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Sandia efforts to measure cryogenic hydrogen dispersion and enable separation distance reduction

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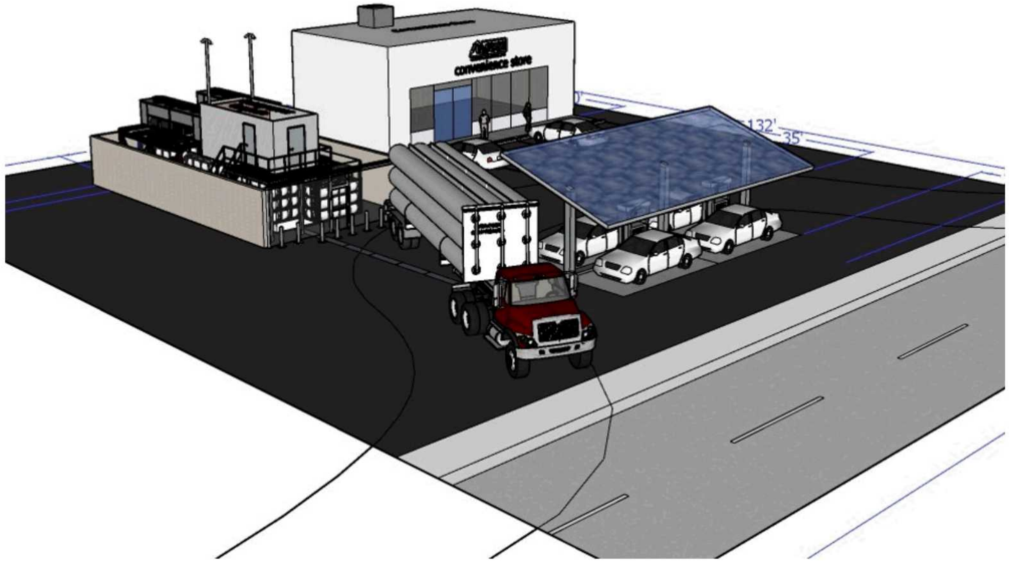
Current separation distances for liquid hydrogen systems in the U.S. are based on consensus rather than a comprehensive scientific basis

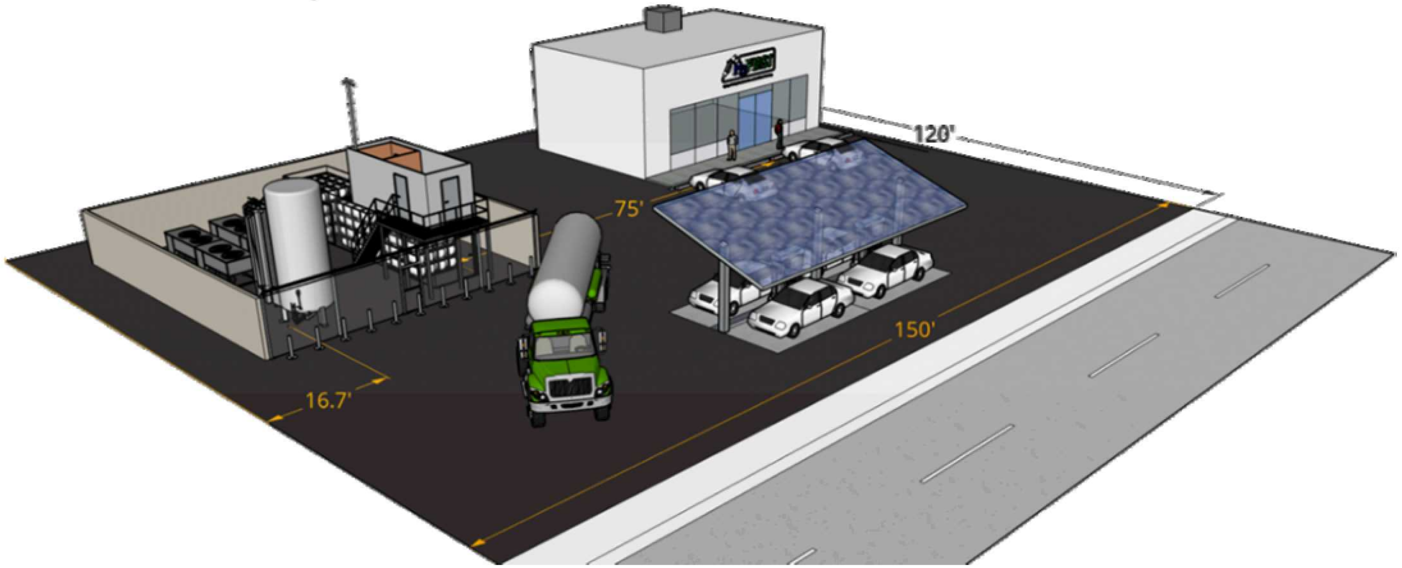
Compressed H_2 storage

- Previous work by Sandia led to science-based gaseous H_2 separation distances



Liquid H_2 storage

- Even with credits for insulation and fire-rated barrier wall, 75 ft. offset to building intakes and parking make footprint large



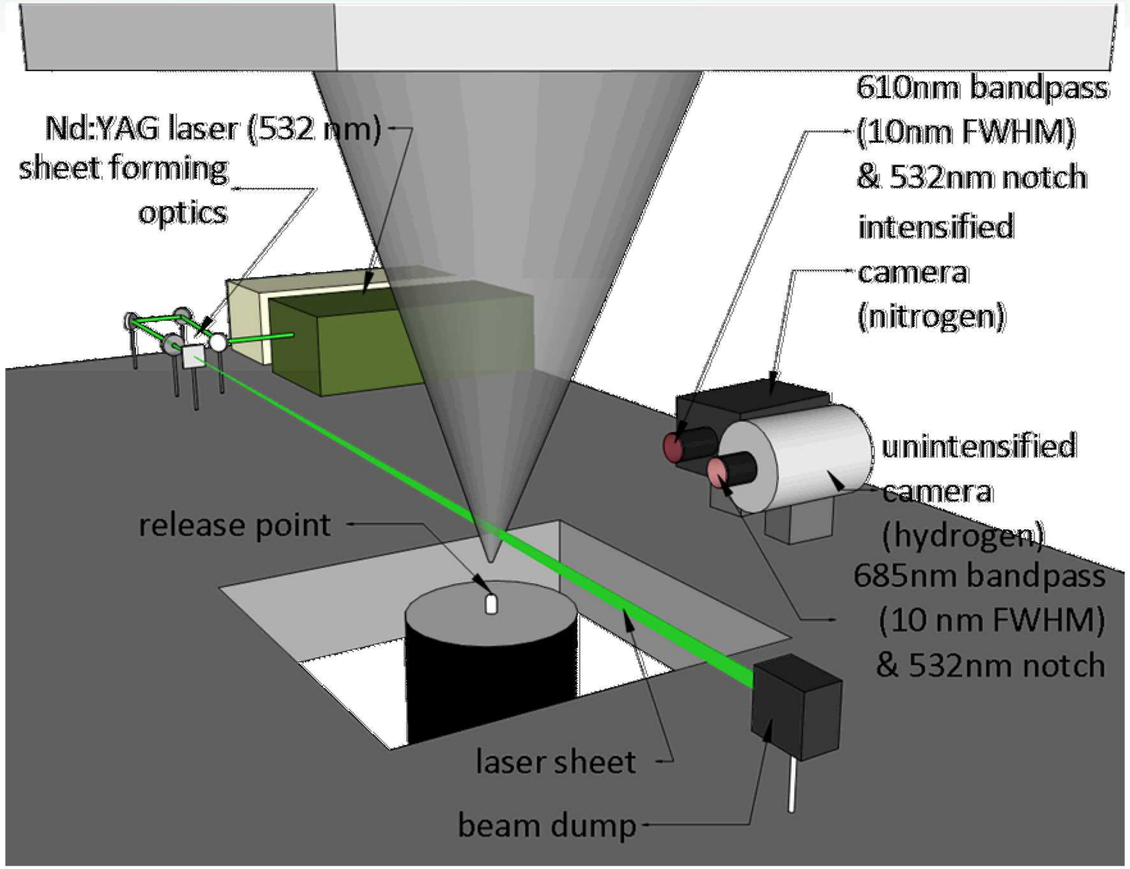
Research objectives

- Develop a diagnostic that can accurately measure the dispersion of cryogenic hydrogen in real-world scenarios
- Gather data and validate models for dispersion
- Understand the worst case scenario for conservative risk estimates
  - Does wind cause channeling and increase the distance to the LFL, or improve mixing to decrease the distance to the LFL?
  - Does high humidity cause increased buoyancy due to the energy transfer from the condensation of moisture, or does the condensed moisture drag the hydrogen down so it’s less buoyant?
  - Is the hydrogen concurrent with the condensed moisture? Does concurrency depend on the humidity?
- Use models to inform safety codes (NFPA 2) and generate proposed changes for the next edition

