# The Science Behind Liquid Hydrogen Fueling Station Footprint Reduction

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Fuel Cell Technologies Office Webinar

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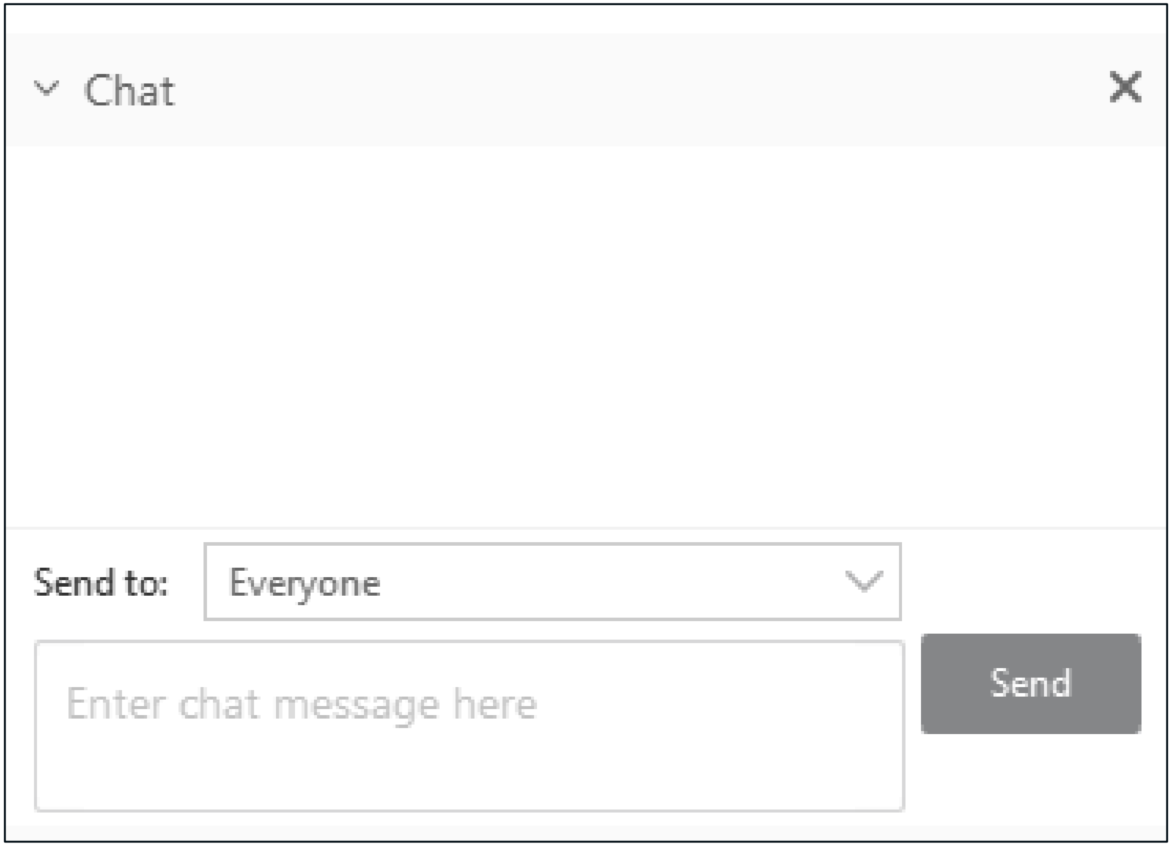
# Question and Answer

- Please type your questions to the chat box. **Send to: (HOST)**



# Acknowledgements

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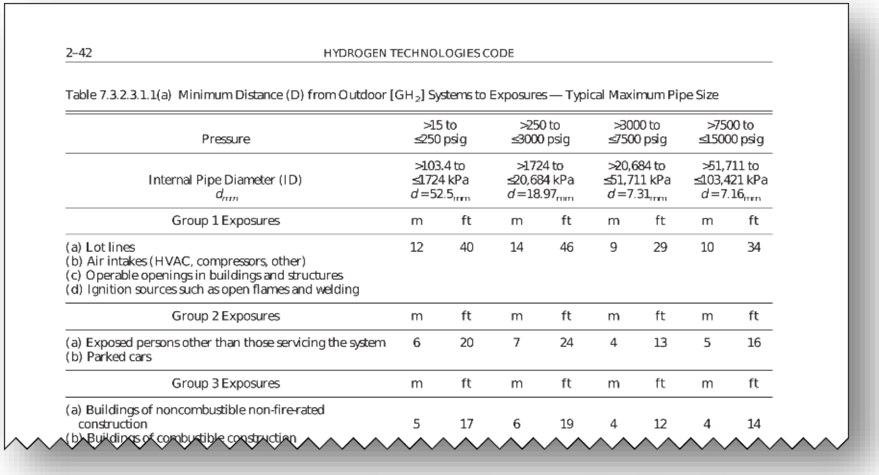
- Hydrogen Research Team at Sandia including:
  - Jon Zimmerman ($H_2$ program manager), Bikram Roy Chowdhury (experiments), Chris LaFleur (Risk, Codes & Standards) , Alice Muna (Risk), Brian Ehrhart ($H_2$FIRST), Gaby Bran-Anleu ($H_2$FIRST), Scott Bisson (optics), Tony McDaniel (experiments), Rad Bozinoski (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: Pratikash Panda, Joe Pratt, Katrina Groth, Isaac Ekoto, Adam Ruggles, Bob Schefer, Bill Houf, Greg Evans, Bill Winters

# In the U.S., authorities look to NFPA 2 for standards on how to site hydrogen fueling stations

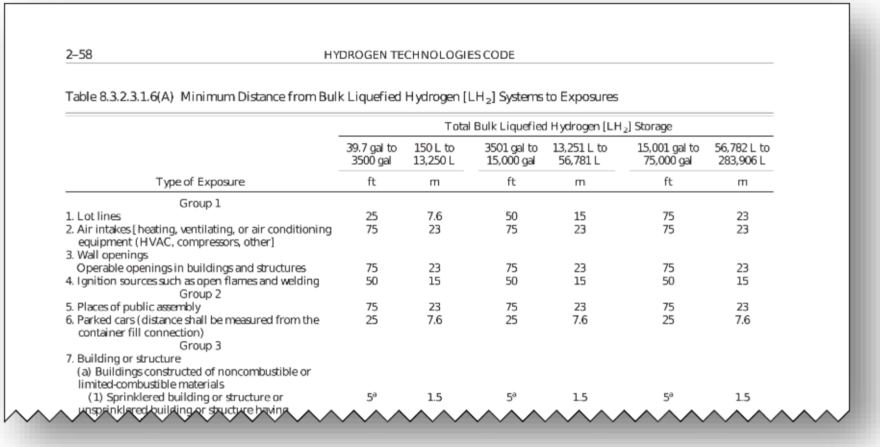
- Different distances for different exposures
- Some distances able to be reduced with mitigations (barrier wall, insulation, etc.)
- Gaseous separation distances related to diameter and pressure
- Liquid separation distances related to storage volume
- Justification for gaseous separation distances provided in annex
  - Separation distance reductions in NFPA 2 2011 (previously based on OSHA tables) and 2020 (under review) enabled by Sandia-led scientific analyses



2–42 HYDROGEN TECHNOLOGIES CODE

Table 7.3.2.3.1.1(a) Minimum Distance (D) from Outdoor [$GH_2$] Systems to Exposures — Typical Maximum Pipe Size

| Pressure | >15 to ≤250 psig | | >250 to ≤3000 psig | | >3000 to ≤7500 psig | | >7500 to ≤15000 psig | |
|---|---|---|---|---|---|---|---|---|
| Internal Pipe Diameter (ID) $d_{mm}$ | >103.4 to ≤1724 kPa $d = 52.5_{mm}$ | | >1724 to ≤20,684 kPa $d = 18.97_{mm}$ | | >20,684 to ≤51,711 kPa $d = 7.31_{mm}$ | | >51,711 to ≤103,421 kPa $d = 7.16_{mm}$ | |
| Group 1 Exposures | m | ft | m | ft | m | ft | m | ft |
| (a) Lot lines<br>(b) Air intakes (HVAC, compressors, other)<br>(c) Operable openings in buildings and structures<br>(d) Ignition sources such as open flames and welding | 12 | 40 | 14 | 46 | 9 | 29 | 10 | 34 |
| Group 2 Exposures | m | ft | m | ft | m | ft | m | ft |
| (a) Exposed persons other than those servicing the system<br>(b) Parked cars | 6 | 20 | 7 | 24 | 4 | 13 | 5 | 16 |
| Group 3 Exposures | m | ft | m | ft | m | ft | m | ft |
| (a) Buildings of noncombustible non-fire-rated construction | 5 | 17 | 6 | 19 | 4 | 12 | 4 | 14 |
| (b) Buildings of combustible construction | | | | | | | | |

