High-Resolution Raman Measurements of Gradients at Interfaces

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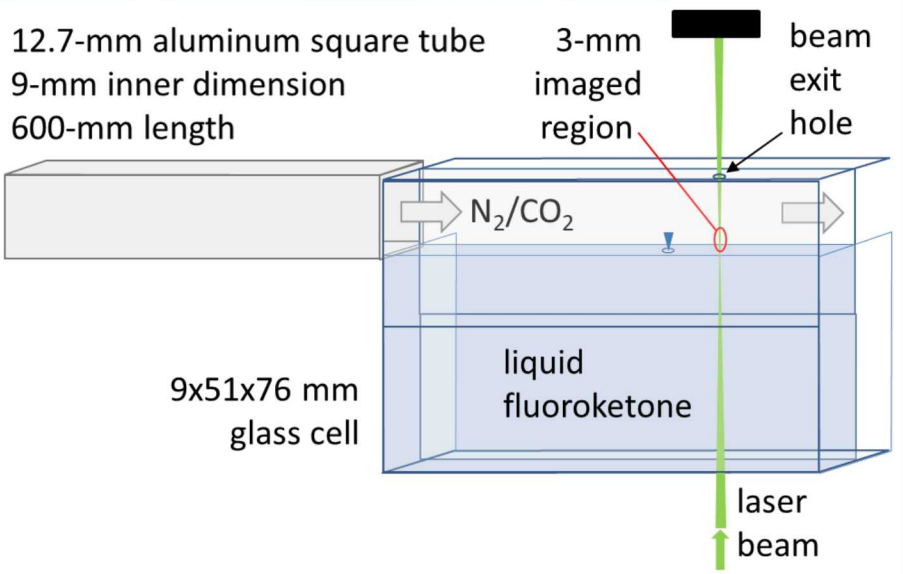
- **Purpose:** Assess feasibility of 1D Raman diagnostics for new area of research on high-pressure gas-liquid interfaces ($C_6F_{12}O$, N_2, CO_2 system)
- **Approach:** Create a compact, modular Raman spectrometer; document spectroscopy of $C_6F_{12}O$
- **Goal:** Demonstrate spatially-resolved species measurements across the gas-phase boundary layer above a liquid fluoroketone surface



Laminar Flow Cell

Key R&D Results and Significance

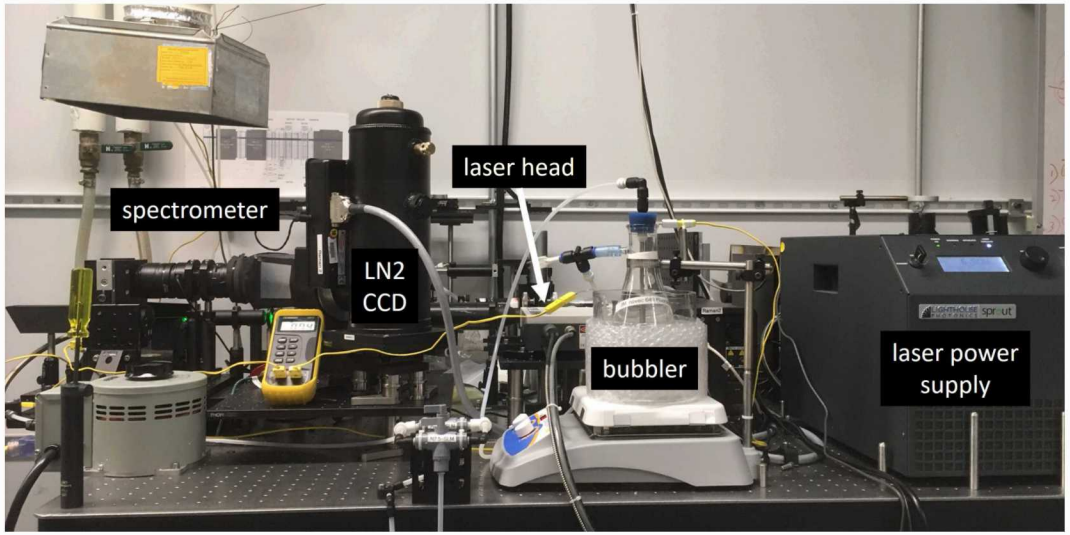
- **All proposed tasks completed successfully**
- **Developed compact modular imaging spectrometer**
  - ✓ $100K of available equipment, including laser
  - ✓ $6K additional optics and mounts
  - ✓ OD-12 rejection at laser wavelength (532 nm)
- **Spectroscopy of fluoroketone**
  - ✓ Raman spectra measured; 300K to 700K
  - ✓ No detectable interference from broadband laser-induced fluorescence
  - ✓ Negligible Raman crosstalk onto N_2
  - ✓ High-resolution spectra in CO_2 overlap region
- **Near-surface boundary layer measurements**
  - ✓ Laminar CO_2/N_2 flow over fluoroketone liquid
  - ✓ Raman spectra measured with 28-μm spacing to within 30-60 μm of the surface
- **No spectroscopic barriers to proposed high-pressure measurements!!**
- **Lessons learned**
  - ✓ Improved bubbler design → lower uncertainty
  - ✓ Deeper cell → higher laser power
- **Follow-on related to BES proposal in review**
  - ✓ Material for compelling rebuttal (if needed)
  - ✓ Big head start if funded
- **Publication**
  - ✓ Spectroscopy; experimental fluids