First efforts showed planar Raman imaging to work well in a lab setting

H_2 Raman cross-section ≈ 10^{-30} cm^2

- Signals are low
  - High powered light source required (~700 mJ/pulse @ 532nm, 12mm tall sheet)
  - Fast optics for collection (F/1.2)
- Large Raman shift enables higher optical density filters to remove unwanted Mie scatter
  - 10 nm FWHM bandpass filters at wavelengths of interest
  - OD of 12 @ all wavelengths
  - OD of 18 @ 532 nm
- Signals for other Raman lines (rotational, etc.) low at cryogenic temperatures



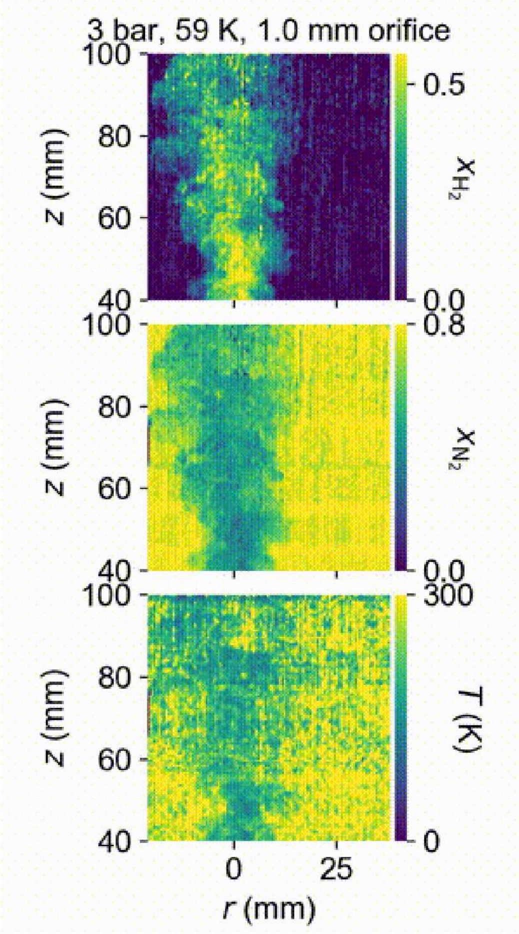
H_2: shift of 4161 cm^{-1} (532nm → 683 nm, 355nm → 416 nm)

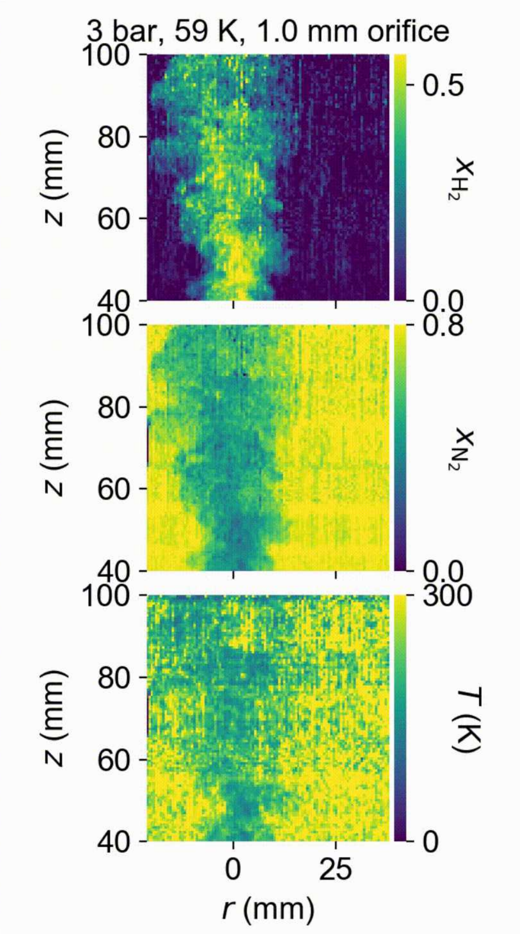
N_2: shift of 2331 cm^{-1} (532nm → 607 nm, 355nm → 387 nm)

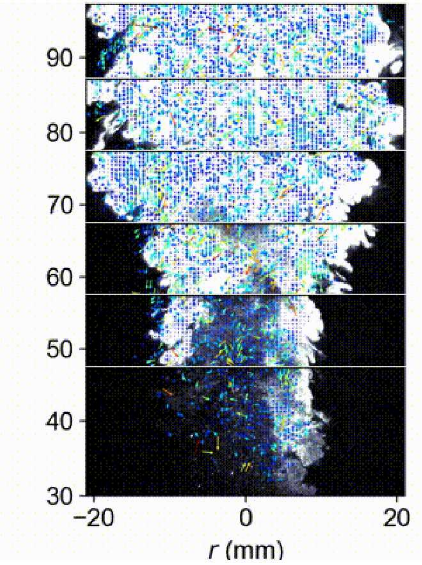
Raman was used in a lab-scale campaign to measure releases from ≈1 mm orifices

T_{noz} [K]	P_{noz} [bar_{abs}]	d [mm]	T_{throat} [K]	n_{hts}
58	2	1	43.5	4
56	3	1	41.9	4
53	4	1	39.6	4
50	5	1	37.4	5
61	2	1.25	45.7	6
51	2.5	1.25	38.2	2
51	3	1.25	38.2	6
55	3.5	1.25	41.2	3
54	4	1.25	40.4	2
43	4	1	32.1	2
59	3	1	44.2	6
56	3.5	1	41.9	1
80	3	1	60.3	5

