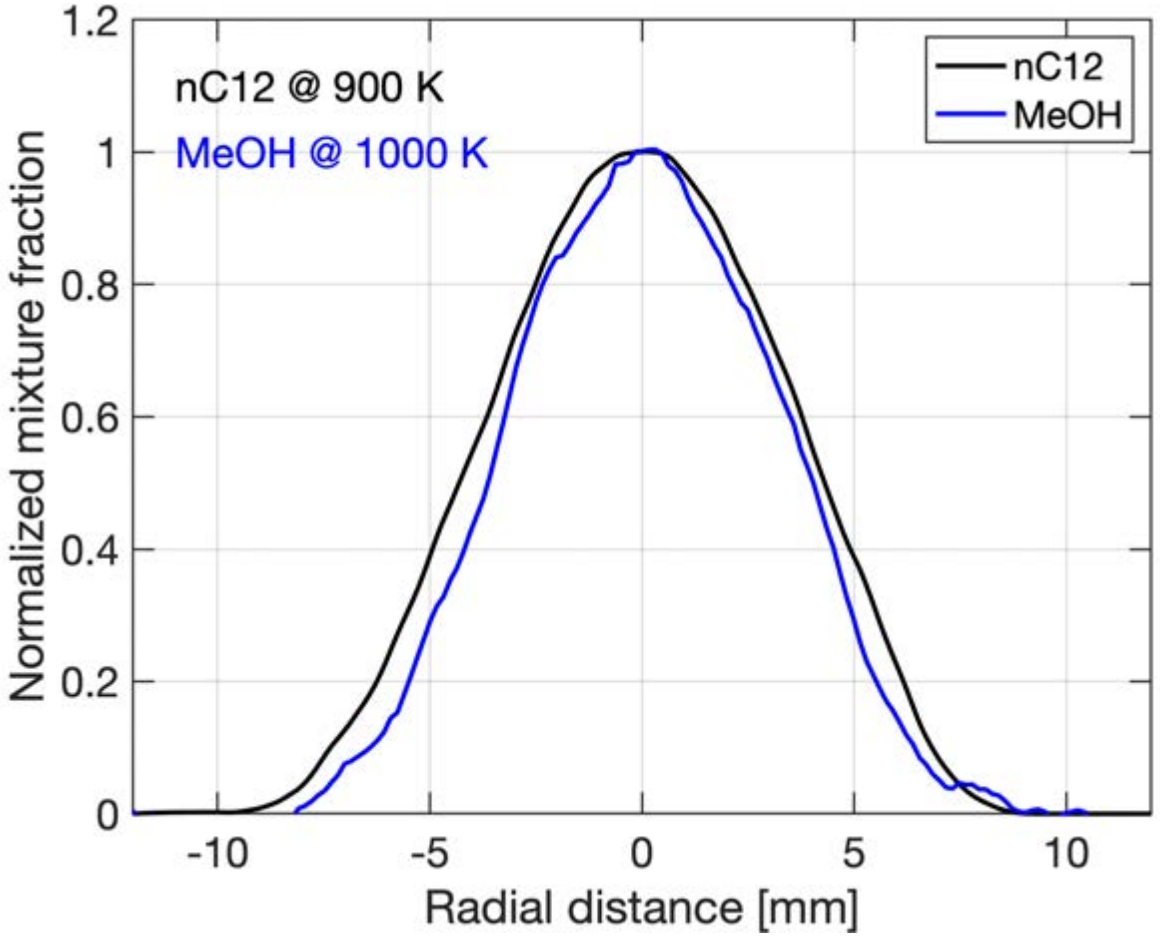
- Ensemble averaging performed
- Uncertainty affected by the number of injections performed
  - Despite the low signal levels, intrinsic noise from the diagnostic is low
    - Uncertainty is similar to equivalent measurements in n-dodecane using plana laser Rayleigh scattering, on the order of 5 to 7%

$$\frac{I_{mix}}{I_{amb}} = \frac{\frac{\sigma'_{fuel}}{\sigma'_{amb}} + \frac{N_{amb}}{N_{fuel}}}{\frac{N_{amb}}{N_{fuel}} + 1} \times \frac{T_{amb}}{T_{mix}}$$



# MIXING QUANTITIES AND COMPARISONS

- Compared to Rayleigh scattering mixing measurements with n-dodecane, the measured methanol jet is more narrow
  - This is in agreement with the faster penetration rate we measured for methanol under these conditions
- Such behavior is likely explained by two aspects, both stemming from methanol's high enthalpy of evaporation:
  - 1) Methanol's longer liquid-phase penetration induces more velocity slip and thus lower momentum exchange between the jet and ambient
  - 2) The higher densities near the jet centerline provides a momentum ratio that is jet dominant



# SUMMARY AND ONGOING ACTIVITIES

- Building on research to understand and predict methanol and diesel fuel sprays, a novel Raman scatter imaging method was developed to quantify two-dimensional vapor-phase mixing in evaporative liquid sprays of small molecules
- Quantitative mixture fraction fields of methanol jets show
  - The sample results highlight the high cooling power of methanol, showing mixture temperatures well below the ambient
  - As a result of the high heat of vaporization, methanol jets appear to be narrower than n-dodecane measurements

# QUESTIONS?

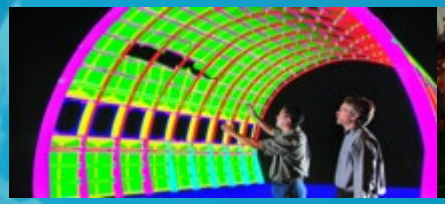
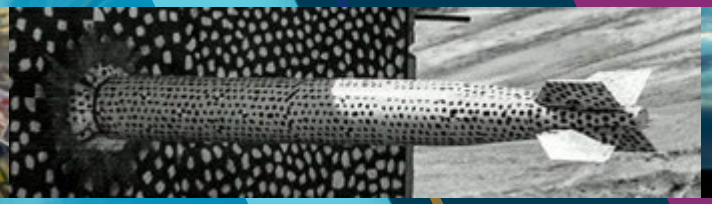
Julien Manin (jmanin@sandia.gov)

Lyle Pickett (LMPicke@sandia.gov)

Sandia National Laboratories

Please visit ecn.sandia.gov

ENGINE COMBUSTION NETWORK

Sandia National Laboratories

*Exceptional service in the national interest*