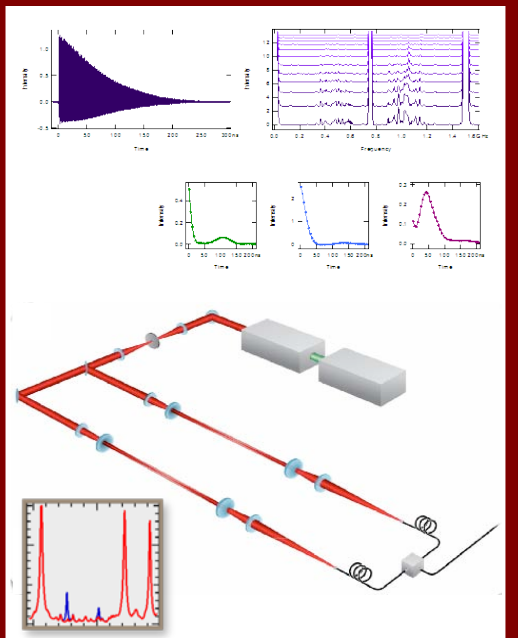
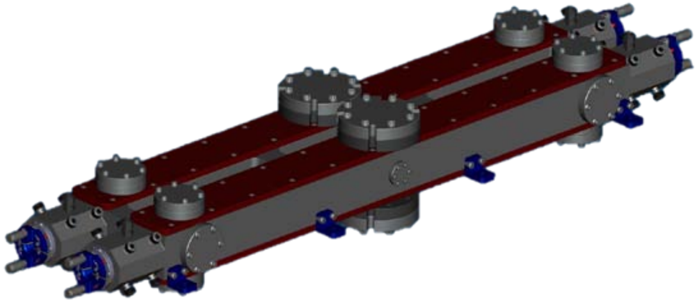


Laser-Based Detection of Trace-Level Contaminants

Alexandra Hoops, Salvatore Birtola, David Chandler, Sean Moore, Brian Patterson, Kevin Strecker

NETL 2012 Crosscutting Research Review Meeting - 3/12/12



Sandia National Laboratories

Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Outline

- Motivation
- Dual-etalon, frequency-comb cavity ring-down spectrometer
- Proof-of-principle experiments: H_2O, O_2
  - Setup I: broadband laser, low-resolution cavity
  - Setup II: narrowband laser, high-resolution cavity
- Application to HCl detection
  - HCl spectroscopy
  - Component selection and next-generation dual-etalon spectrometer design
- Summary and next steps

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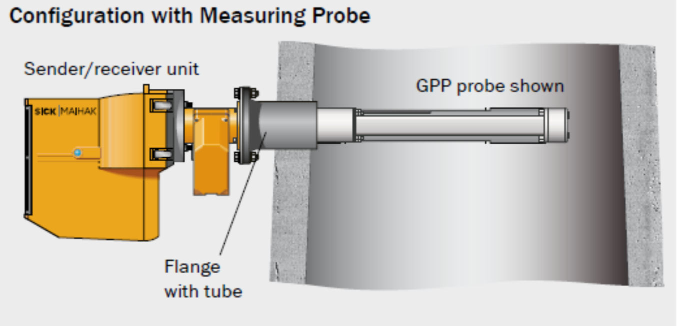
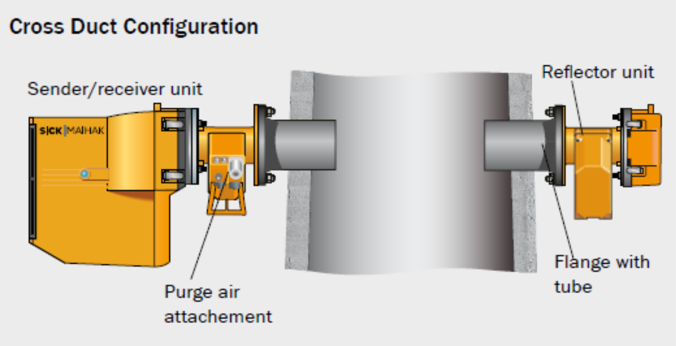
Motivation

- Recently promulgated regulations regarding hazardous-air-pollutant (HAP) emissions from utility coal boilers include:
  - Substantial reductions in allowable emission levels, especially for new plants
  - Increased monitoring and reporting requirements
- Determination of HAP emission limits based on:
  - Environmental and health effects
  - Capabilities of monitoring approaches
- Potential for greater emissions control with advanced sensors that can operate with high-sensitivity, specificity, and with a fast time response
- HCl identified as a key HAP for which current continuous emission monitors (CEMs) are inadequate