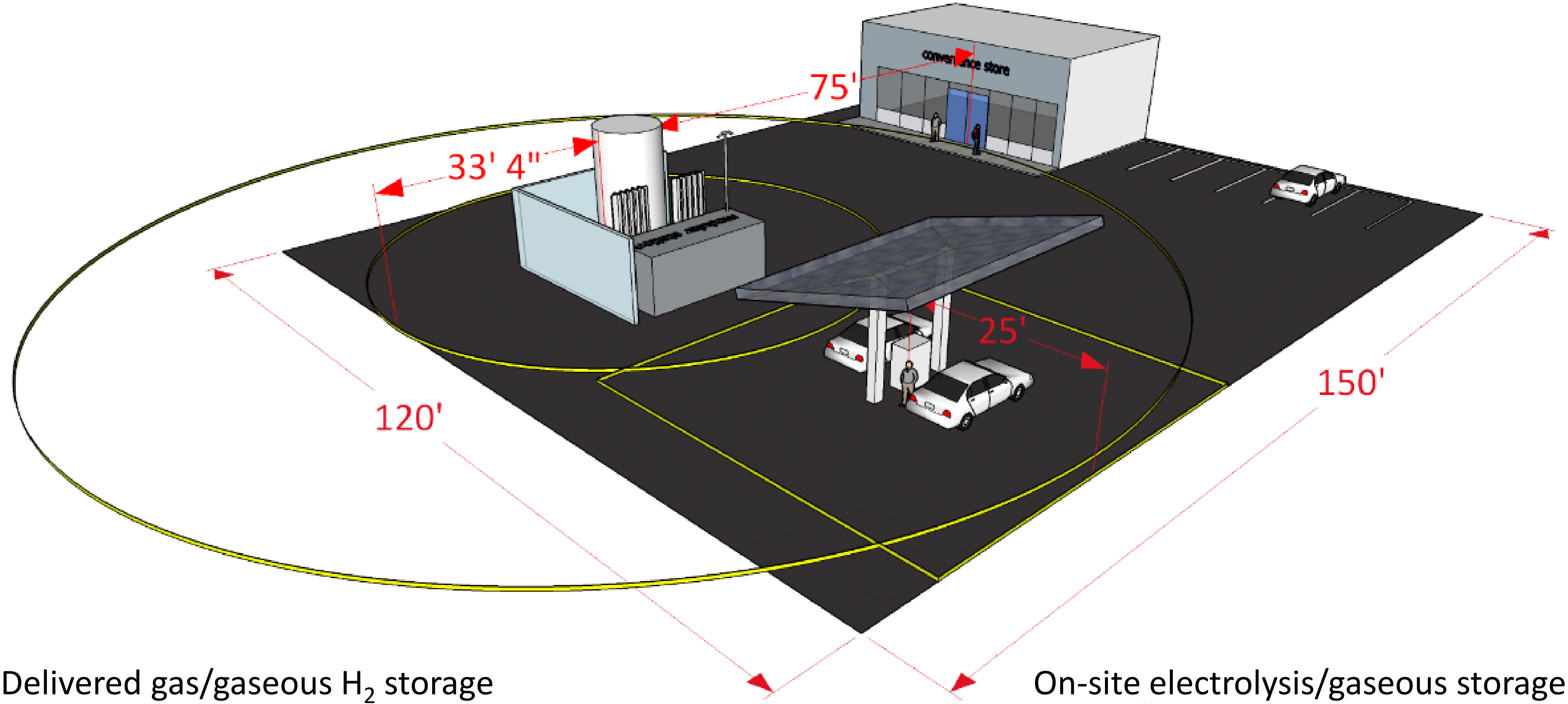


2–58 HYDROGEN TECHNOLOGIES CODE

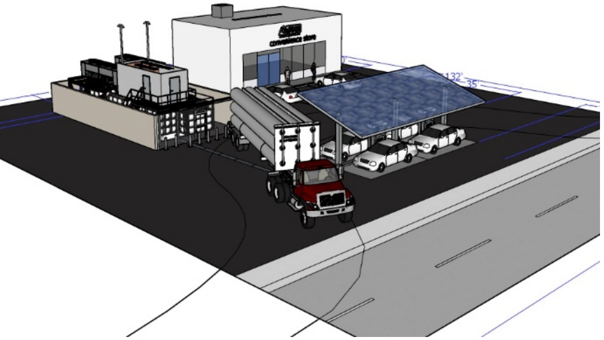
Table 8.3.2.3.1.6(A) Minimum Distance from Bulk Liquefied Hydrogen [$LH_2$] Systems to Exposures

| | Total Bulk Liquefied Hydrogen [$LH_2$] Storage | | | | | |
|---|---|---|---|---|---|---|
| | 39.7 gal to 3500 gal | 150 L to 13,250 L | 3501 gal to 15,000 gal | 13,251 L to 56,781 L | 15,001 gal to 75,000 gal | 56,782 L to 283,906 L |
| Type of Exposure | ft | m | ft | m | ft | m |
| Group 1 | | | | | | |
| 1. Lot lines | 25 | 7.6 | 50 | 15 | 75 | 23 |
| 2. Air intakes [heating, ventilating, or air conditioning equipment (HVAC, compressors, other] | 75 | 23 | 75 | 23 | 75 | 23 |
| 3. Wall openings | | | | | | |
| Operable openings in buildings and structures | 75 | 23 | 75 | 23 | 75 | 23 |
| 4. Ignition sources such as open flames and welding | 50 | 15 | 50 | 15 | 50 | 15 |
| Group 2 | | | | | | |
| 5. Places of public assembly | 75 | 23 | 75 | 23 | 75 | 23 |
| 6. Parked cars (distance shall be measured from the container fill connection) | 25 | 7.6 | 25 | 7.6 | 25 | 7.6 |
| Group 3 | | | | | | |
| 7. Building or structure | | | | | | |
| (a) Buildings constructed of noncombustible or limited-combustible materials | | | | | | |
| (1) Sprinklered building or structure or unsprinklered building or structure having | $5^a$ | 1.5 | $5^a$ | 1.5 | $5^a$ | 1.5 |

# Separation distances for liquid hydrogen are onerous and lack detailed scientific justification



Delivered gas/gaseous $H_2$ storage



On-site electrolysis/gaseous storage

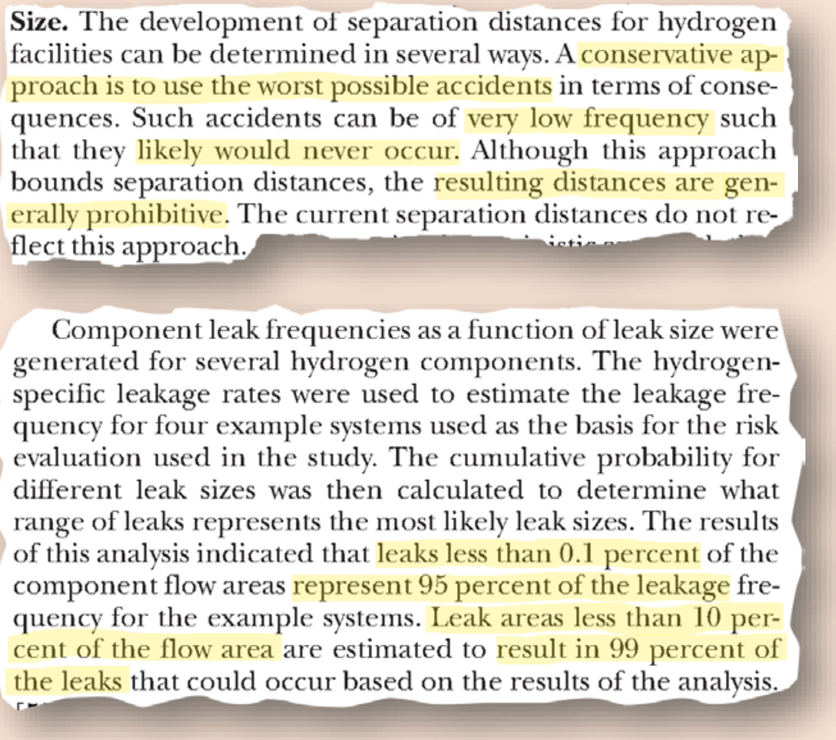
# Quantitative risk assessment (QRA) forms a basis for gaseous hydrogen separation distances

- Conservative: assess worst possible accident scenario(s) (e.g., full line shear, tank rupture)
  - Low frequency
  - Prohibitive distance
  - Separation distance does not *(and should not*)* protect against this scenario

** Author's opinion*

- Risk informed
  - Factor in leak frequency
  - Potential methods:
    - Perform QRA on each system of interest
    - Use QRA results from typical system to relate deterministic distance(s) to acceptable risk
    - Determine probable maximum leak size and assess accident scenario(s) (cover 95%, 99%, etc. of probable leaks)

**Selected text from annex (I - NFPA 2, H – NFPA 55)**

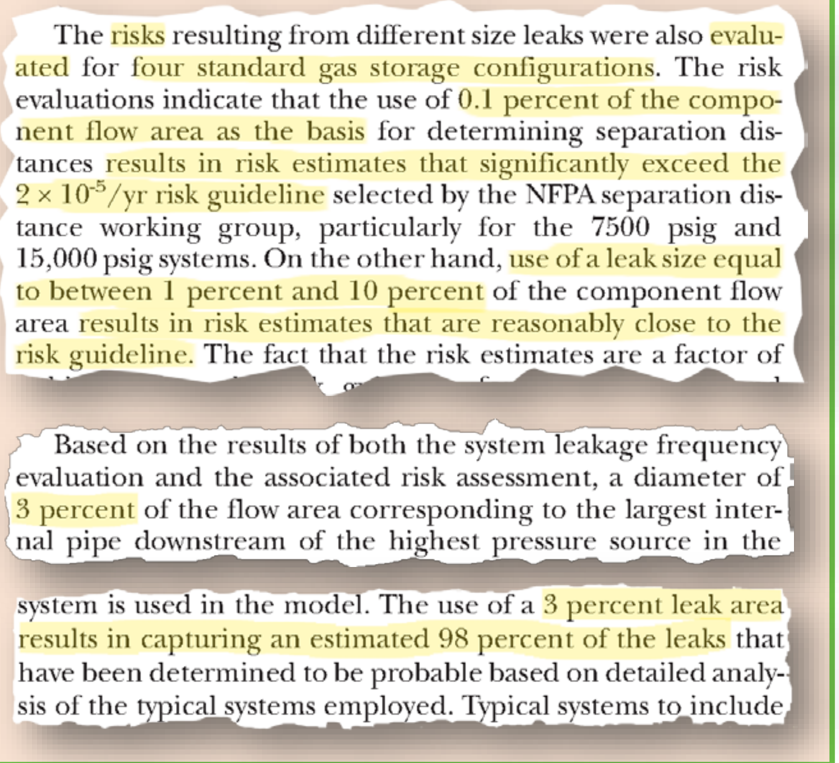


**Size.** The development of separation distances for hydrogen facilities can be determined in several ways. A conservative approach is to use the worst possible accidents in terms of consequences. Such accidents can be of very low frequency such that they likely would never occur. Although this approach bounds separation distances, the resulting distances are generally prohibitive. The current separation distances do not reflect this approach.

Component leak frequencies as a function of leak size were generated for several hydrogen components. The hydrogen-specific leakage rates were used to estimate the leakage frequency for four example systems used as the basis for the risk evaluation used in the study. The cumulative probability for different leak sizes was then calculated to determine what range of leaks represents the most likely leak sizes. The results of this analysis indicated that leaks less than 0.1 percent of the component flow areas represent 95 percent of the leakage frequency for the example systems. Leak areas less than 10 percent of the flow area are estimated to result in 99 percent of the leaks that could occur based on the results of the analysis.

# Risk informed approach: acceptable risk must be decided along with a 'typical' system

## Selected text from annex (I - NFPA 2, H – NFPA 55)

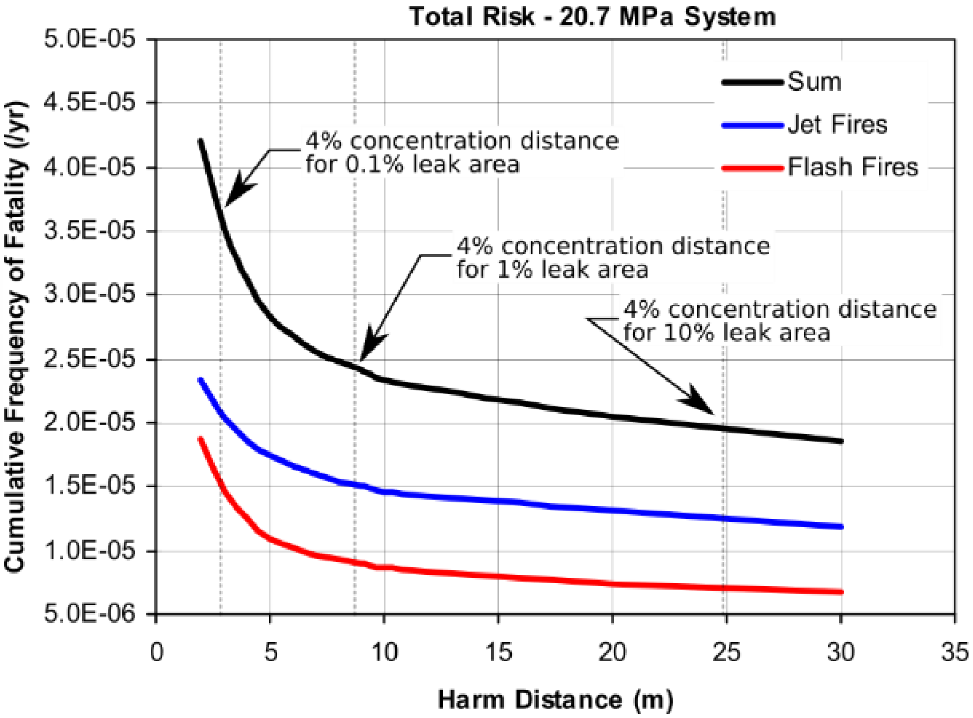


The risks resulting from different size leaks were also evaluated for four standard gas storage configurations. The risk evaluations indicate that the use of 0.1 percent of the component flow area as the basis for determining separation distances results in risk estimates that significantly exceed the $2 \times 10^{-5}$/yr risk guideline selected by the NFPA separation distance working group, particularly for the 7500 psig and 15,000 psig systems. On the other hand, use of a leak size equal to between 1 percent and 10 percent of the component flow area results in risk estimates that are reasonably close to the risk guideline. The fact that the risk estimates are a factor of