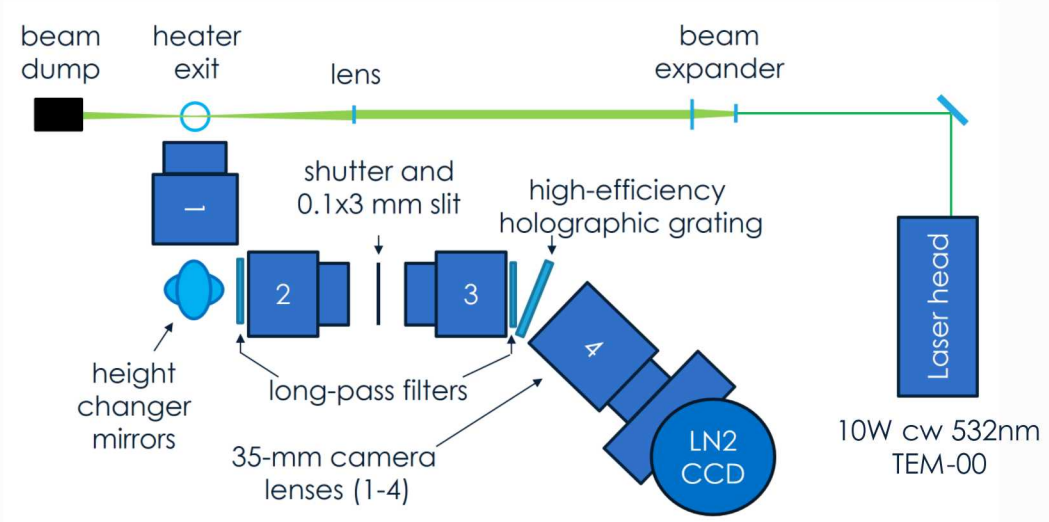
LDRD Approach

- **Experimental setup:**
  - $100K available equipment
  - $9K total purchases

- **Modular spectrometer:**
  - Four 35-mm camera lenses
  - Two long-pass filters; OD-12 @ 532nm
  - Low and high-dispersion holographic transmission gratings
  - Low-noise CCD (1300x1340 pixels)
  - Projected pixel size (14.06 μm)

- **Measure:**
  - Raman spectra of gas-phase fluoroketone in carrier (N_2, CO_2) over temperature range 300K – 700K
  - Spatially resolved spectra across boundary layer above a fluoroketone liquid surface