HCl CEMs

- Optical approaches offer high sensitivity and specificity
  - Tunable diode laser spectroscopy
  - Fourier transform infrared spectroscopy (FTIR)
- Detection sensitivities of currently available HCl CEMs
  - Extractive: 0.1 ppm
  - Probe: 0.2 ppm
  - Cross duct: 60 ppm
- Existing technology sufficient to meet monitoring requirements for existing utility coal boilers, but inadequate for new units
- Goal: to develop an *in situ* monitoring approach with detection sensitivity < 0.1 ppm





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Traditional Cavity Ring-Down Spectroscopy (CRDS)

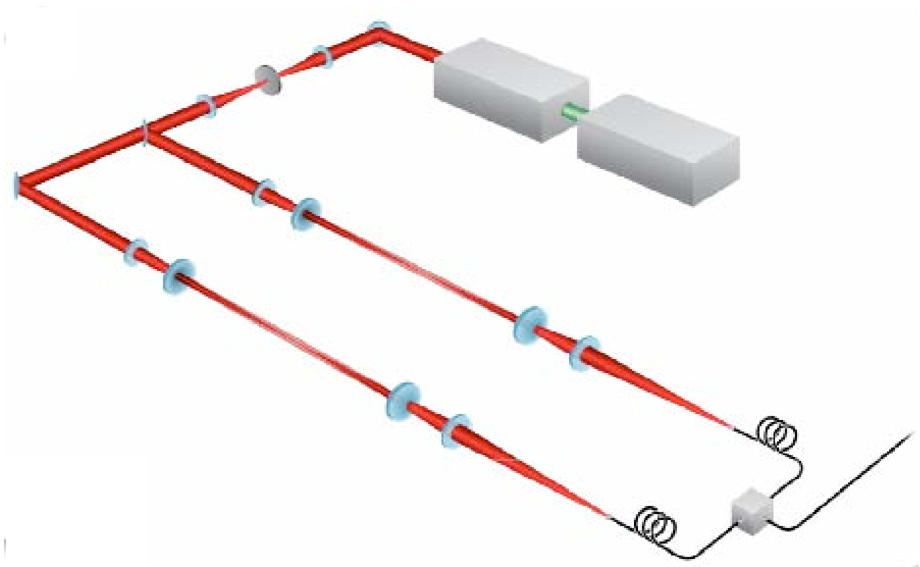
- Principles of operation:
  - Laser pulse is injected into a high finesse cavity and the decay of light intensity, I(t), leaked out of the cavity is monitored:

$$I(t) = I_0 e^{-t/\tau}$$

  - Decay constant, τ, of the cavity depends on the mirror reflectivity, scattering, and absorption by the background gas
  - Absorption by analyte present in cavity increases decay rate
- Advantages
  - High sensitivity: long path length from multiple passes through the cavity
  - Ring down time not sensitive to variations in laser intensity
- Key disadvantages
  - Observed intensity decay not spectrally resolved → to acquire a spectrum, the laser wavelength must be scanned
  - Spectral resolution limited by laser linewidth, necessitating high-quality laser source