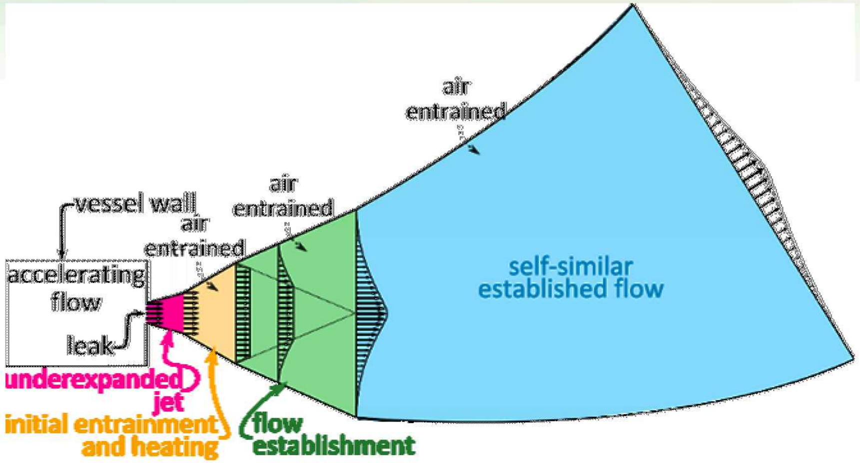
With PIV

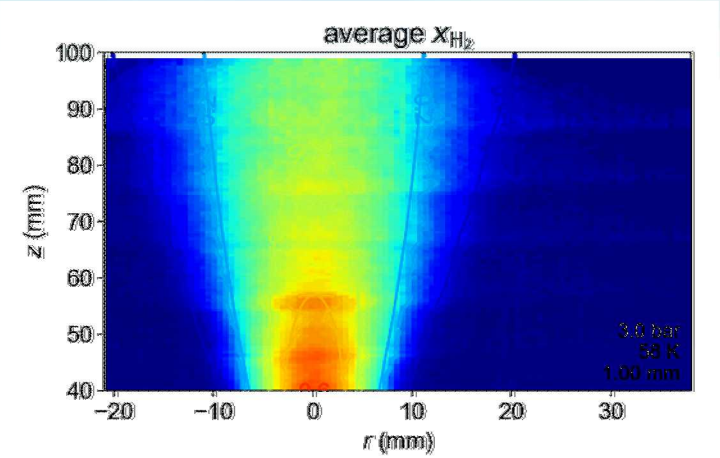




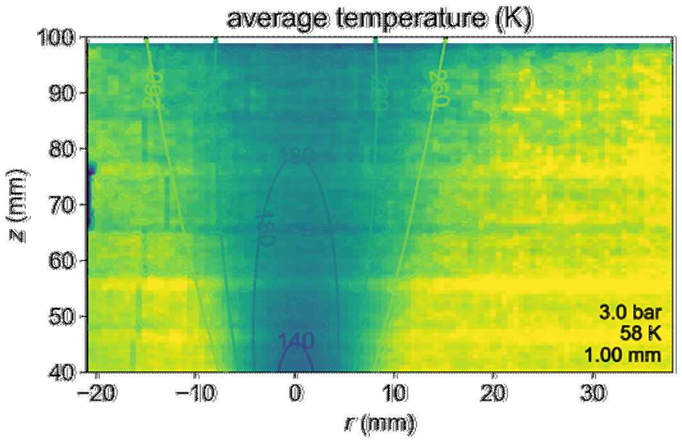


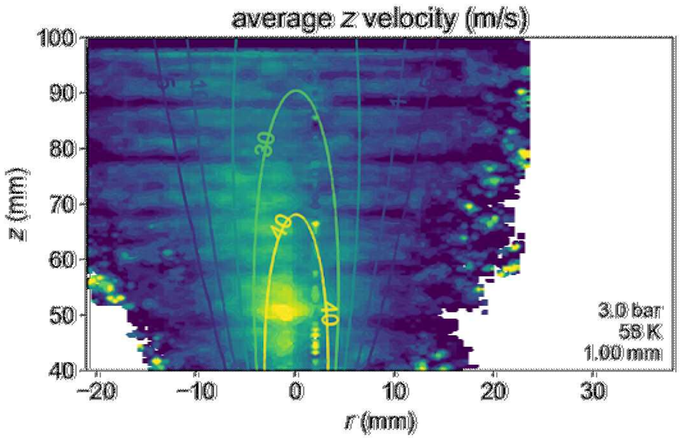
ColdPLUME model has been validated with laboratory data





- Experimental results shown by shading and thick, dashed lines
- ColdPLUME model results are thin, solid lines

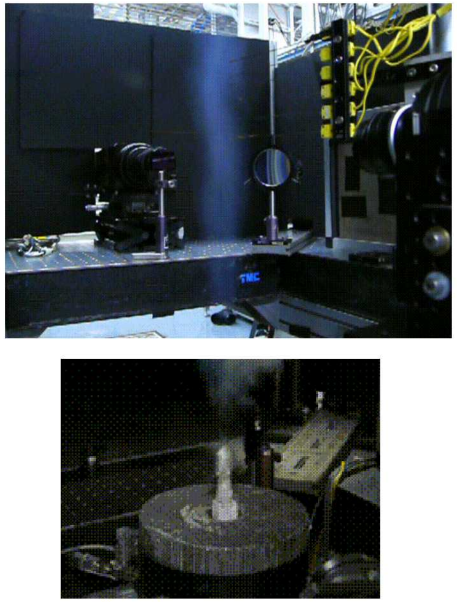




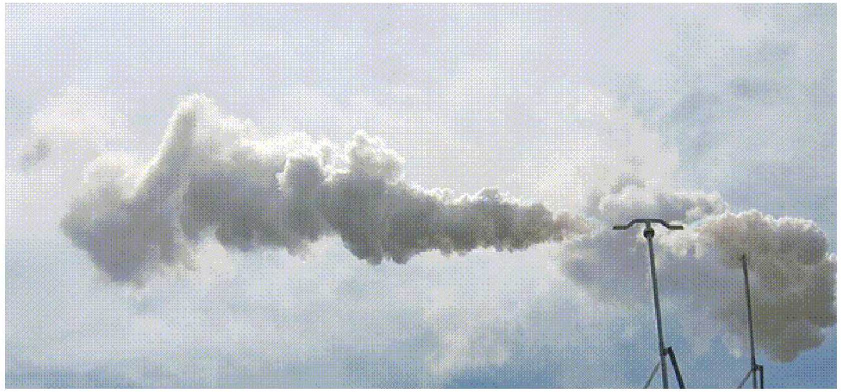
➢ Model accurately simulates mole fraction, temperature, and velocity - can be used as predictive tool

We have scaled the laboratory setup to measure Raman scattering from larger experiments

- Enables application of diagnostic to releases with more flow (larger orifices or higher-pressures)
  - Details of plume interactions with ambient air
- Future experiments to explore additional LH_2 physics:
  - Pooling
  - Evaporation from LH_2 pools
  - Impact of barrier walls as a mitigation



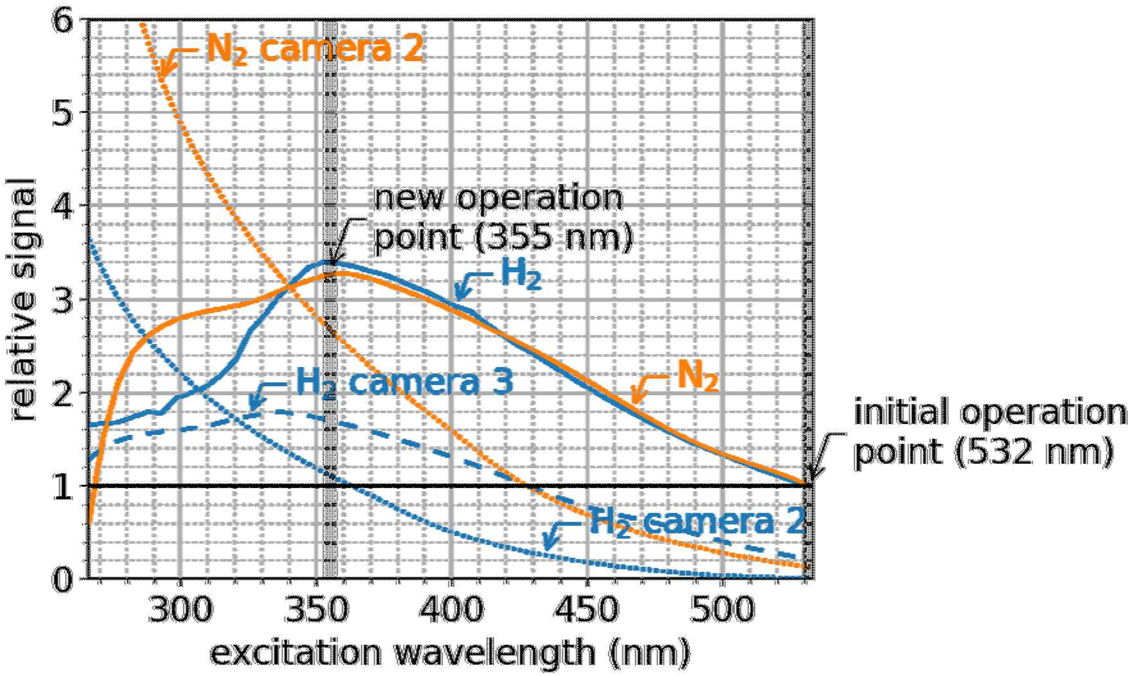
≈ 1 mm orifice, ≈ 0.5 g/s



≈ 50 mm orifice, ≈ 15 g/s

Signal-to-noise ratio from Raman imaging can be boosted by utilizing the wavelength dependency

- $\text{Raman signal} \propto (incident\ energy)(cross - section)(number\ density)$
- $cross - section \propto (1/\text{wavelength} + \Delta energy)^4$