Based on the results of both the system leakage frequency evaluation and the associated risk assessment, a diameter of 3 percent of the flow area corresponding to the largest internal pipe downstream of the highest pressure source in the

system is used in the model. The use of a 3 percent leak area results in capturing an estimated 98 percent of the leaks that have been determined to be probable based on detailed analysis of the typical systems employed. Typical systems to include

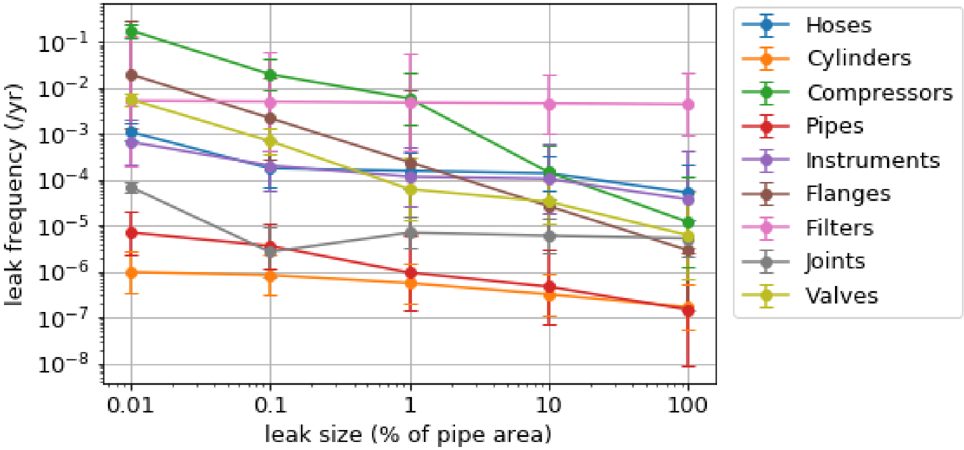
3% leak area reduced to 1% in proposed NFPA 2 update – gaseous hydrogen setback distances further reduced

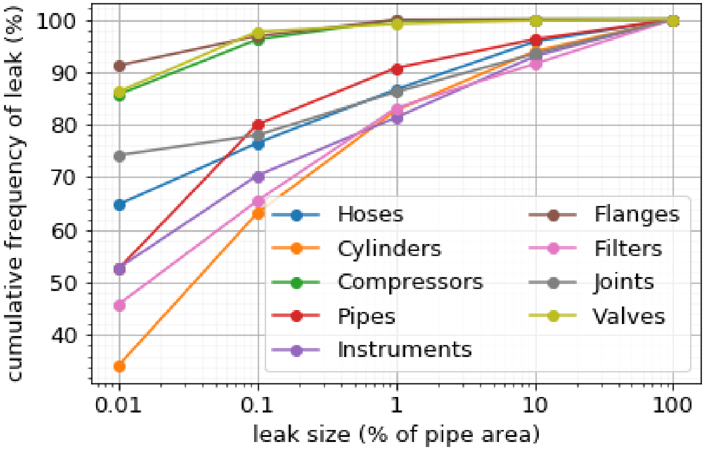


Gaseous distance reduction method:

- QRA performed on typical system
- Overall risk compared to deterministic hazard distances (jet flame radiation, unignited flammable concentration)

# Key component of QRA is leak frequency





- More 'leaky' components -> more risk
- Hazard/harm distance related to pressure (and temperature for $LH_2$) and flow area
  - Separation distances for gas also related to pressure and flow area
  - Separation distance for liquid related to capacity – analysis may show this to be poor criteria
- More specificity could improve accuracy – compression joint not going to have the same leak frequency as threaded as weld, etc.
- Lack of leak frequency data for liquid hydrogen components

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

## Gaseous

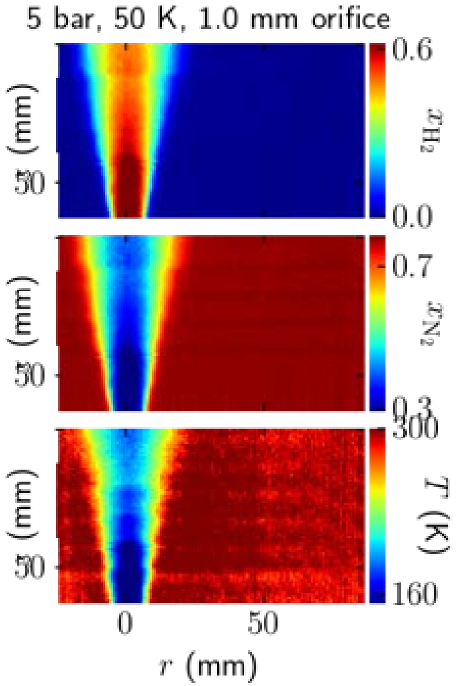
- ✓ Determine list of exposures
- ✓ Conduct hazard analysis
- ✓ Create representative system
- ✓ Acquire leak data
- ✓ Calculate leak frequency (using representative system and leak data)
- ✓ Calculate consequence distances using physics models and representative leak parameters
  - Unignited concentration 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

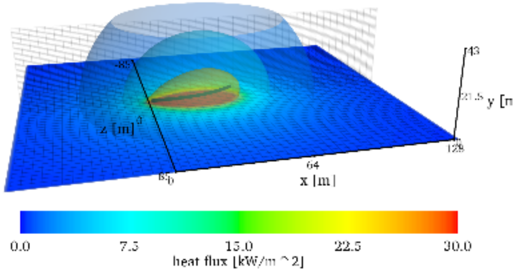
- ✓ Determine list of exposures
- ✓ Conduct hazard analysis
- ✓ Create representative system – additional parameters for $LH_2$
  - Temperature
  - Phase (liquid or gas)
- ☐ Acquire leak/vent data
  - ☐ Unanticipated leaks
  - ☐ Vent rates
- ☐ Calculate leak/vent frequency
- ☐ Calculate consequence distances 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?

# Sandia $H_2$ Safety Codes and Standards research includes coordinated activities that facilitate deployment of hydrogen technologies

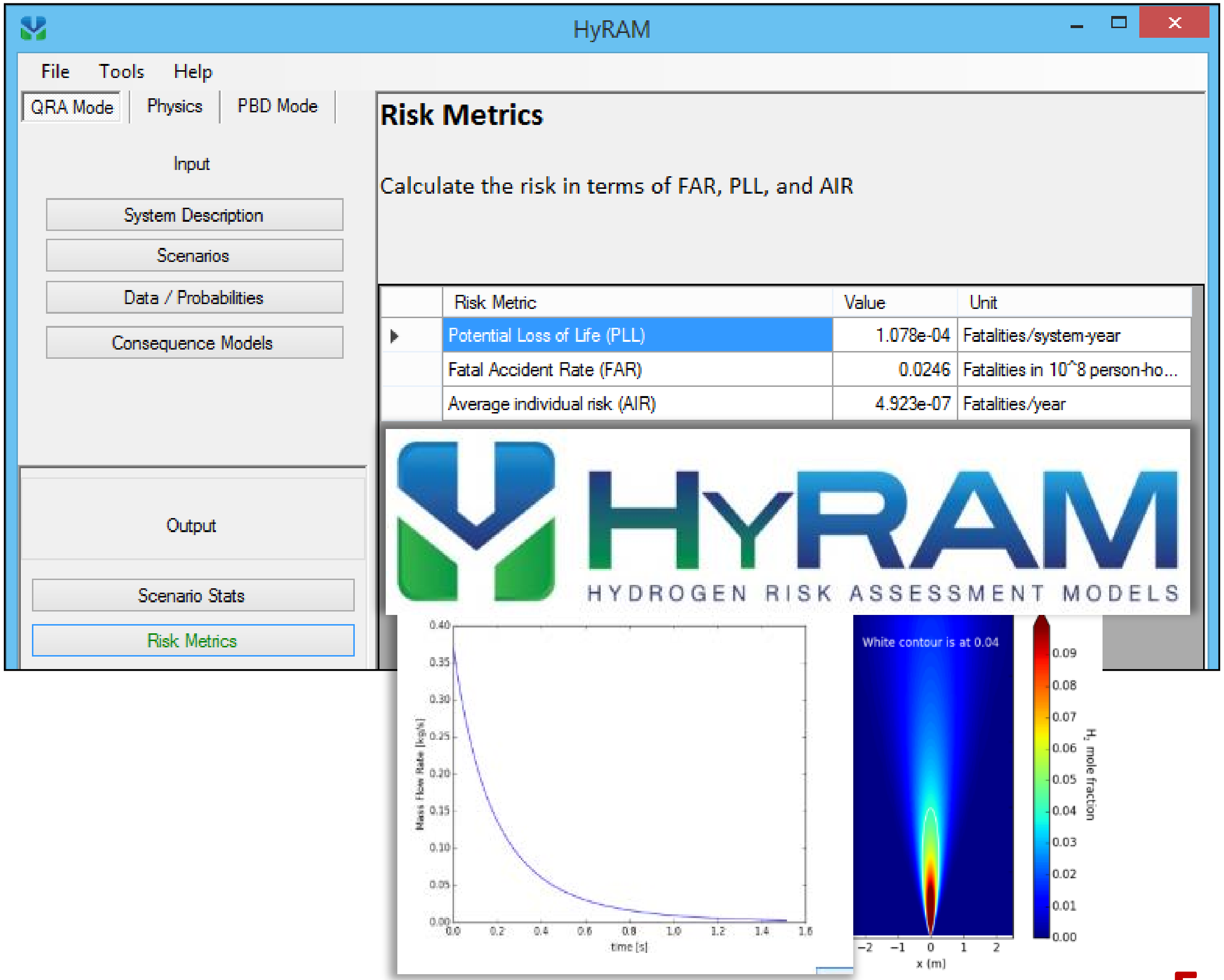
- Hydrogen Behavior
  - **Develop and validate scientific models** to accurately predict hazards and harm from liquid releases, flames, etc.
- Quantitative Risk Assessment, tools R&D
  - **Develop integrated methods and algorithms** enabling consistent, traceable, and rigorous QRA (Quantitative Risk Assessment) for $H_2$ facilities and vehicles
- Enable Hydrogen Infrastructure through Science-based Codes and Standards
  - **Apply QRA and behavior models to real problems** in hydrogen infrastructure and emerging technology
  - **Facilitate updates to NFPA 2** through deep technical analyses