Dual-Etalon, Frequency-Comb Cavity Ring-Down Spectroscopy

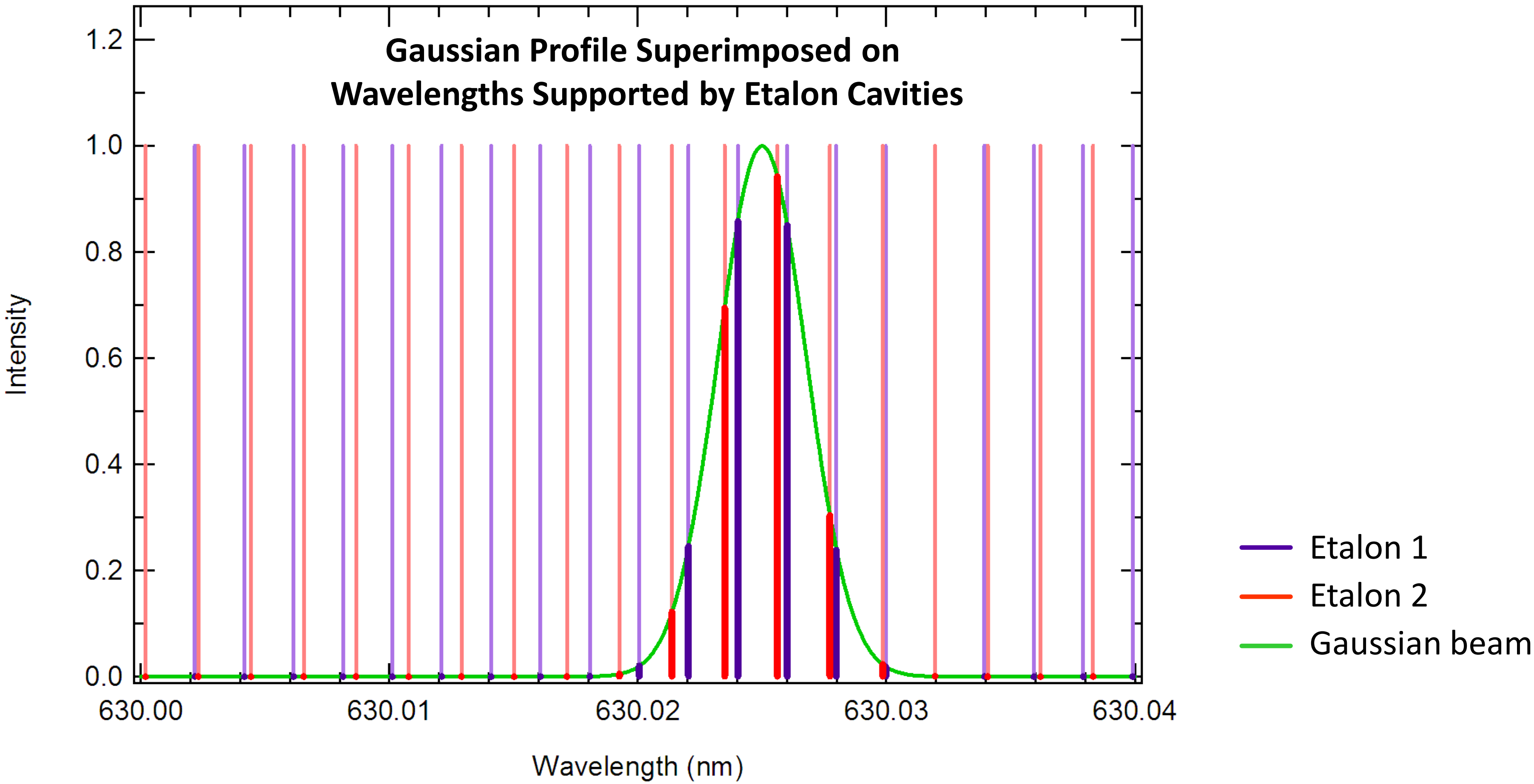
- New technique* recently developed at Sandia to generate a broad-bandwidth, high-resolution spectrum with the sensitivity of CRDS in a single laser pulse
- Broad bandwidth laser beam directed through two etalon cavities of slightly different lengths
- Output beams are two frequency combs with spacings set by free spectral ranges (FSRs) of etalon cavities
- Difference in spacing between the frequency combs generates beat frequencies when signals from the the two cavities are combined
- Absorption spectrum can be reconstituted from the observed interference pattern