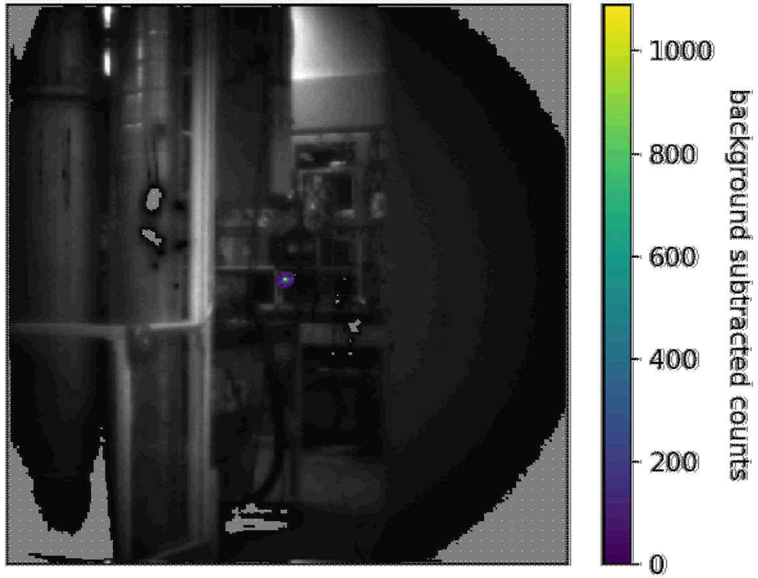


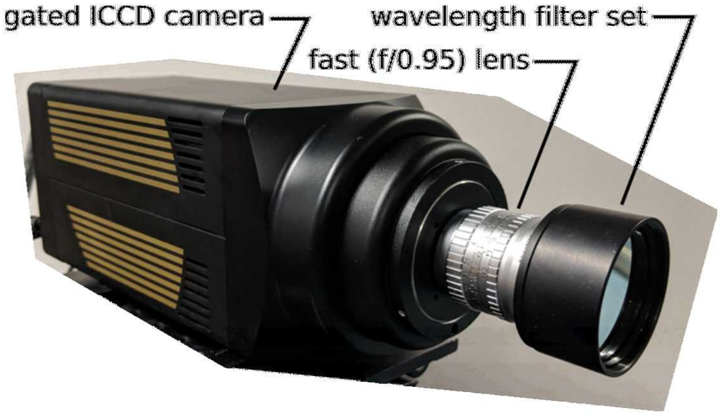
- Signal scales inversely with wavelength to the 4th power
- Cameras/sensors can have reduced efficiency at low wavelength
- Laser harmonic generation reduces output power
- Net win in signal (>3x) going from 532→355 nm

Demonstrated acceptable signal to noise in the laboratory

- Iterated through a range of lens and filter combinations
- Imaged hydrogen from 40 foot standoff distance in the laboratory
- Observed nearly 30 degree field of view (20 ft scene from 40 ft distance)
- Shot-to-shot variation in the laser pulse monitored by usin a fast-photodiode and box-car integrator setup

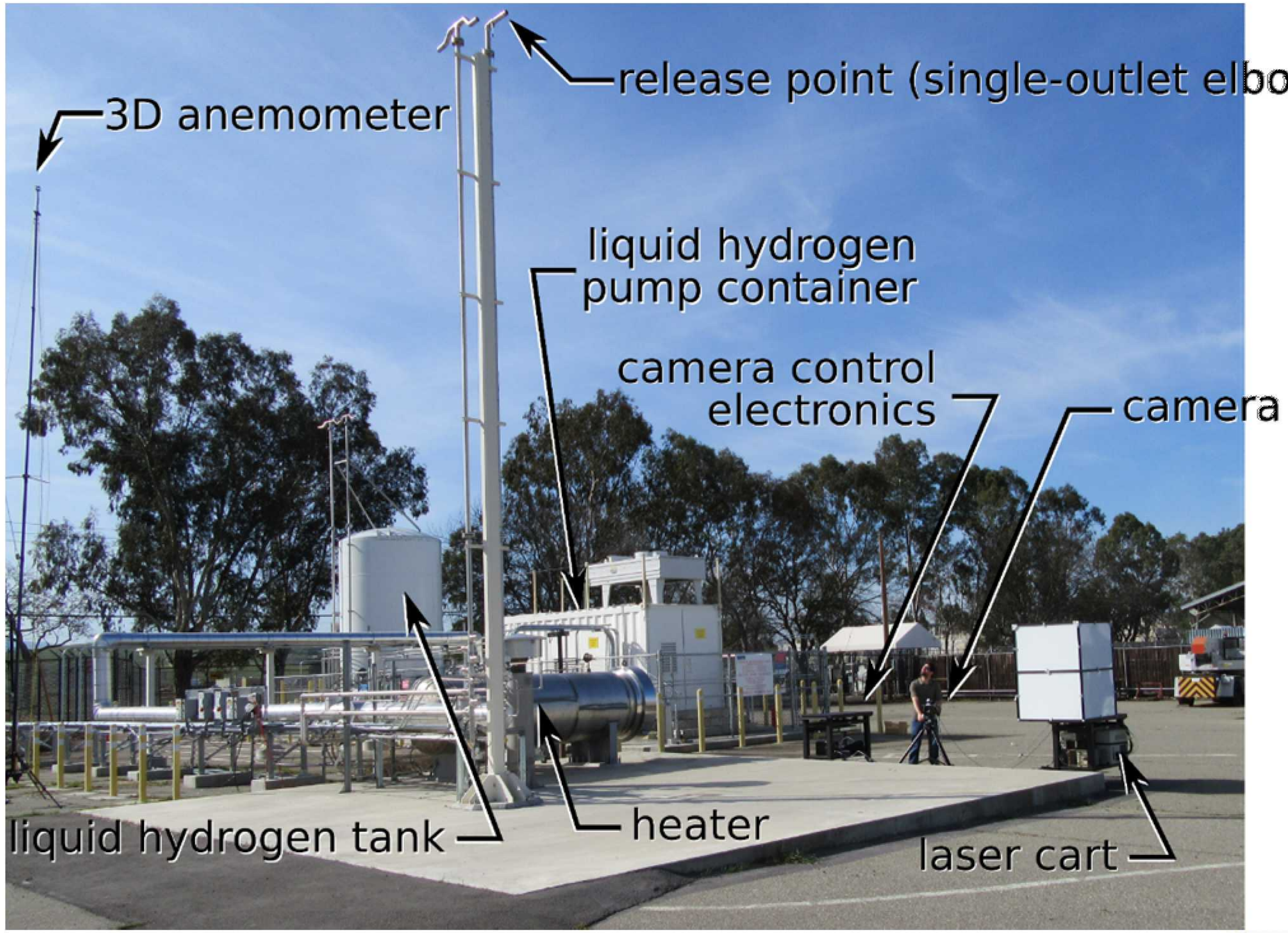
Raman signal overlaid on laboratory scene