HyRAM
HYDROGEN RISK ASSESSMENT MODELS



# Sandia developed software – HyRAM – enables QRA of gaseous hydrogen systems



**Risk Metrics**

Calculate the risk in terms of FAR, PLL, and AIR

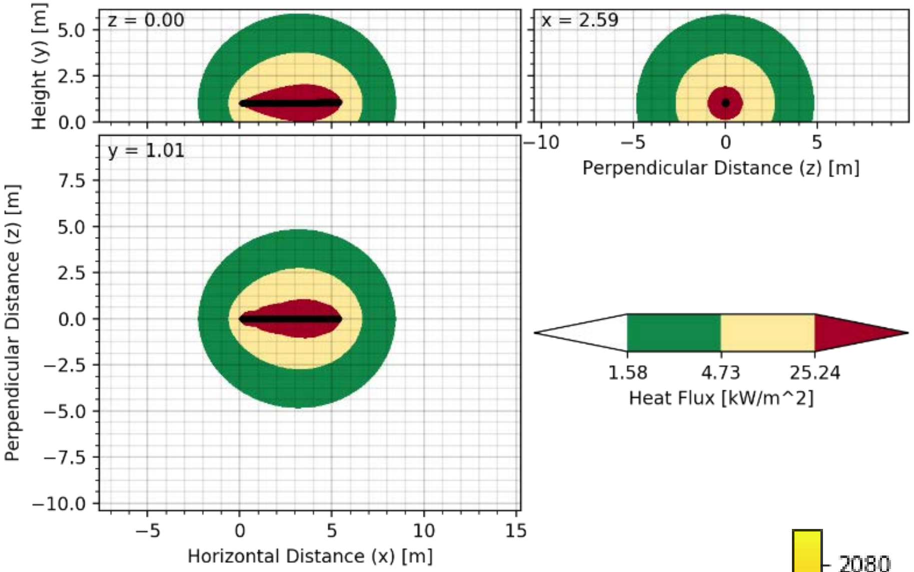
| Risk Metric | Value | Unit |
|---|---|---|
| Potential Loss of Life (PLL) | 1.078e-04 | Fatalities/system-year |
| Fatal Accident Rate (FAR) | 0.0246 | Fatalities in 10^8 person-ho... |
| Average individual risk (AIR) | 4.923e-07 | Fatalities/year |

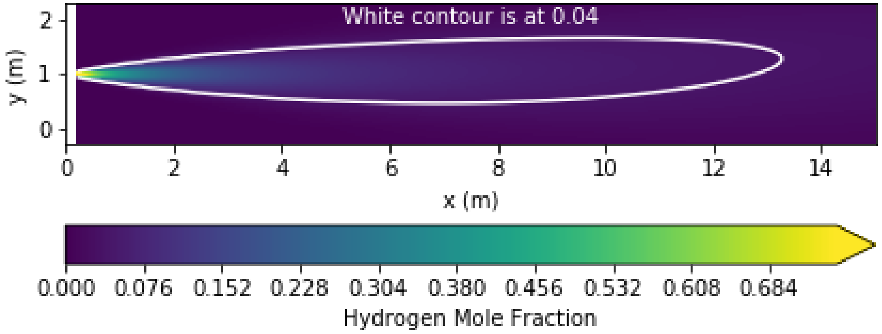
- Documented, repeatable QRA methodology
- Frequency & probability data for hydrogen component failures
- Fast-running models of hydrogen gas and flame behaviors

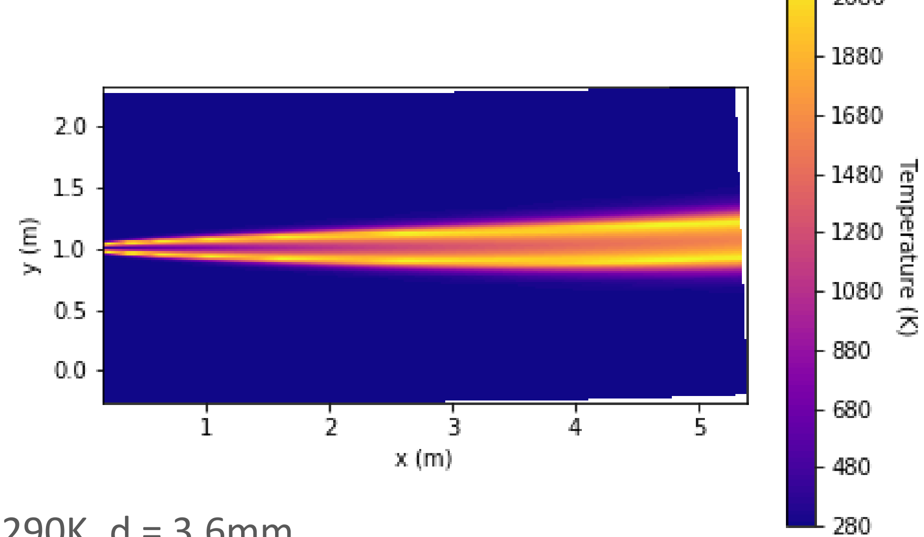
**Free download at http://hyram.sandia.gov**

# A variety of validated physical models are used in HyRAM

- Unignited dispersion
  - Distance to certain concentration
- Flame model
  - Temperature field
  - Heat flux field
- Overpressure for delayed ignition of indoor releases







P = 134 bar, T = 290K, d = 3.6mm

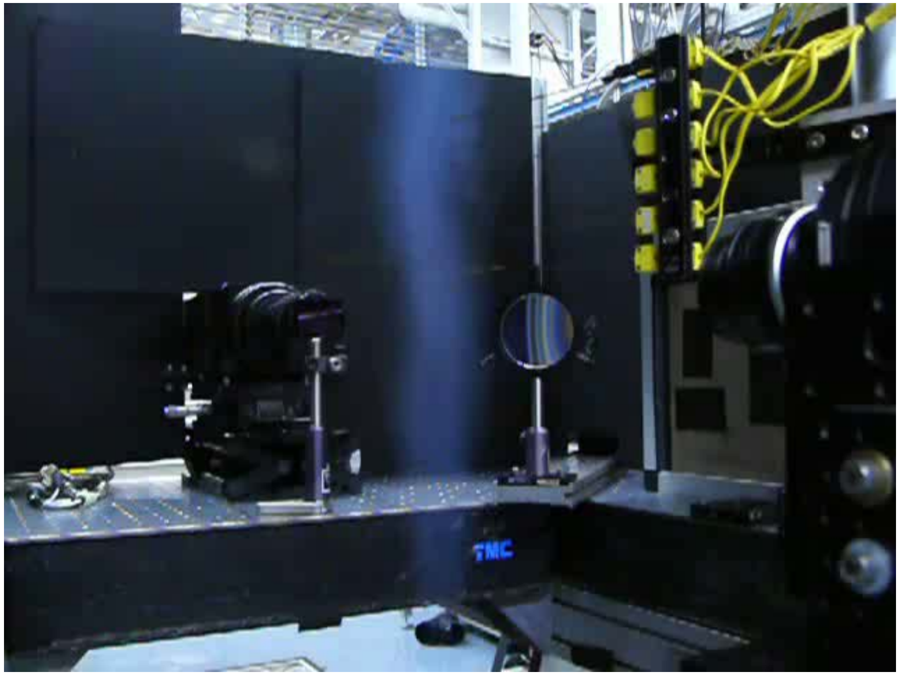
# Model validation is a priority

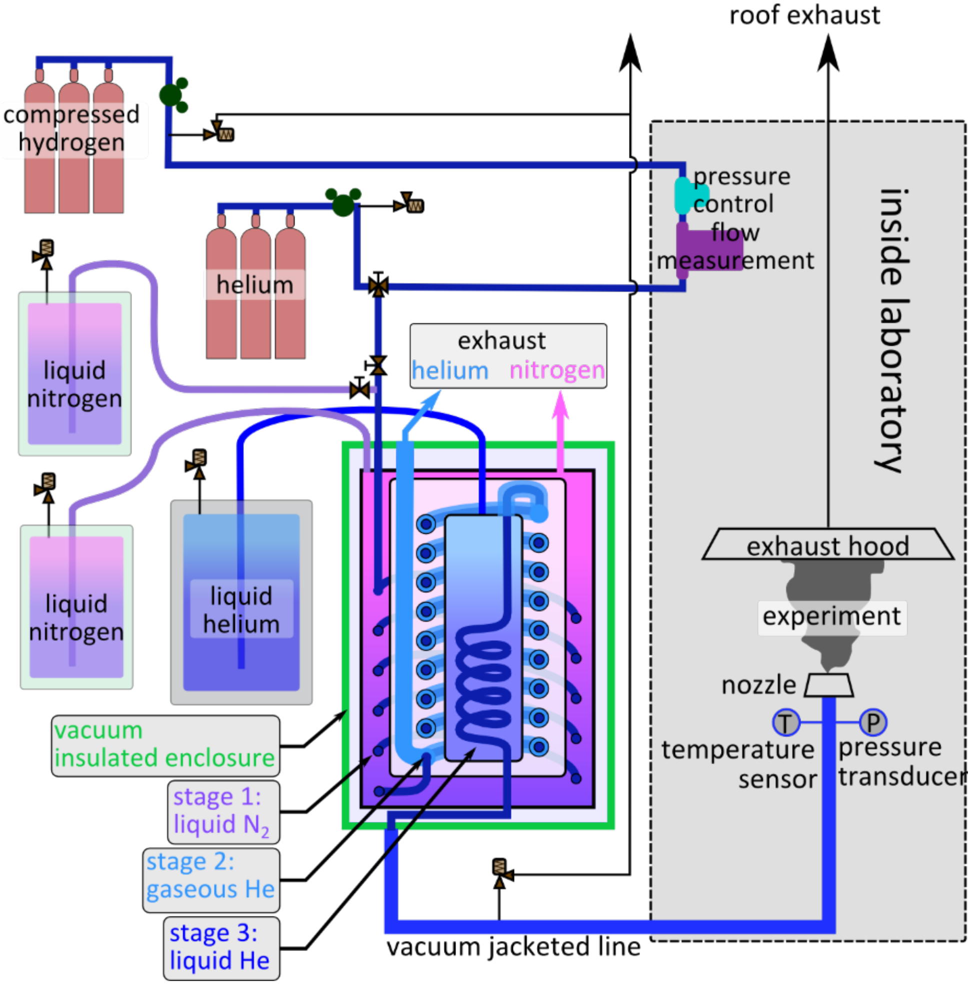
A unique experimental platform has been developed at Sandia to release cryogenic hydrogen through approximately 1 mm orifices at up to 10 bar

Research and validation for models of:

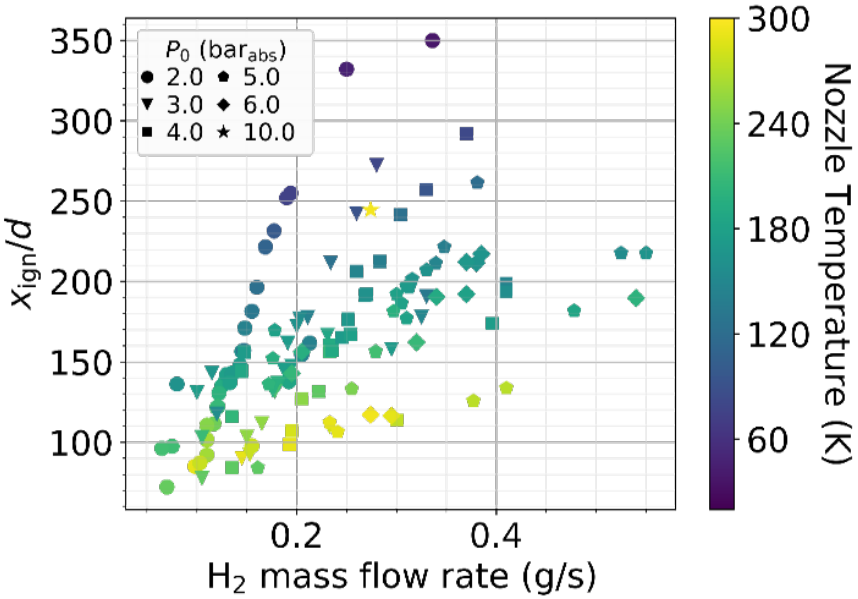
- Ignition
- Flames
- Dispersion

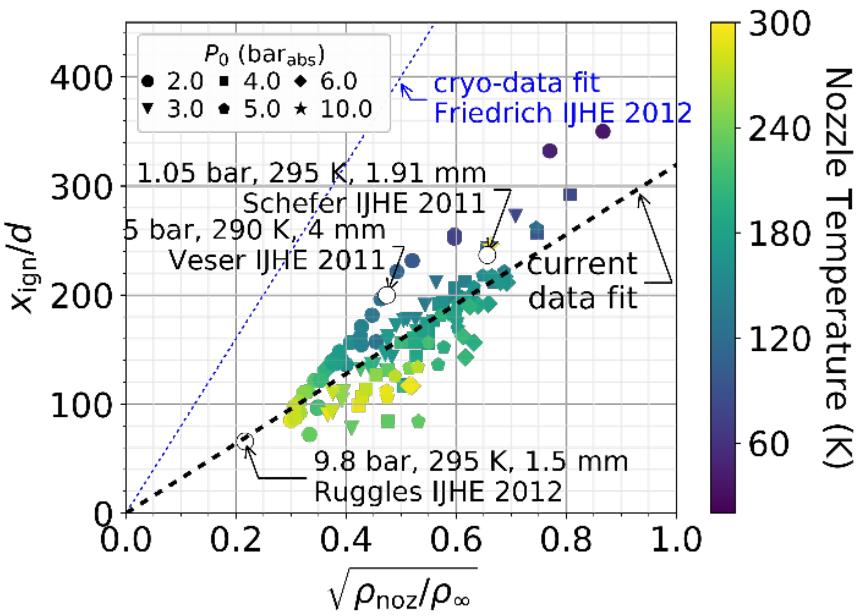
P = 1 bar, T = 37 K, ignition distance = 325 mm





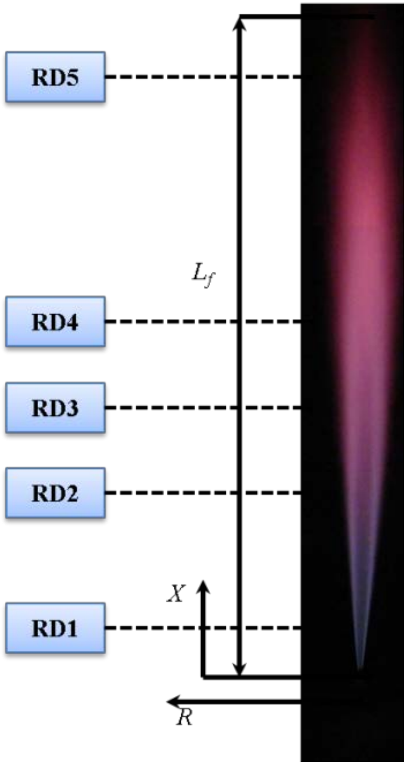
# We have measured and can calculate the maximum ignition distance for cryogenic hydrogen

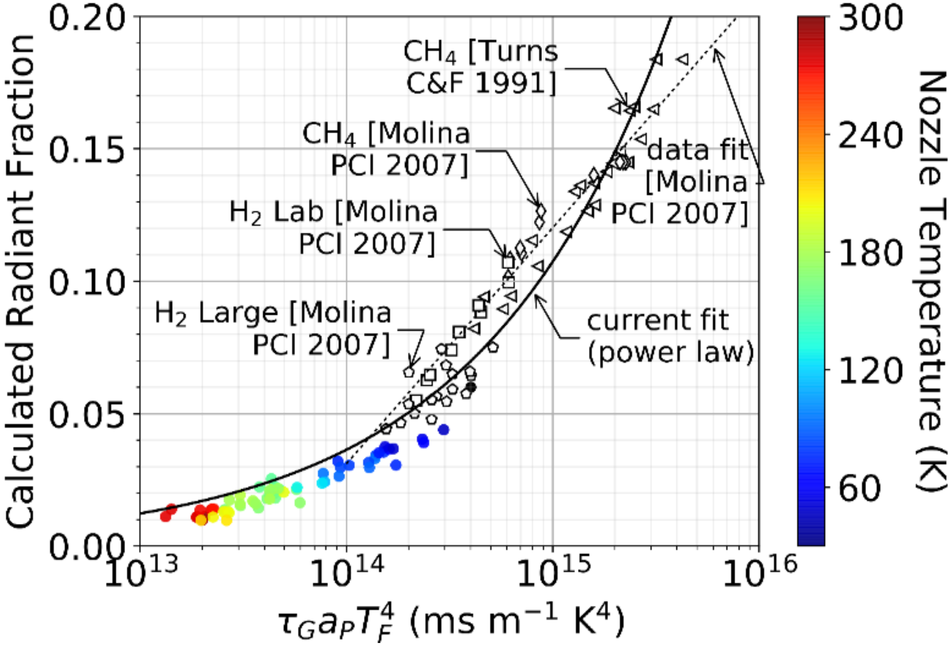




- for a given mass flow, ignition of cold $H_2$ occurs much further from the release point
- a larger ignition distance is observed at a lower mass flow rate of hydrogen for the colder jets
- Ignition distance linearly varies as a function of effective diameter (same as literature reported room temperature releases)

# We have measured and can calculate the radiant heat flux for cryogenic hydrogen jet flames



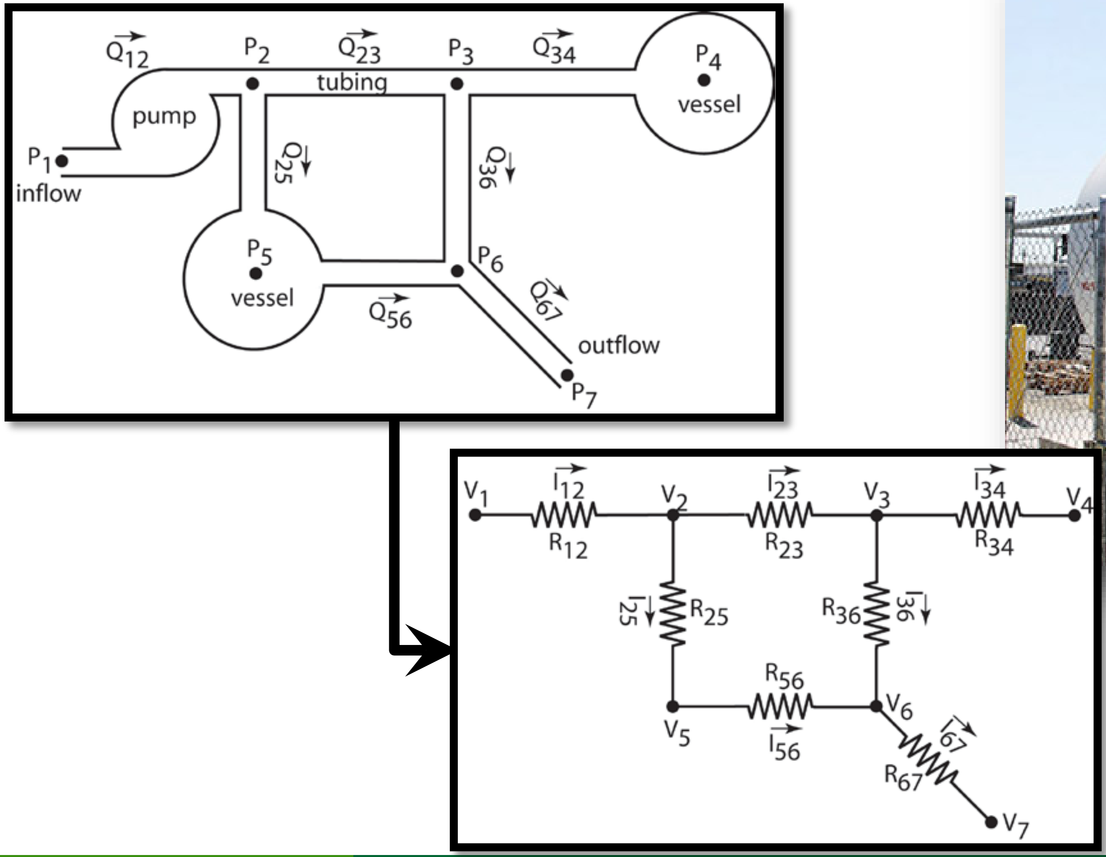


- Radiometers placed at 5 axial locations along the flame length to measure radiative heat flux
- Hydrogen flames have lower radiant heat flux compared to methane or syngas flames
- An increase in radiant fraction is observed for colder $H_2$ jets (for a given nozzle size and pressure) due to longer flame residence time (more mass flux)

$$\text{radiant heat flux} \propto (\text{radiant fraction})(\text{mass flow})(\text{heat of combustion})(\text{transmissivity})$$

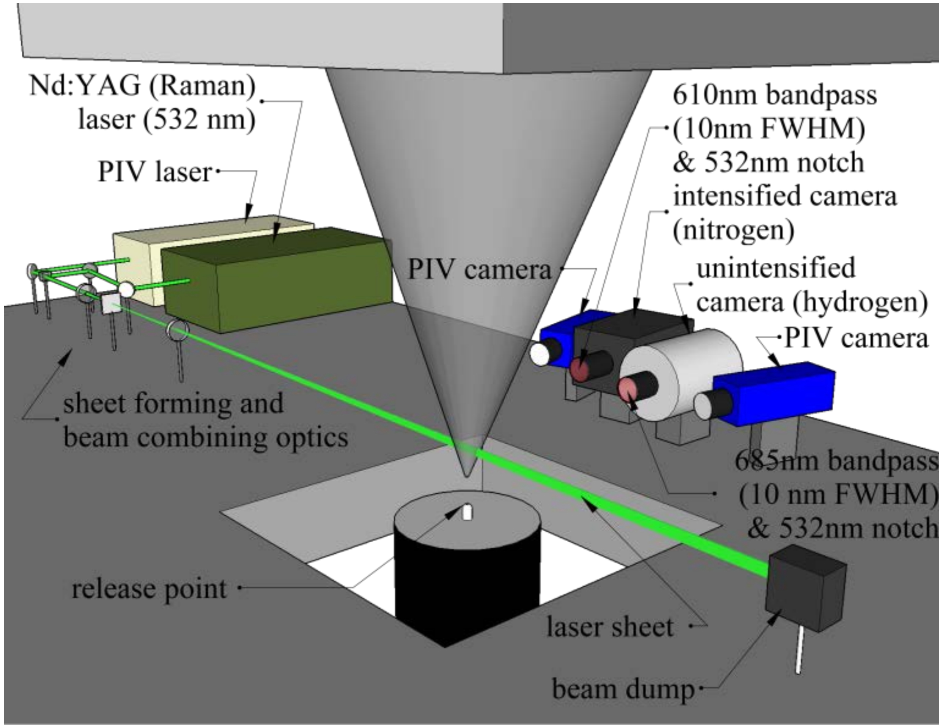
# We have a model (MassTran) for internal, phase-changing flow