*Patent submitted 2011

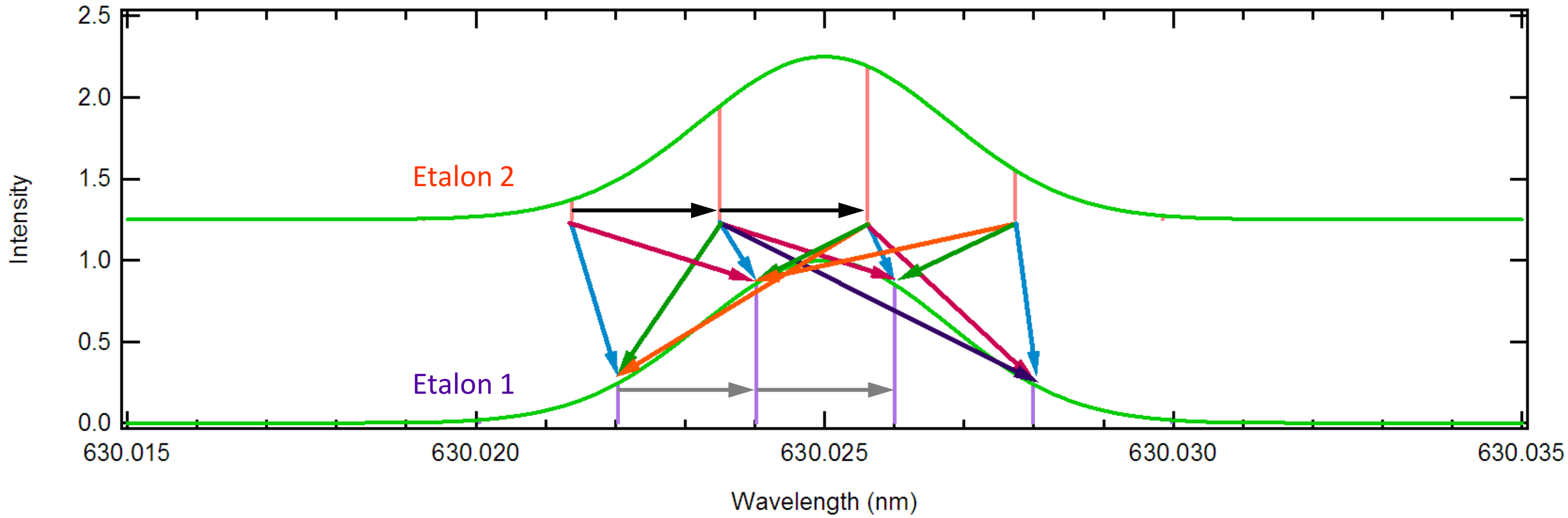
Simulated Etalon Output

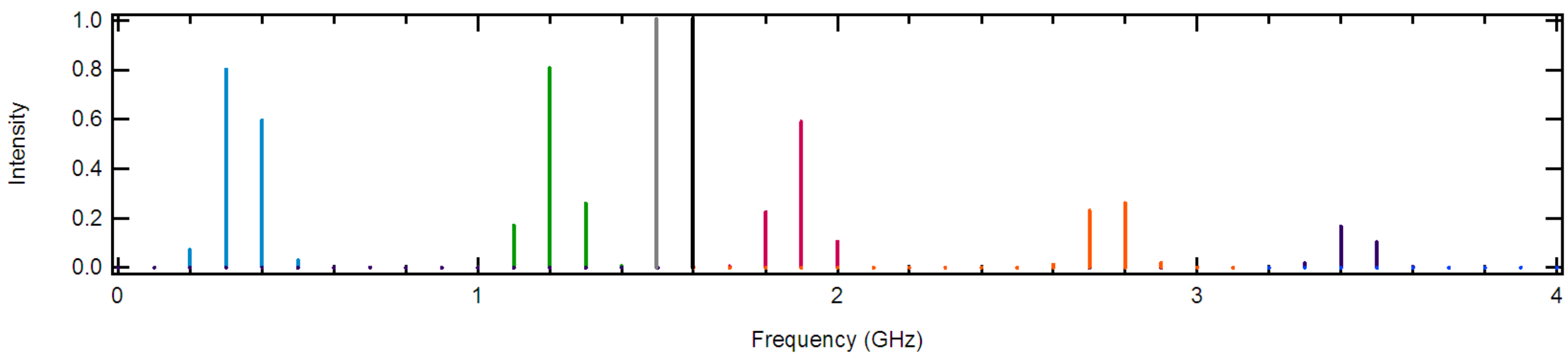
- Etalon 1 free spectral range: 1.5 GHz
- Etalon 2 offset: 100 MHz