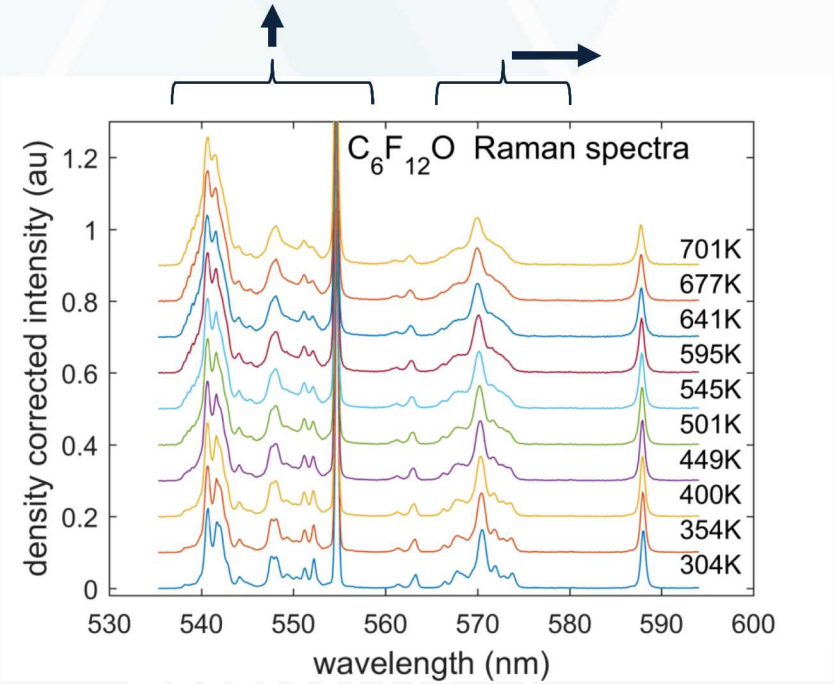


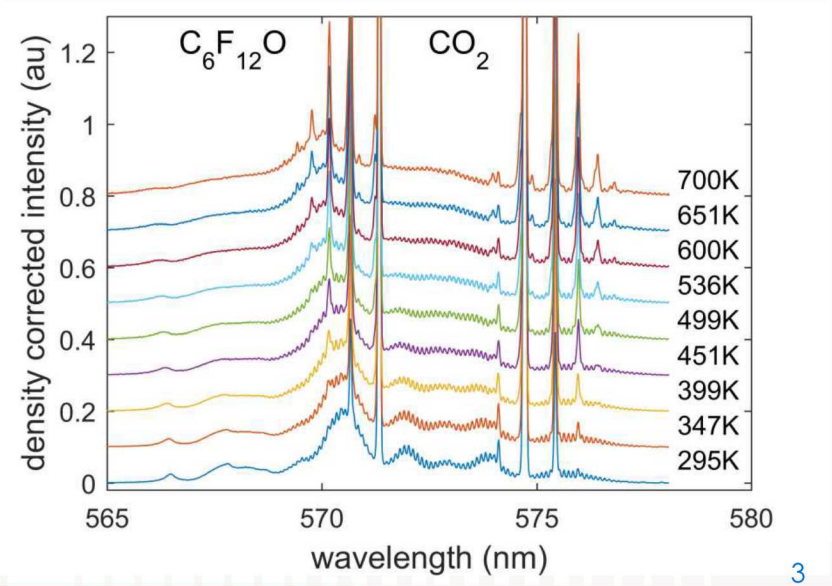


top view

Raman Spectra of Flouroketone

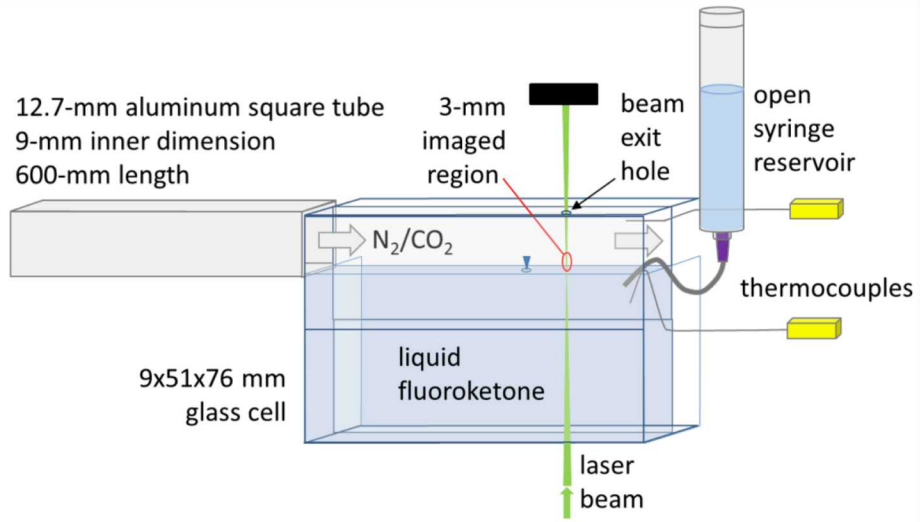
- **No detectable fluorescence**
- **No detectable crosstalk onto N_2**
- **Normalized $C_6F_{12}O$ spectra vs. T**
  - Fluoroketone mole fraction determined from integrated N_2 intensity
  - Integrated response vs. T for interval 535–560 nm increases linearly from 7.2 at 300K to 13 at 700K relative to N_2 at 294K
- **$C_6F_{12}O$ spectrum overlaps CO_2**
- **High-dispersion measurements**
- **Strategy for future work**
  - Build temperature-dependent spectral library for fluoroketone
  - Apply spectral fitting to quantify CO_2