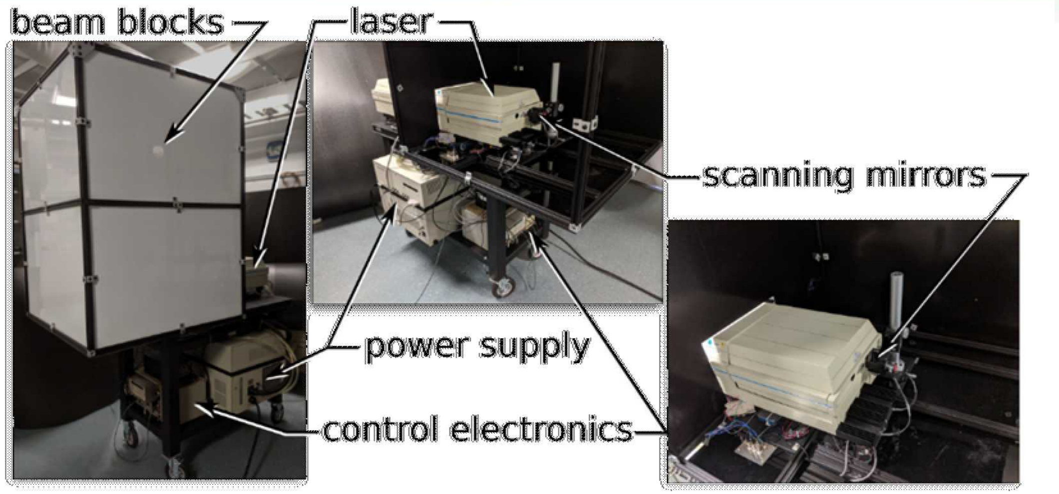


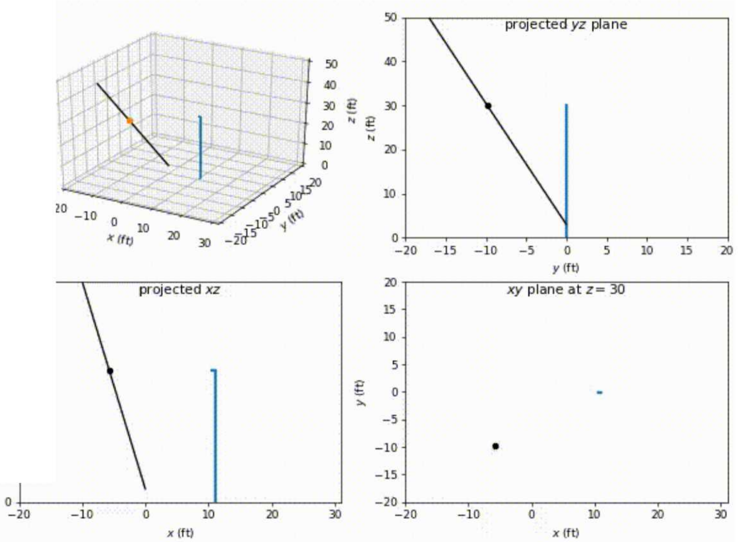


➢ Uniquely fast optics enable collection of small Raman signal

A mobile laser scanning system is at the LLNL liquid hydrogen pad







Experimental campaign to commence in a matter of days to weeks

- Heaters and pump enable a wide range of flow rates and temperatures at vent stack
- Proximity to SNL enables experiments to be run on short notice (when weather is right – for a range of conditions)

- Liquid hydrogen tank has been filled
- Laser system is at LLNL
- Bullhorns have been replaced by single outlet elbow (horizontal release)
- Additional thermocouples have been installed along the flow path
- Liquid pump tested
- Safety documentation awaiting final approval

A series of tests are planned, representative of a range of operations

Notes:
maximum pump flow rate: 120 kg/hr = 2 kg/min = 33 g/s,
normal boil-off is 4-8 kg/day

description	flow rate (g/s)	duration (mins)	total H2 (kg)	Wind	Humidity	Purpose	Note
high-flow warm plume dispersion	16.67	30	30	low (< 5 MPH)	any	validate diagnostic (high flow-rate/concentration, no condensation)	Use heater to warm H2 to as high a T as possible, repeat until diagnostic deemed ready
high flow cold dispersion	16.67	30	30	low (< 5 MPH)	low	simulate vent release during transfer	Possibly repeat with high and low ambient temperatures
high flow cold dispersion	16.67	30	30	high (> 5 MPH)	low	simulate vent release during transfer	
high flow cold dispersion	16.67	30	30	low (< 5 MPH)	high	simulate vent release during transfer	
high flow cold dispersion	16.67	30	30	high (> 5 MPH)	high	simulate vent release during transfer	
simulated high-boiloff	0.56	30	1	low (< 5 MPH)	low	simulate high level of boiloff	Possibly repeat with high and low ambient temperatures. May need to precool vent lines with higher flows before reducing flow rate.
simulated high-boiloff	0.56	30	1	high (> 5 MPH)	low	simulate high level of boiloff	
simulated high-boiloff	0.56	30	1	low (< 5 MPH)	high	simulate high level of boiloff	
simulated high-boiloff	0.56	30	1	high (> 5 MPH)	high	simulate high level of boiloff	
normal boiloff	0.07	30	0.125	low (< 5 MPH)	any	normal boilff measured by meter	May need to scrap if diagnostic not sensitive enough.
normal boiloff	0.07	30	0.125	high (> 5 MPH)	any	normal boilff measured by meter	

4 weather conditions: high and low wind, high and low humidity. Each day when the weather is right, can perform 4 experiments: high-flow cold dispersion, simulated high boil-off, and normal boil-off. This means there are 4 actual days of testing (8 if we do high and low ambient temperatures). If everything goes right, we need approximately 160 kg/H2.

We will be able to answer key questions at the end of the campaign

- Does wind cause channeling and increase the distance to the LFL, or improve mixing to decrease the distance to the LFL?
- Does high humidity cause increased buoyancy due to the energy transfer from the condensation of moisture, or does the condensed moisture drag the hydrogen down so it’s less buoyant?
- Is the hydrogen concurrent with the condensed moisture? Does concurrency depend on the humidity?
- Is our model accurate enough for risk calculations for larger releases?

The NFPA 2 liquid hydrogen setback distance task group has a path for separation distance reduction, but there are gaps for LH_2

Gaseous

- ✓ Determine list of exposures
- ✓ Conduct hazard analysis
- ✓ Create representative system
- ✓ Acquire leak data
- ✓ Calculate leak frequency (using representative system and leak data)
- ✓ Calculate consequence distances using physics models and representative leak parameters
  - Unignited concentration of 8%
  - Heat flux of 4.7 kW/m^2
- ✓ Determine separation distance using frequency calculations and consequence calculations
  - – Function of size and pressure

Liquid

- ✓ Determine list of exposures
- ✓ Conduct hazard analysis
- ✓ Create representative system – additional parameters for LH_2
  - Temperature
  - Phase (liquid or gas)
- ☐ Acquire leak/vent data
  - ☐ Unanticipated leaks
  - ☐ Vent rates
- ☐ Calculate leak/vent frequency
- ☐ Calculate consequence distances using physics models and representative leak/vent parameters
- ☐ Determine separation distance using frequency calculations and consequence calculations
  - – Function of LH_2 volume or something else?

Placeholder data for proposal varied to see if overall risk changes

this work enables

QUESTIONS

COMMENTS

DISCUSSION

Thanks for funding support from:

- United States Department of Energy, Energy Efficiency &Renewable Energy, Fuel Cell Technologies Office, Safety, Codes, and Standards subprogram managed by Laura Hill
- Industry support including the OEM Group at the California Fuel Cell Partnership, Linde, and Shell
- Air Liquide and partners

And thanks to the hydrogen research team at Sandia including:

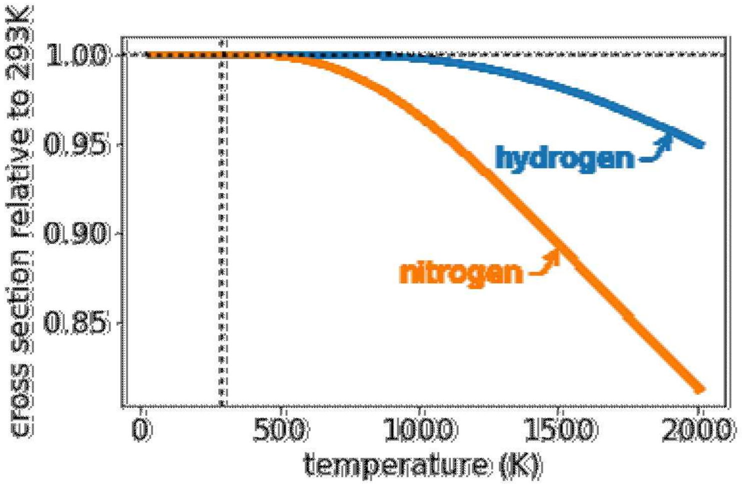
- Jon Zimmerman (H_2 program manager), Chris LaFleur (Risk, Codes & Standards) , Alice Muna (Risk), Brian Ehrhart (H_2FIRST), Gaby Bran-Anleu (H_2FIRST), Scott Bisson (optics), Tony McDaniel (experiments), Rad Bozinoski (modeling), Myra Blaylock (CFD), Chris San Marchi (materials/metal interactions with H_2), Joe Ronevich(materials/metal interactions with H_2), John Reynolds (HyRAM), Nalini Menon (polymer interactions with H_2)
- Previous researchers: , Bikram Roy Chowdhury, Pratikash PandaJoe Pratt, Katrina Groth, Isaac Ekoto, Adam Ruggles, Bob Schefer, Bill Houf, Greg Evans, Bill Winters

Ideas to improve system

- Currently 10 Hz scan rate
- Pulse-burst laser with polygonal beam scanner
  - Increase overall power
  - Improve temporal resolution
- Camera with bigger sensor – enables more photons to be collected

Quantification of Raman signals

- Signal is proportional to number density of molecules
- We use the ideal gas law to relate temperature and mole fraction to number density
  - $\frac{n_{total}\Sigma x}{V} = \frac{P_{total}\Sigma x}{RT}$
  - other equation of state could be used but may not have analytical solution
- Cross-section dependence matters for high-T (flames), but not low-T (cryogenic)