Generation of Beat Frequencies

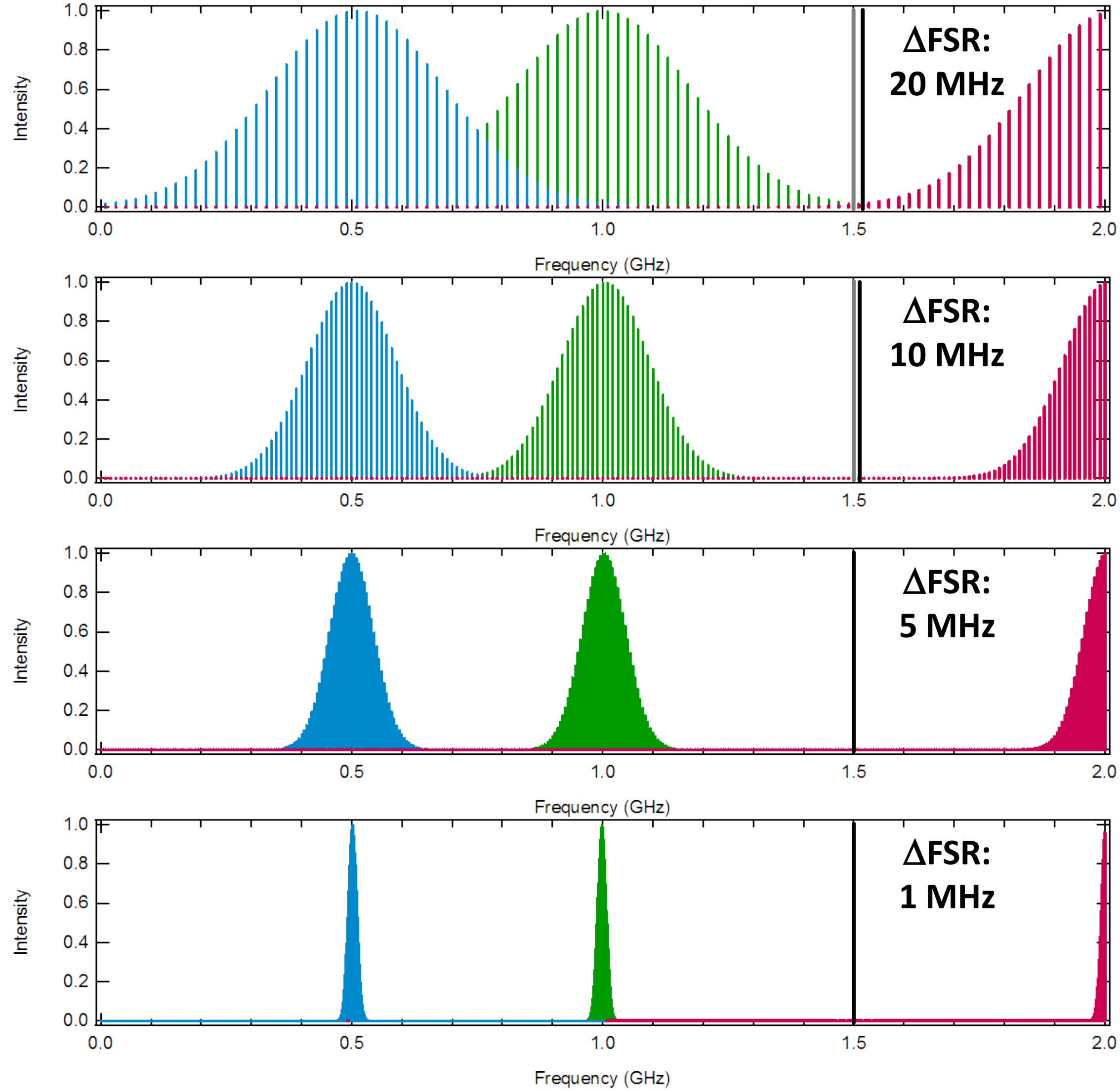
- Heterodyning two frequency combs results in additional beat frequencies, shifting spectrum to lower frequencies
- Key to high resolution: frequency walk-off of the two combs ensures that each optical frequency corresponds to a unique rf frequency





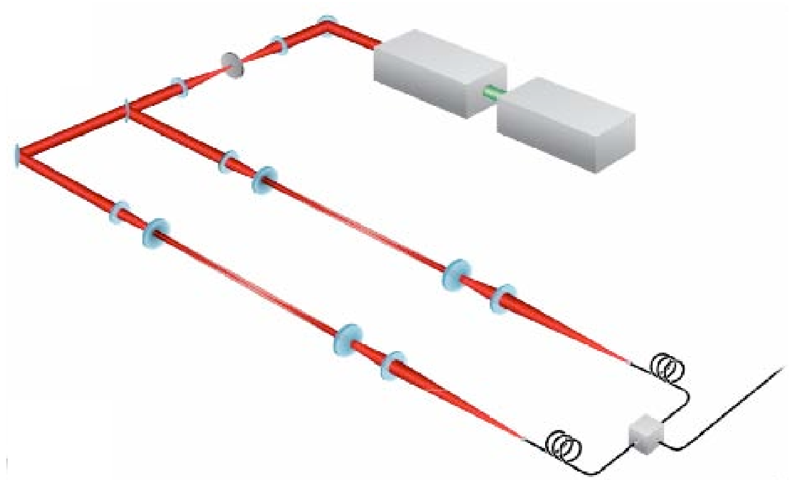
Impact of Etalon FSR Offset

- Simulated Gaussian profile width: 0.1 nm
- Decreasing difference in free spectral ranges of cavities increases width of captured spectrum
- Upper limit: spectral overlap
  - Non-overlapped spectral width: FSR×N_{BF}
  - N_{BF} : number of beat frequencies in non-overlapped region (N_{BF} = 0.5 FSR / ΔFSR)
- Lower limit: resolving power for features of interest (function of ring-down time)



Dual-Etalon, Frequency-Comb CRDS Characteristics

- Width of single-shot spectrum determined by laser bandwidth
- Maximum spectral resolution equals free spectral range of etalons, not laser linewidth
- Laser requirements (spatial beam quality, linewidth, stability) relaxed in comparison to traditional CRDS
- Sensitivity of CRDS with a single laser shot
- Additional sensitivity can be achieved with signal averaging