- Flow out a vent stack is no longer at $LH_2$ temperature
- Valves, piping, and other components represented as an electrical network
- Need details (heat transfer rate, component orifice sizes, etc.) to accurately calculate conditions at release point



Liquid hydrogen storage tank

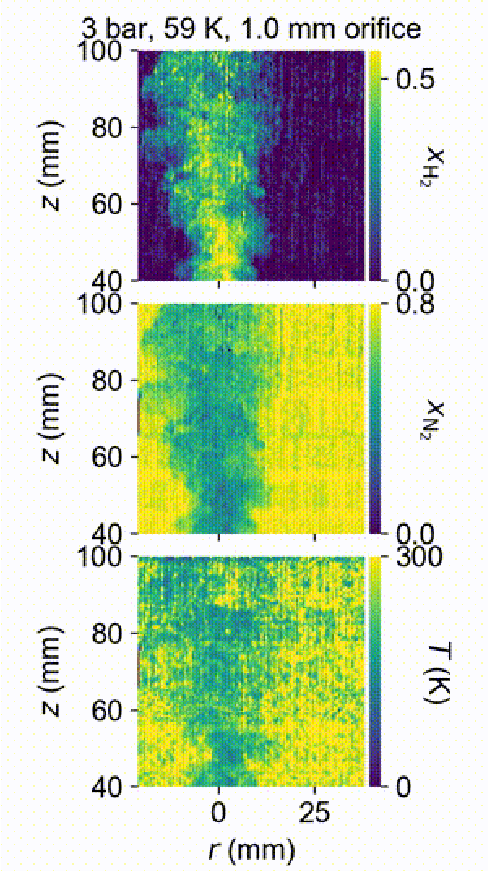
# $H_2$-$N_2$ Raman imaging and particle imaging velocimetry are used to measure concentration, temperature, and velocity of cryogenic $H_2$



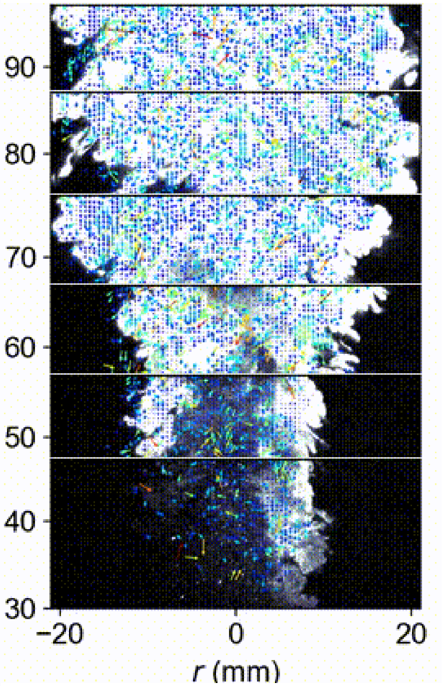
Independent model parameters measured:

- ✓ $T$ - temperature
- ✓ $x$ - mole fraction
- ✓ $v$ - velocity
- ✓ $B$ - halfwidth (both velocity and concentration)

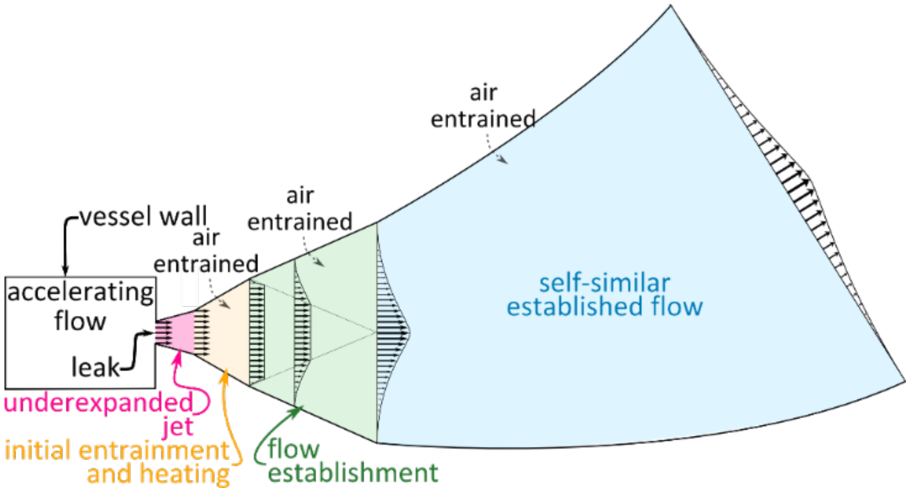
Concentration and temperature fields from Raman imaging

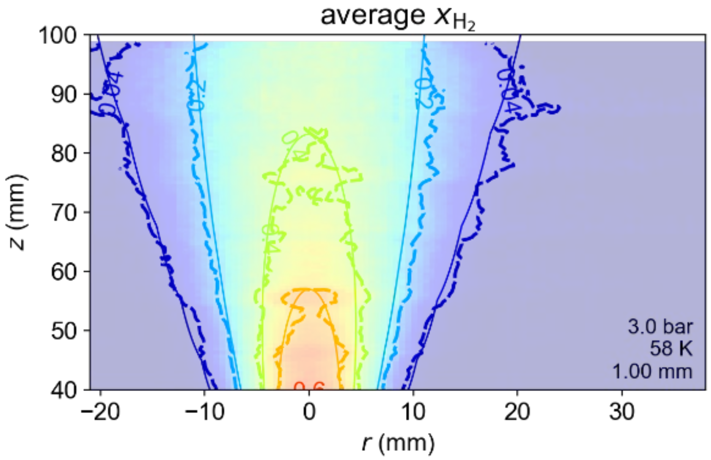


Velocity vectors superimposed on Mie scattering

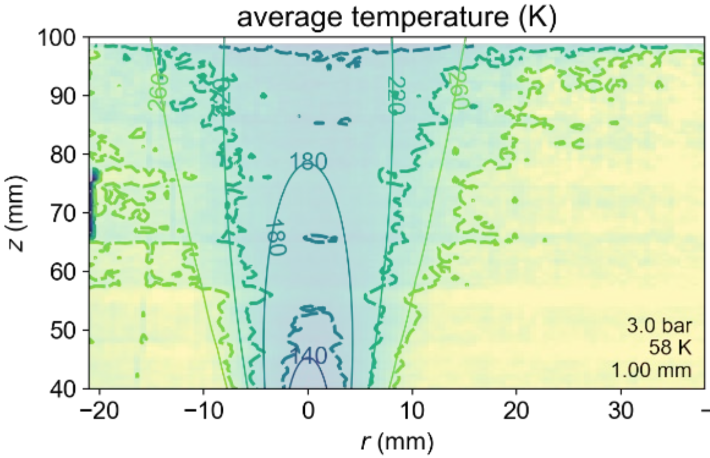


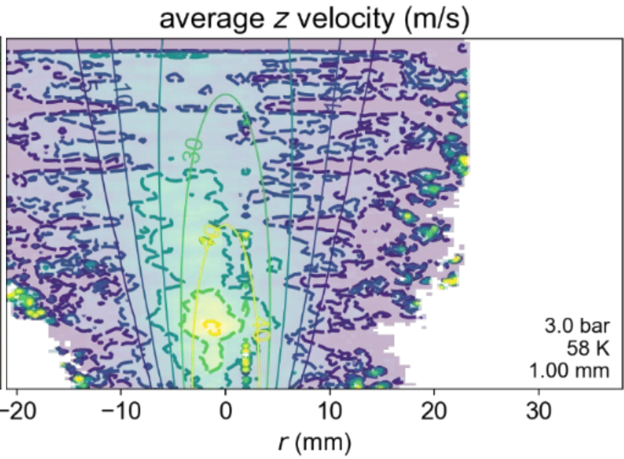
# ColdPLUME model shows good agreement with the data





- 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 a predictive tool

# Lab-scale experiments have been used to validate the model, but larger experiments are needed to study interactions with wind and vaporization