Eq. 1: $\frac{I_{H_2}}{I_0} = k_{H_2}\frac{x_{H_2}}{T}$ ← unknown 1 (x_{H_2}), ← unknown 2 (T)

measured values

calibration constants

Eq. 2: $\frac{I_{N_2}}{I_0} = k_{N_2}\frac{x_{N_2}}{T}$ ← unknown 3 (x_{N_2})

based on the composition of air

Eq. 3: $1 = x_{H_2} + 1.28x_{N_2}$

$$\begin{cases} x_{H_2} = \dfrac{\mathrm{I}_{\mathrm{H}_2}}{k_{H_2}\left(\dfrac{\mathrm{I}_{\mathrm{H}_2}}{k_{H_2}} + \dfrac{1.28\mathrm{I}_{\mathrm{N}_2}}{k_{N_2}}\right)} \\ x_{N_2} = \dfrac{\mathrm{I}_{\mathrm{N}_2}/\mathrm{I}_0}{k_{N_2}\left(\dfrac{\mathrm{I}_{\mathrm{H}_2}}{k_{H_2}} + \dfrac{1.28\mathrm{I}_{\mathrm{N}_2}}{k_{N_2}}\right)} \\ T = \dfrac{1}{\dfrac{\mathrm{I}_{\mathrm{H}_2}}{k_{H_2}} + \dfrac{1.28\mathrm{I}_{\mathrm{N}_2}}{k_{N_2}}} \end{cases}$$

How to develop a diagnostic tool for capturing high-fidelity quantitative data for large scale LH_2 experiments?

- **Required**: quantitative concentration measurements with < 1 m resolution
- **Desired**: non-intrusive concentration, temperature and velocity measurements in 3-dimensions + time

sensors

👍

- Low cost
- Reasonably straightforward implementation

👎

- Placed in flow, or suction, disturbs flow
- Point measurement (challenging to get spatial resolution)
- Usually slow response time (poor temporal resolution)
- Can be affected by environmental factors (not specific to only H_2)

optical diagnostic

👍

- High spatial resolution possible
- High temporal resolution possible
- Non-intrusive

👎

- H_2 is difficult to measure optically (no strong absorption features, no fluorescence transitions)

➢ Decision: pursue optical techniques

There are several potential technologies to visualize gas flows

Technique	Principle
Shadowgraphy	Refractive index gradients bend light rays as they pass through density variations.
Schlieren	Same as shadowgraphy. Knife edge enables focused image to form rather than simply shadow.
Fluorescence	Photons are absorbed by molecules at a resonant transition and light is reemitted at a shifted wavelength
Absorption	Gases have absorption features for certain wavelengths of light.
Rayleigh scattering	Elastic scattering off of different molecules is proportional to their cross-sections and number density.
Raman scattering	Inelastic scattering off of different molecules gives each component a spectral fingerprint.

Schlieren imaging

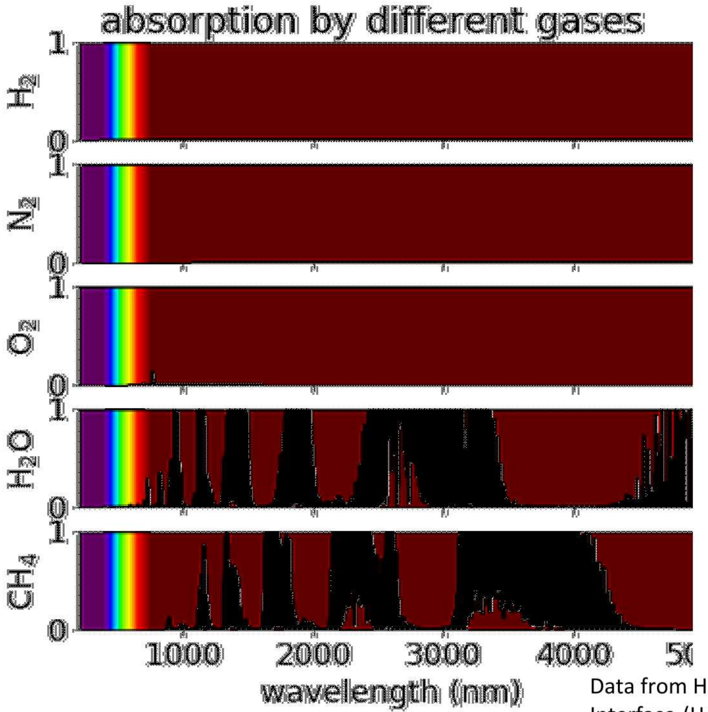
- Measures gradients in density (1st derivative)
- For quantitative measurements:
  - Calibrated schlieren – uniform light source, light intensity quantifies refraction angles
  - Rainbow schlieren – color cutoff filter in place of knife edge, color quantifies refraction angles
  - Diverging light background oriented schlieren (BOS) – pixel offset from original position determines refraction angle
- BOS (using sunlight) possible for H_2, however:
  - Need semi-ordered background
  - Density gradients caused by both temperature and composition
  - Line-integrated, total refraction measured, extremely complex to quantify, even with tomography
  - No symmetries for an open plume

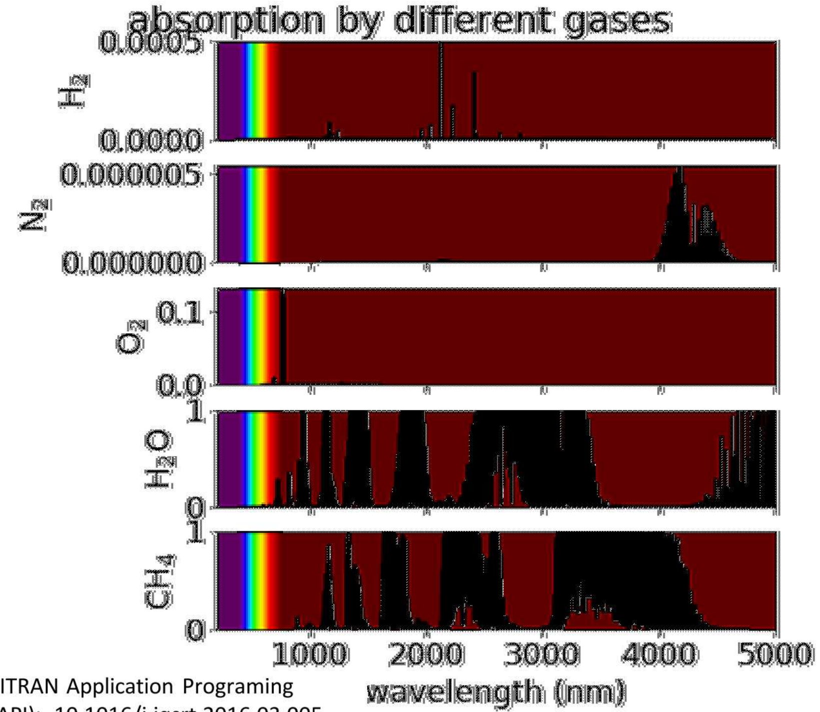
Fluorescence

- OH fluorescence possible, but only for flames, not unignited H_2
- Unignited concentration measurement would require seeding hydrogen with fluorescent tracer material (aliphatic ketones like acetone or 3-pentanone often used)
  - For cryogenic H_2, no gaseous or liquid options at LH_2 temperatures
  - Very challenging to get solid particles dispersed in liquid, and get them to follow gas flow during phase change

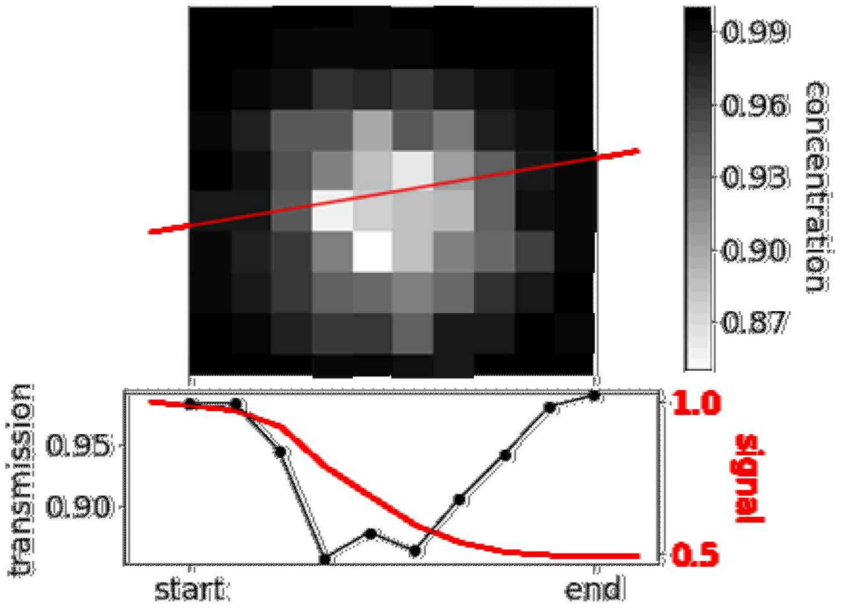
Absorption

- H_2 lacks strong absorption features (unlike CH_4)
- Would require illumination and light collection on opposite sides of plume (or mirror to reflect light)
- Line-integrated absorption, to quantify, requires multiple angles, tomography