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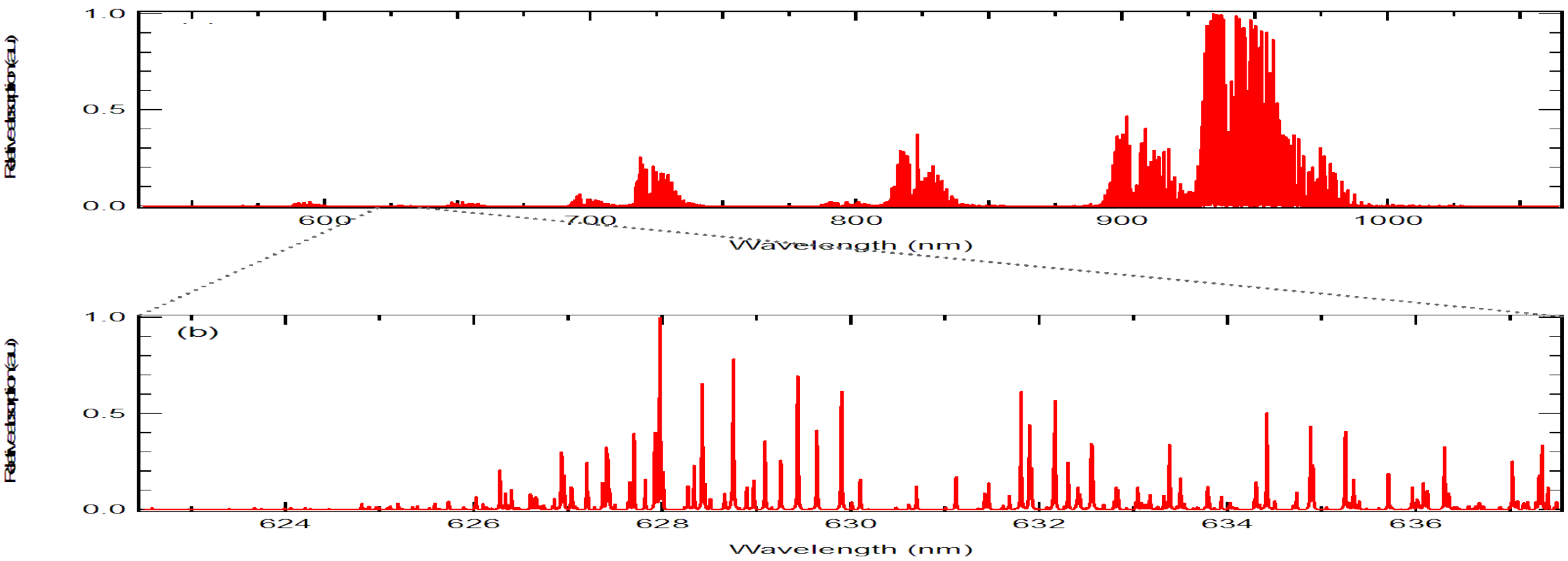
Proof-of-Principle Experiments

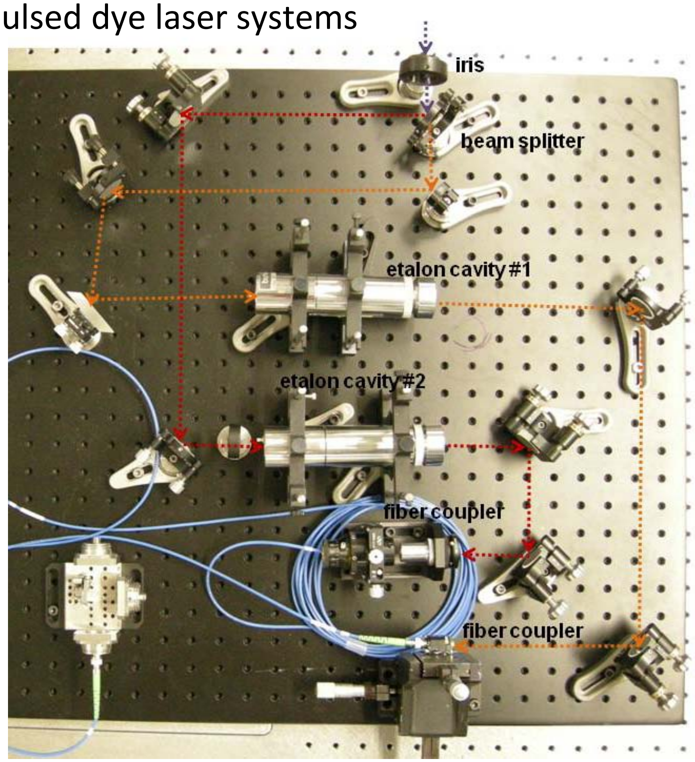
- Goal: demonstrate feasibility of dual-etalon, frequency-comb cavity ring-down spectrometer
- Target: weak H_2O absorption overtones accessible with readily available dye lasers