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

## sensors

👍

- Low cost
- 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

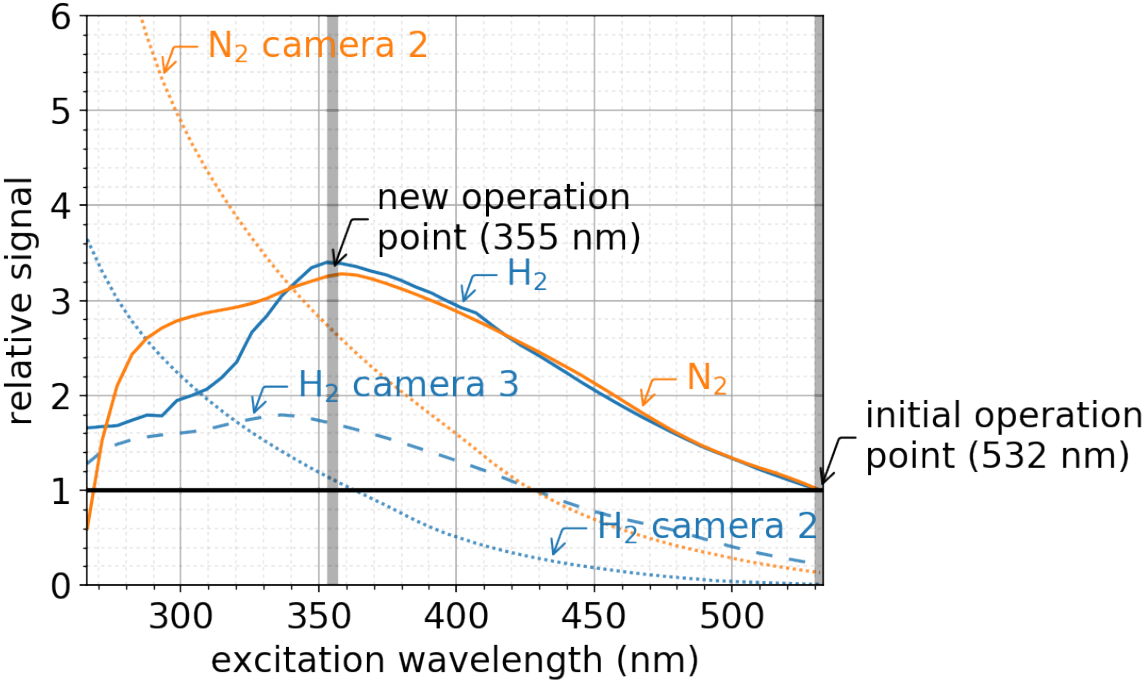
👎

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

➢ Decision: pursue optical techniques

# The large-scale diagnostic will take advantage of a powerful Raman signal dependence on wavelength

- 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

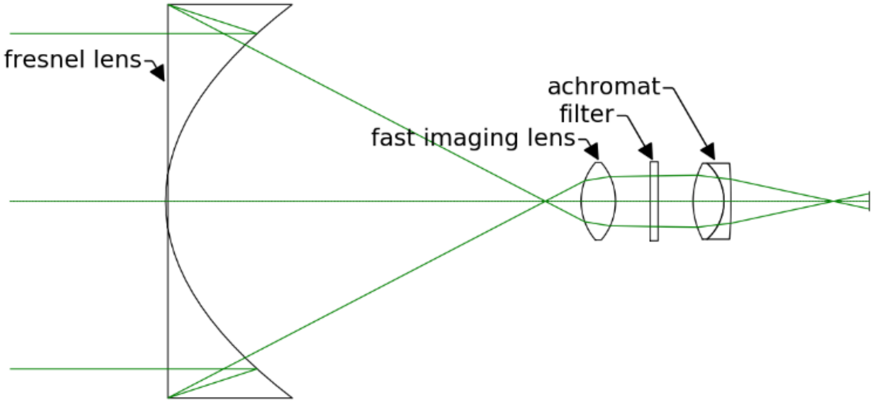


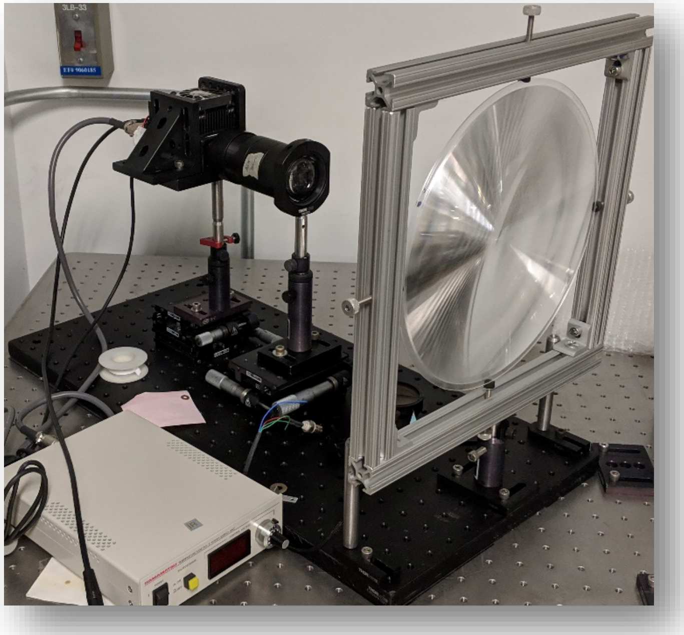
$$\text{Raman signal} \propto (\text{incident energy})(\text{cross}-\text{section})(\text{number density})$$

$$\text{cross}-\text{section} \propto (1/\text{wavelength} + \Delta\text{energy})^4$$

# A Fresnel lens will be used as the primary collector

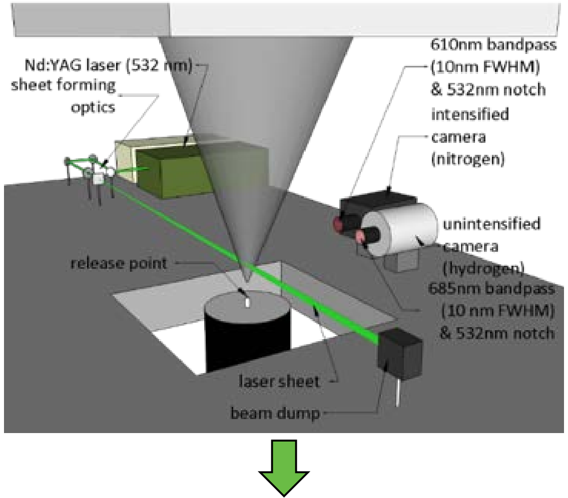
- Large diameter – large solid angle of collection
- Fast (f/0.8)
- Off-the-shelf
- Low cost
- Field lenses to achieve larger field of view, maintaining parallel rays for filter
- Signal detected @ > 20 ft in the lab

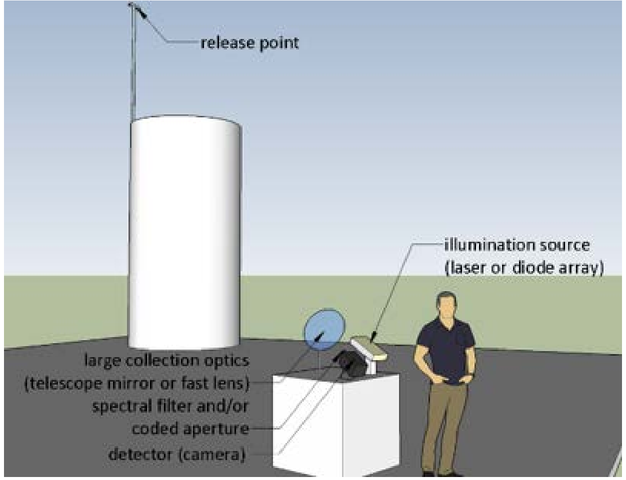




# The diagnostic will be applied to $LH_2$ vents and large-scale experiments

- **Remaining priorities for $LH_2$:**
  - Lab-scale:
    - Develop models relating concentration data to ignition distance
    - Study non-circular orifices
  - Characterization and modeling of
    - Interactions with ambient (i.e. wind)
    - Pooling
    - Evaporation from $LH_2$ pools





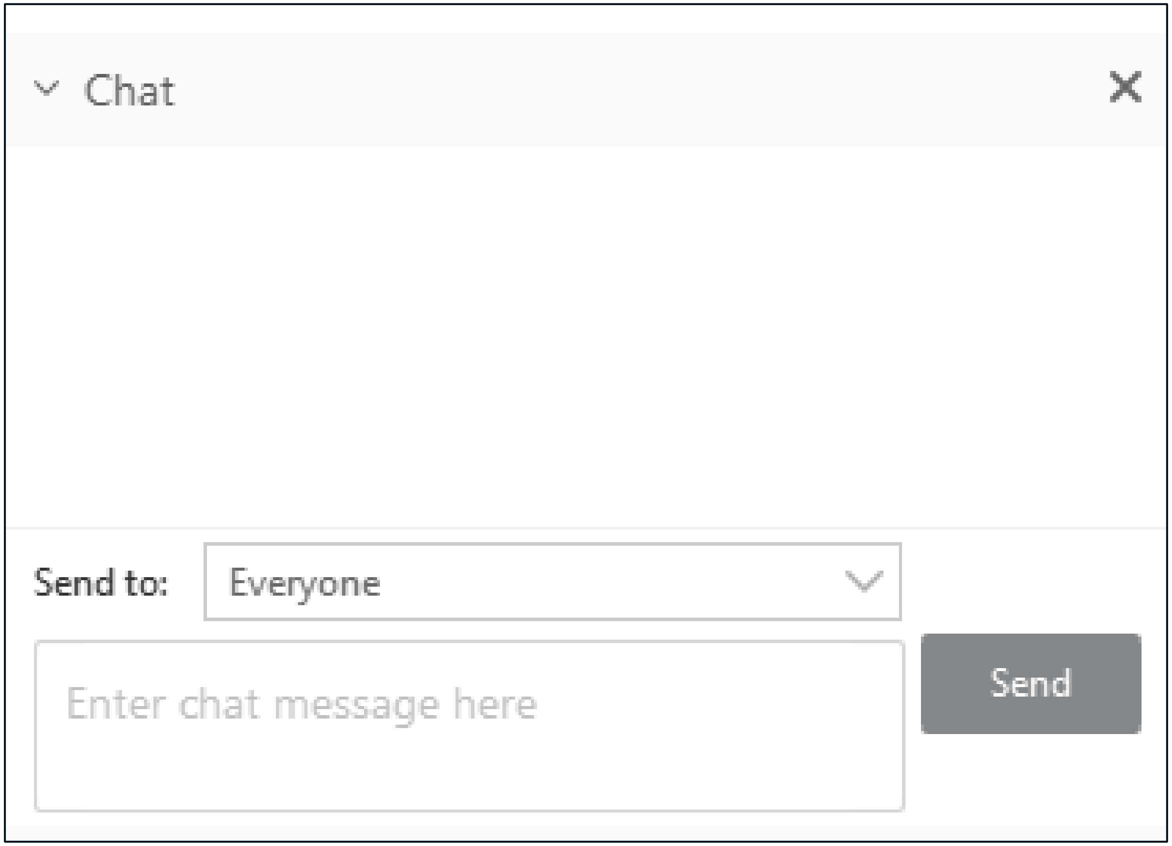
- Apply diagnostic to high-frequency outdoor releases (normally occurring events such as venting after $LH_2$ fill, this summer) to validate ColdPLUME model in non-ideal conditions
- Dedicated validation experiments (pooling, cross-wind) at well-controlled facilities next fiscal year (late 2019-early 2020)

# Summary of liquid $H_2$ research and modeling efforts towards fueling station footprint reduction

- Coordinated research and development activities that facilitate deployment of hydrogen technologies by developing validated physical models, integrating models into HyRAM (risk assessment toolkit), applying models and analyzing real-world scenarios
- Close coordination with NFPA 2 liquid hydrogen setback distance task group
- Measured and developed correlation for the centerline light-up boundary for cryogenic hydrogen
- Measured and developed models to calculate the heat flux from cryogenic hydrogen flames
- Developed a model for internal (pipe, pump, etc.), multi-phase flows
- Validated ColdPLUME model for cryogenic hydrogen dispersion by simultaneous Raman imaging and particle imaging velocimetry
- Continued lab-scale experiments to study other cryogenic hydrogen phenomena (e.g., non-circular releases)
- Developing large-scale diagnostic for quantifying real-world, full-scale cryogenic hydrogen dispersion