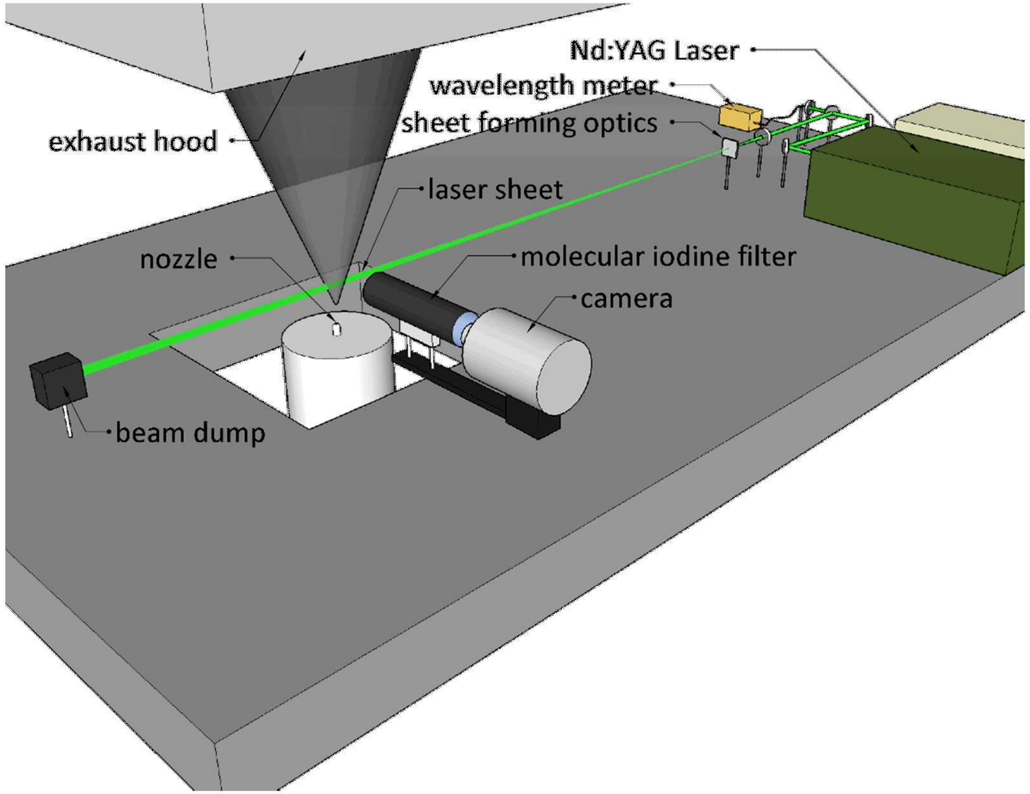
Data from HITRAN Application Programing Interface (HAPI): 10.1016/j.jqsrt.2016.03.005



Rayleigh scattering

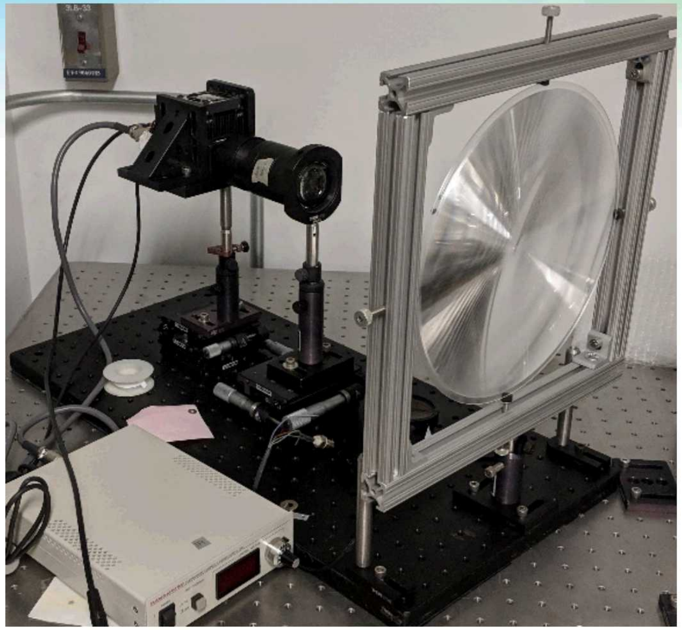
H_2 Rayleigh cross-section ≈ 10^{-27} cm^2

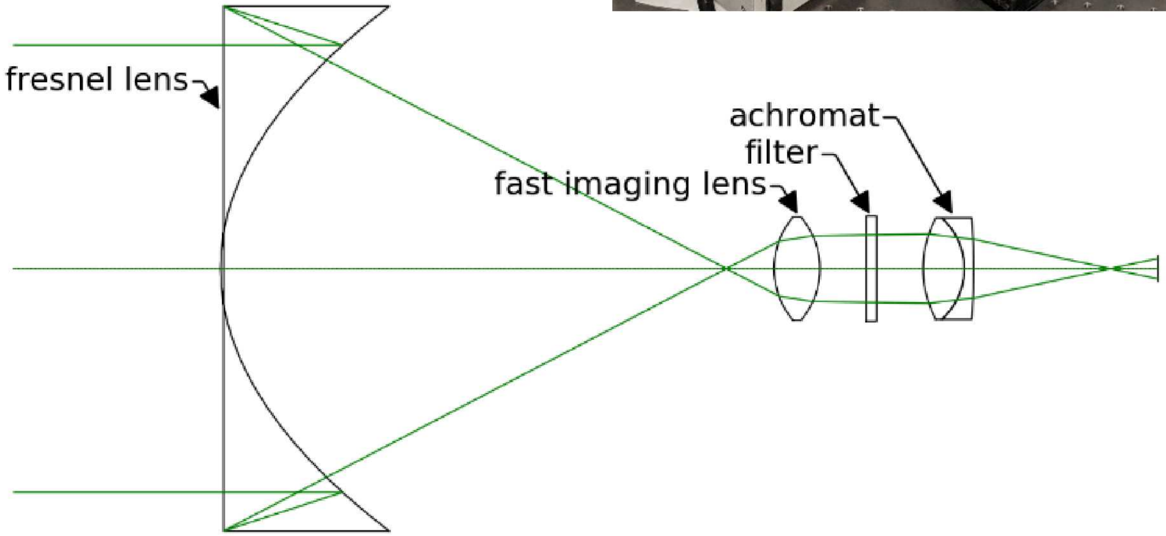
- Planar laser Rayleigh scattering used at Sandia for atmospheric temperature hydrogen releases
- Scatter proportional to number density; variations are caused by both composition and temperature
- For warm releases, always measured in atmospheric temperature region to eliminate this variable and enable composition quantification
- Not feasible to wait until cryogenic plume has warmed back to atmospheric temperature
- Rayleigh imaging will have signal overwhelmed by Mie scattering off of condensed entrained moisture in cryogenic plume
- Filtered Rayleigh has insufficient Mie scattering (condensed, entrained moisture) light suppression (OD≈3)



Explored use of a Fresnel lens as the primary collector

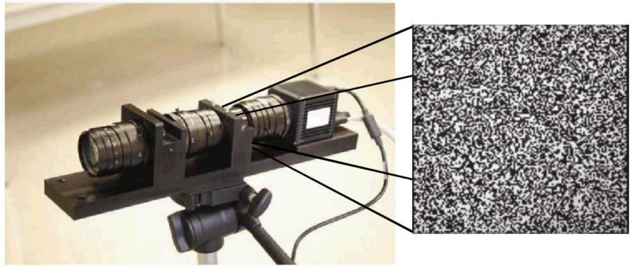
- Large diameter – large solid angle of collection
- Fast (f/0.8)
- Off-the-shelf
- Low cost
- Field lenses to achieve larger field of view, maintaining parallel rays for filter
- Signal detected @ > 20 ft in the lab