HITRAN-generated H_2O Absorption Spectrum



Experimental Setup I

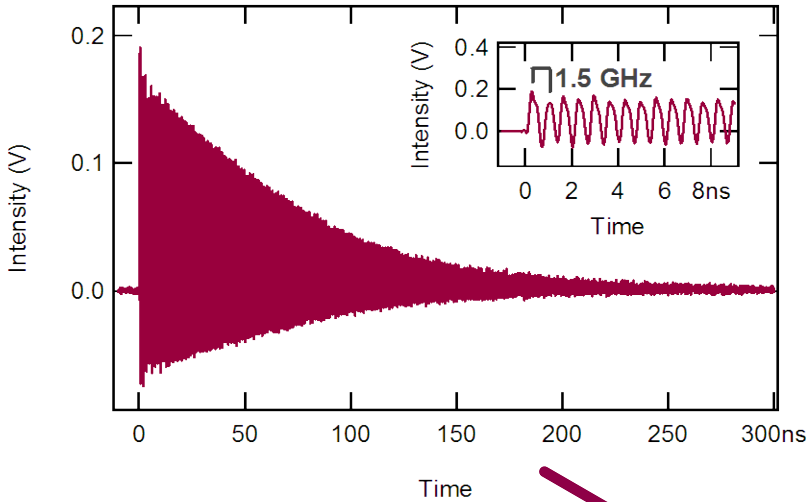
- Laser: amplified broadband dye laser w/DCM
  - Laser thought to lack longitudinal mode structure common in pulsed dye laser systems
  - Pulse energy: 10 mJ
  - Pulse width: 65 ps
  - Repetition rate: 20 Hz
  - Bandwidth: 15 nm



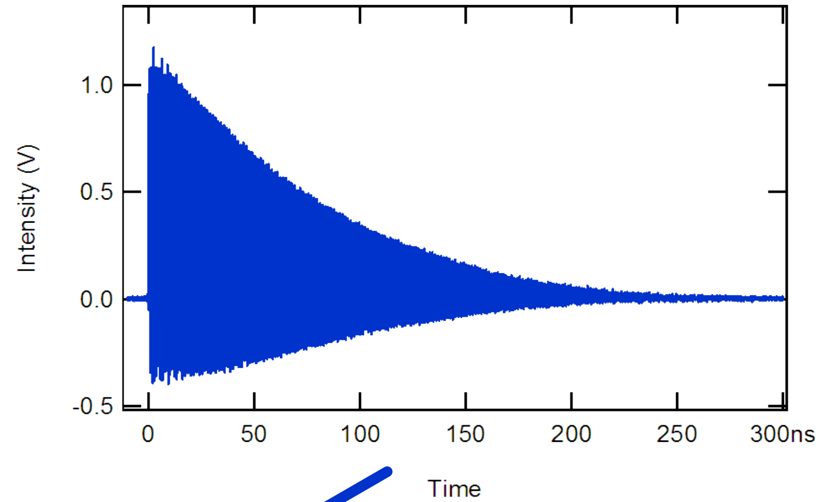
- Bandpass filter to prevent spectral overlap
  - 1 ± 0.2 nm FWHM
  - Center λ: 632.8 nm
  - Peak transmission: 50%
  - Out-of-band transmission (200-1100 nm): <0.01%
- Etalon cavities:
  - Length: 10 cm (1.5-GHz FSR)
  - Mirror reflectivity: >99.5%
  - Confocal configuration: beam collimated in forward direction and focused in cavity center on return
- Fiber coupling for spatial filtering of higher-order cavity modes
- Detector: 1.2-GHz photodiode coupled to 4-GHz oscilloscope