# Question and Answer

- Please type your questions to the chat box. **Send to: (HOST)**



# Thank you

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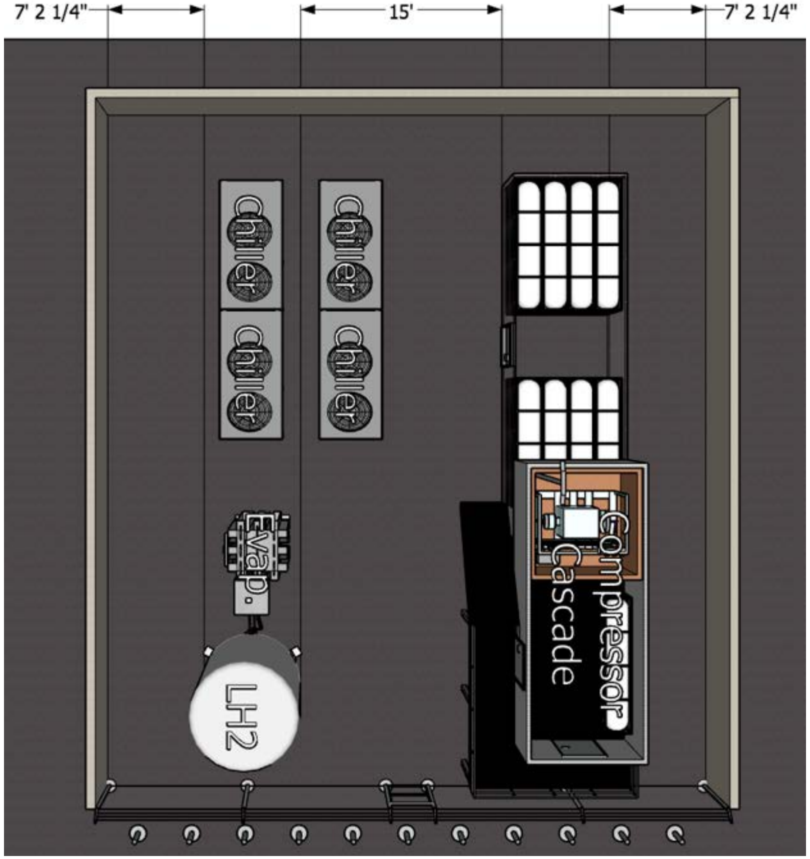
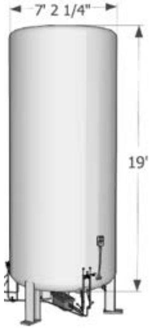
# General NFPA 2 Requirements for Hybrid Hydrogen System

- The hybrid hydrogen system includes both liquid and compressed gas storage
  - Compressor
  - Evaporator
  - Cryogenic pump
- Liquid and gaseous portions of the combined system must be separated by at least 4.6 m (15 ft)



- Vertical tanks shall be located at a distance not less than 1 tank diameter from the enclosing walls



# Moisture and air freeze on the nozzle as the temperature drops

Air and moisture icing around liquid $H_2$ jet column – improves dispersion and reduces hazard distance

# Fast-running, first order models are used in HyRAM to predict hydrogen trajectory and concentration contours (and flames)

- Captures buoyancy effects without full CFD
- Makes it possible to rapidly run many scenarios
- Physical plume/jet (and flame) model coupled to probability of component failure and ignition models to ***quantify*** risk

HyRAM
HYDROGEN RISK ASSESSMENT MODELS

# Common optical techniques 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

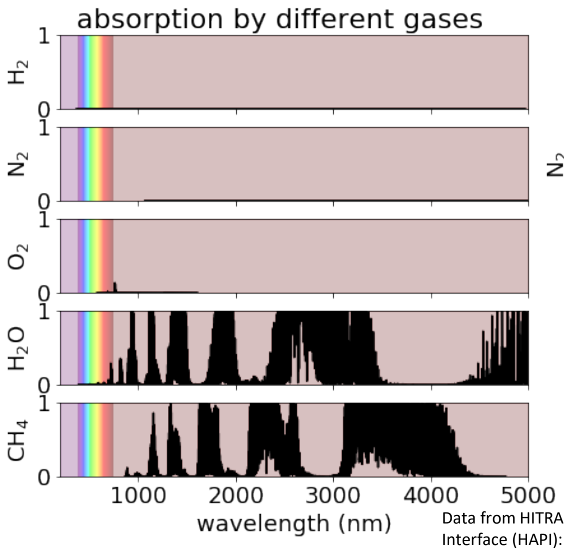
- Measures gradients in density (1st derivative)
- For quantitative measurements:
    - Calibrated schlieren – uniform light source, light intensity quantifies refraction angles
    - Rainbow schlieren – color cutoff filter in place of knife edge, color quantifies refraction angles
    - Diverging light 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

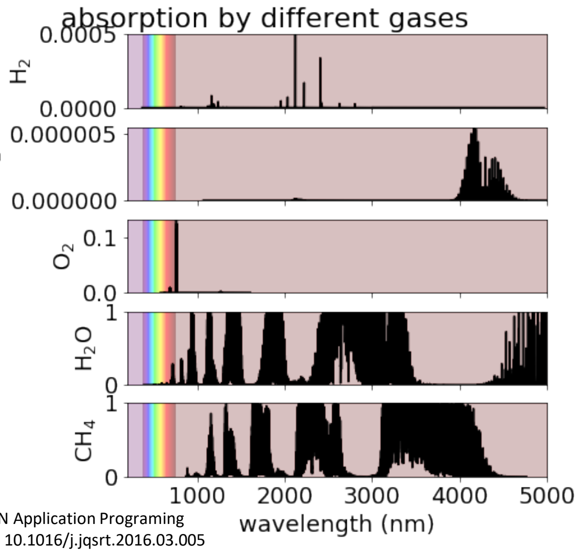
# Fluorescence

- 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

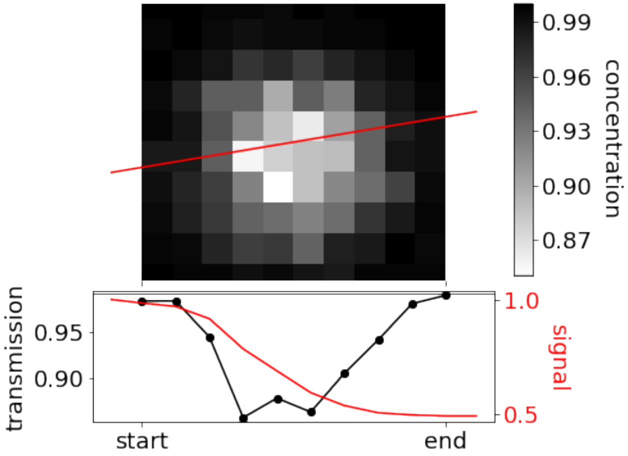
# Absorption

- $H_2$ 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





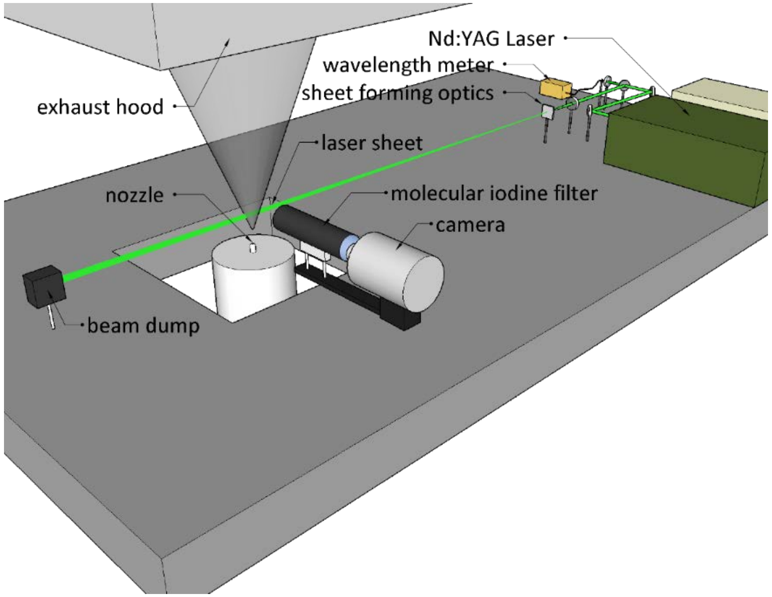
Data from HITRAN Application Programing Interface (HAPI): 10.1016/j.jqsrt.2016.03.005



# Rayleigh scattering

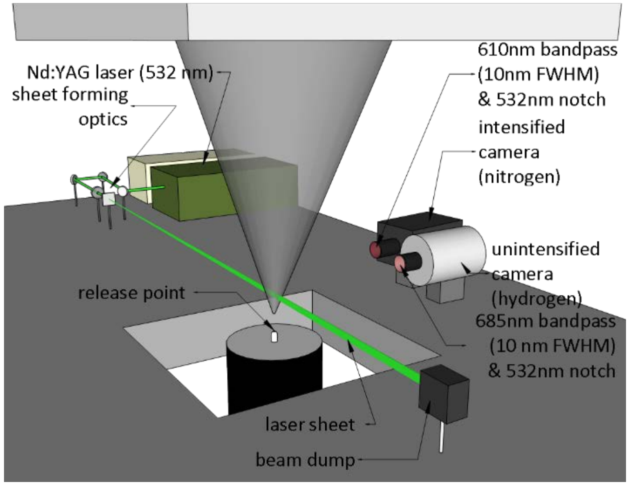
## $H_2$ Rayleigh cross-section ≈ $10^{-27}$ $cm^2$

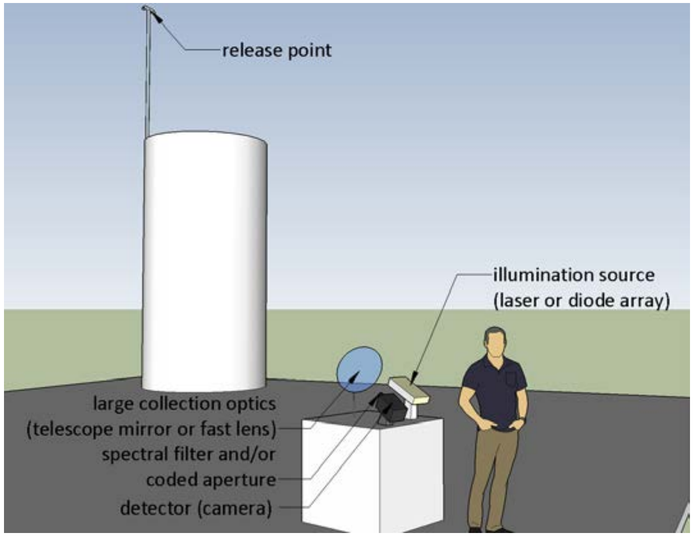
- Planar laser Rayleigh scattering used at Sandia for atmospheric temperature hydrogen releases
- Scatter proportional to number density; variations are caused by both composition and temperature
- For warm releases, always measured in atmospheric temperature region to eliminate this variable and enable 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)



# Challenges abound for technical hardware solutions to enable the large-scale diagnostic

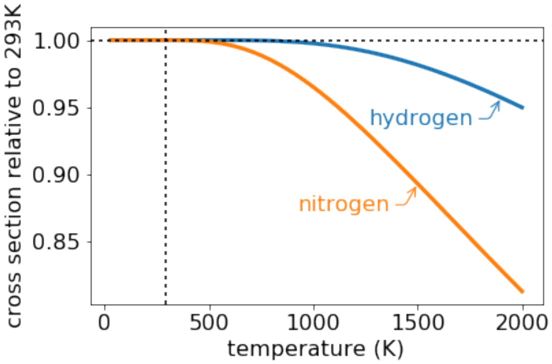
- Challenge: need large field of view and large aperture to collect small number of photons emitted
  - Reflective optics (large telescope mirror)
  - Refractive optics (Fresnel lens)
- Challenge: reasonable cost illumination system with high-power, low-wavelength, pulsed system
  - High-power laser with volumetric illumination
  - High-repetition rate laser scanned across the area quickly
  - High-power diodes/diode arrays
- Challenge: Effective background light suppression (both sunlight and reflected illumination light from condensed water vapor)
  - Time gating
  - Spectral gating
- Challenge: Improved temporal, spectral, and/or spatial resolution
  - Coded aperture sensing
  - Tomography





# 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 ← unknown 2

measured values

calibration constants

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

based on the composition of air

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

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