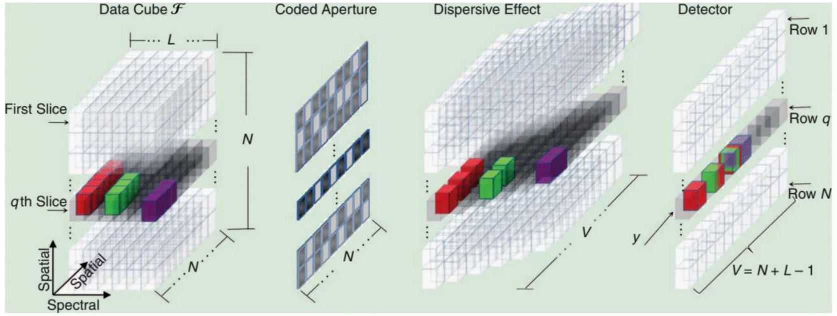


Considered coded-aperture Raman imaging

Pursuing coded-aperture Raman imaging

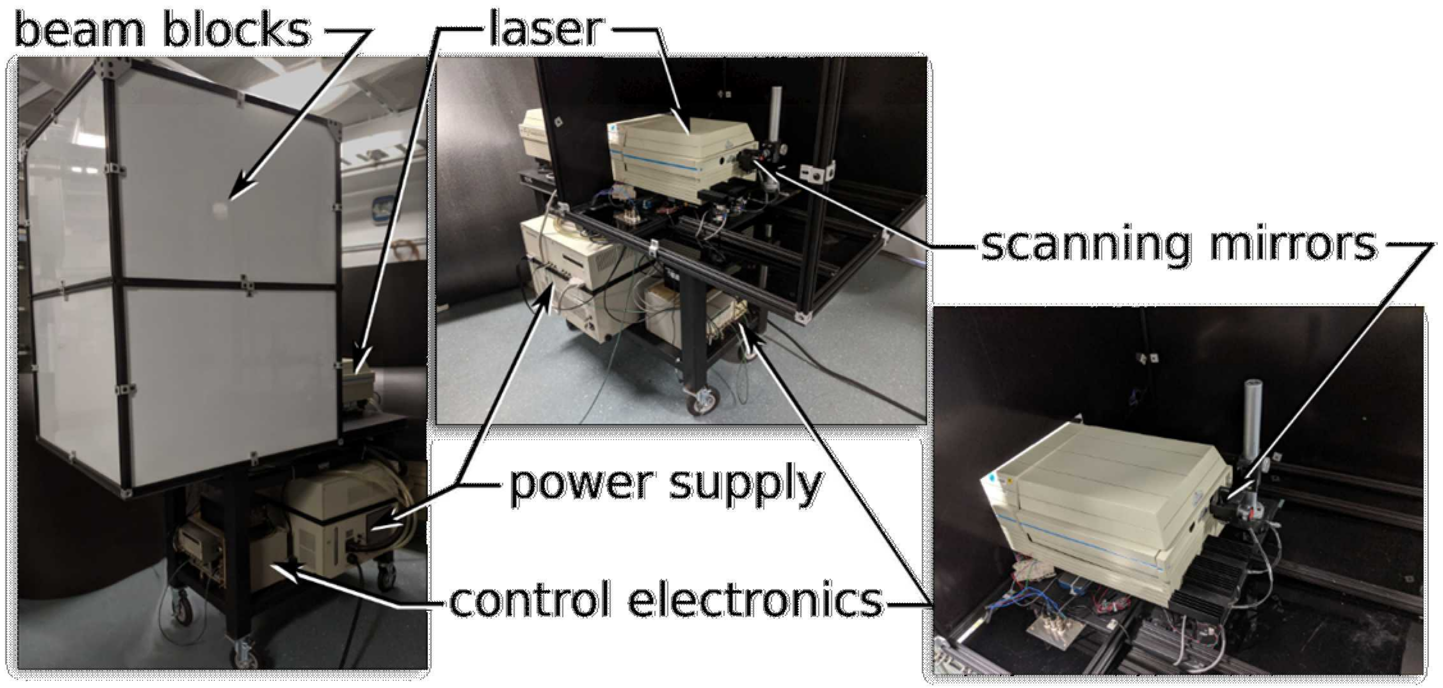


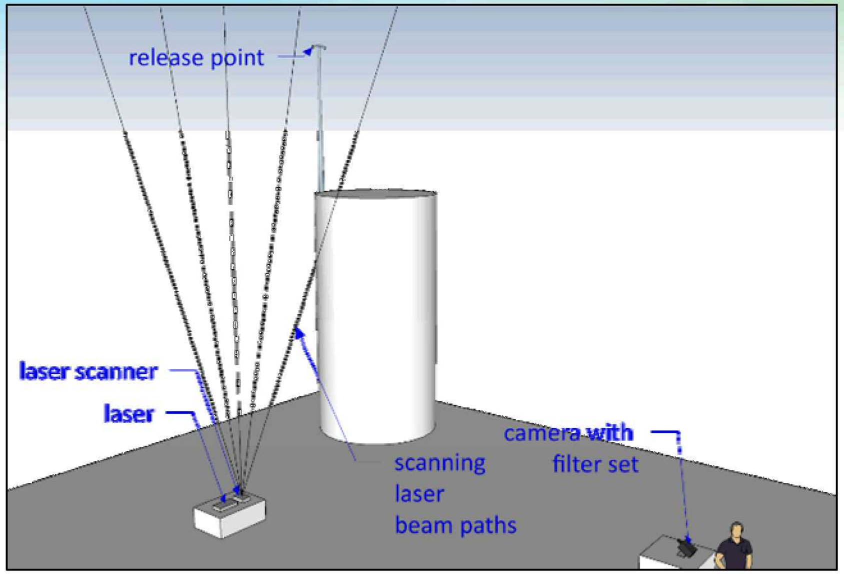
dx.doi.org://10.1117/12.919292

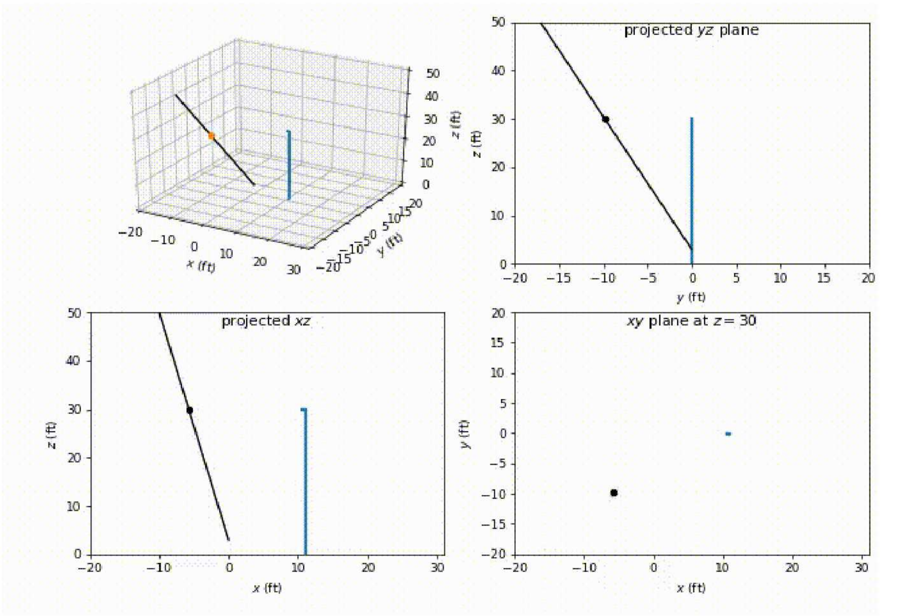


dx.doi.org://10.1109/MSP.2013.2278763

A mobile laser scanning system has been developed







- Self-contained cart only requires electrical power
- Beam-blocks to protect personnel from exposure to laser
- Concentrations measured along a series of lines