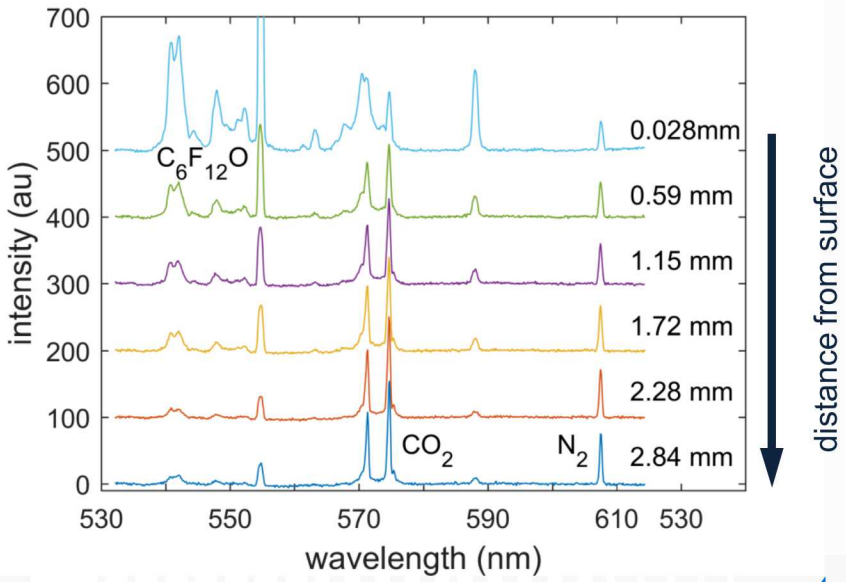


Boundary Layer Measurement

- **Experimental Setup:**
  - Low dispersion grating
  - Height changer removed
  - Laser beam passes through the interface
  - 0.028-mm data spacing (binned by 2)
  - Laminar flow of CO_2/N_2 over liquid $C_6F_{12}O$
  - Surface level constant within ±15 μm



- **Key Achievement:**
  - **Gas phase spectra acquired to within 30-60 microns of the surface**



Project Metrics

- Presentations and Publications
  - LDRD report will be refined for journal submission
  - Possible split into spectroscopy paper and experimental fluids paper

- Tools and Capabilities
  - Compact spectrometer design for near-surface Raman scattering
  - Spectroscopic data for future high-pressure interface research

Project Legacy

Key technical accomplishment

- Feasibility of 1D Raman imaging for spatially-resolved measurements of the gas-phase boundary layer very close to a liquid surface was successfully demonstrated for the target system (fluoroketone, N_2, CO_2)

Engaging Sandia missions

- Specific relevance to pending BES proposal to launch a new program of fundamental research on high-pressure gas-liquid interfaces
- Broad relevance to problems involving gas-liquid and gas-solid interactions (e.g., coupled gas and surface kinetics in catalytic oxidative methane coupling)
- Similar demonstration at a solid surface (laser through a small hole)

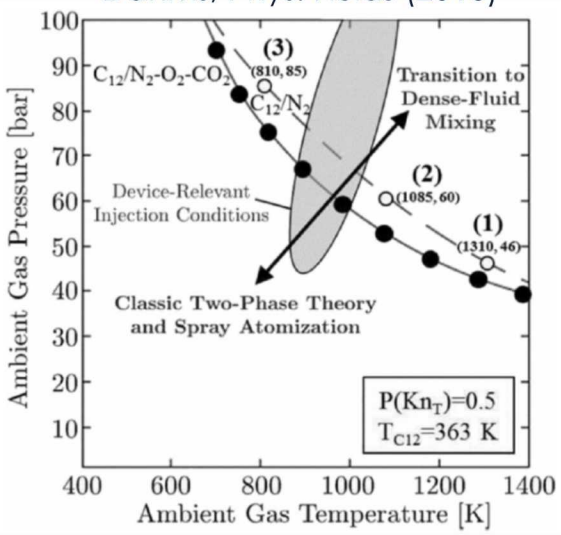
Plans for follow-on and partnerships

- Proposed BES program (head start or added evidence of feasibility, if needed)
- AFOSR has strong interest in high-pressure gas-liquid interface science
- Potential university collaborations

Background and Motivation

- **Theory predicts broadening of gas-liquid interfaces to 10s or 100s of nm**
  - in multi-component systems
  - at elevated (near-critical) pressure
  - in the presence of high temperature gradients
- **No quantitative experimental confirmation of the theory**
- **Proposal to BES** for a new program of fundamental research on high-pressure, non-equilibrium, gas-liquid interfaces is under review
- **Hypothesis:** The relationship of species mole fractions and temperature in the gas phase will change measurably (O(0.1)) when the interface broadens
- **1D Raman scattering:** Species concentrations, temperature, and their gradients in the gas phase
- **Risks addressed by Exploratory Express LDRD:**
  - **No published Raman spectra for fluoroketone** (feasible?)
  - **No literature examples** of 1D Raman measurements made close to a liquid surface in the surface-normal direction (how close?)

Dahms, Phys. Fluids (2016)



Concept for High-P Experiments