Ring-Down Signals

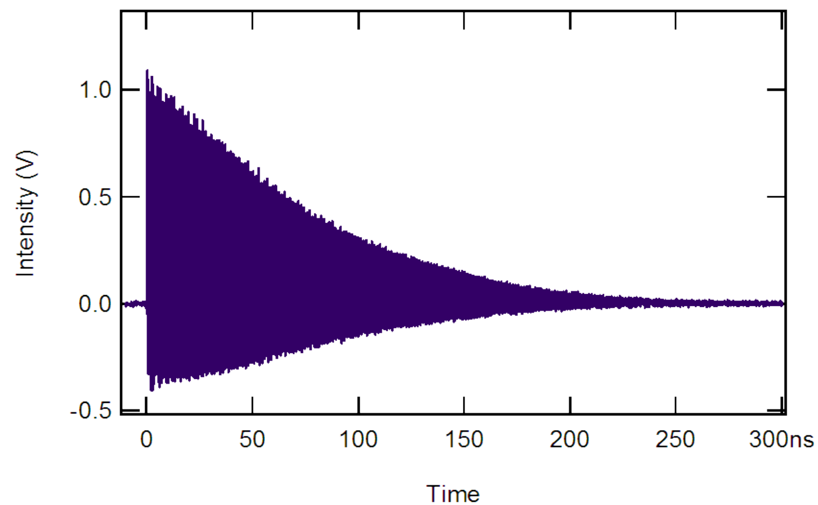
Cavity 1



Cavity 2



Both Cavities



FSR: 1.5 GHz

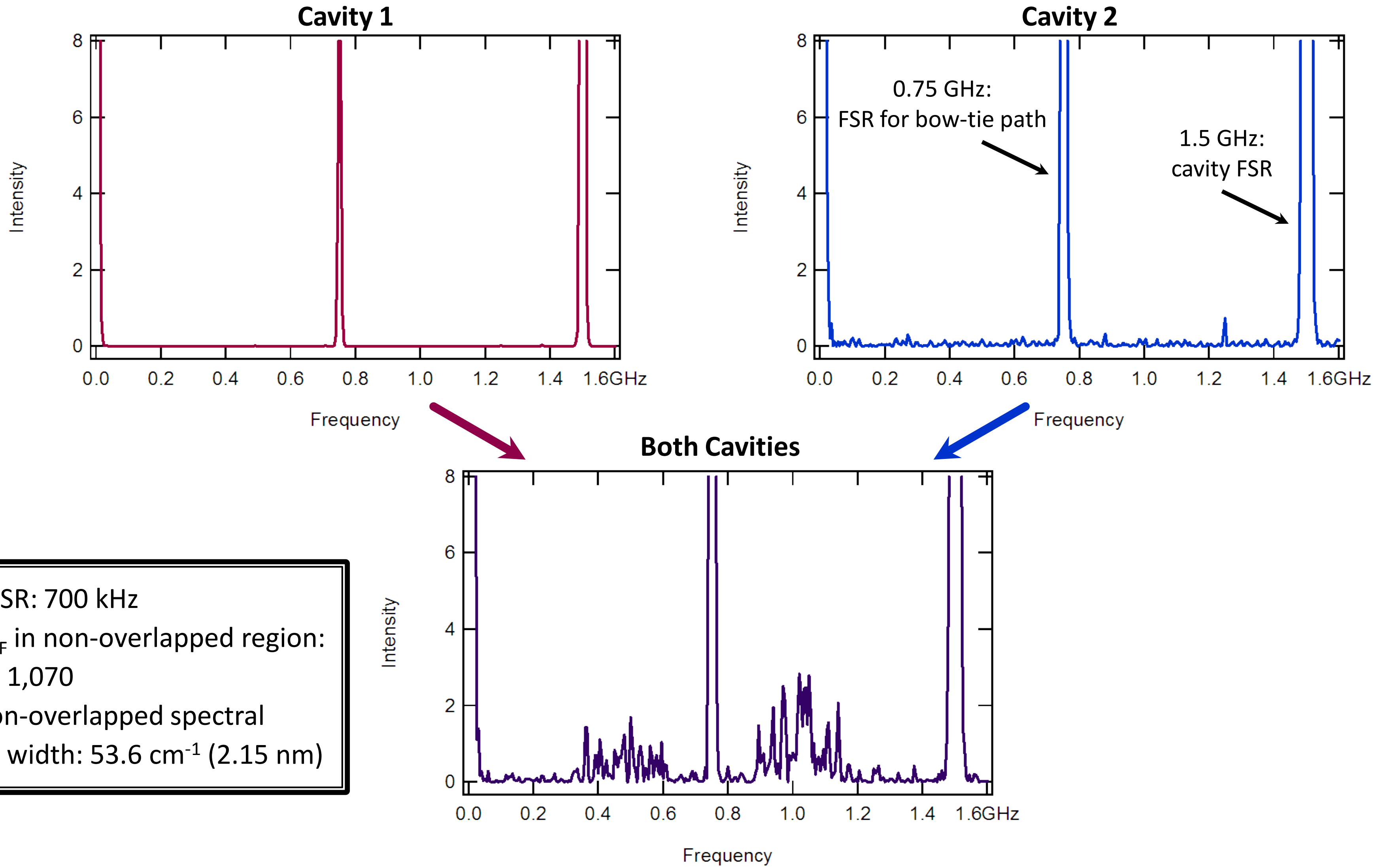
Fit ring-down decay to:

$I(t) = I_0 e^{-t/\tau}$

Cavity decay constant:

$\tau = 75$ ns

Interaction of Frequency Combs Apparent in Fourier Transforms of Ring-Down Signals

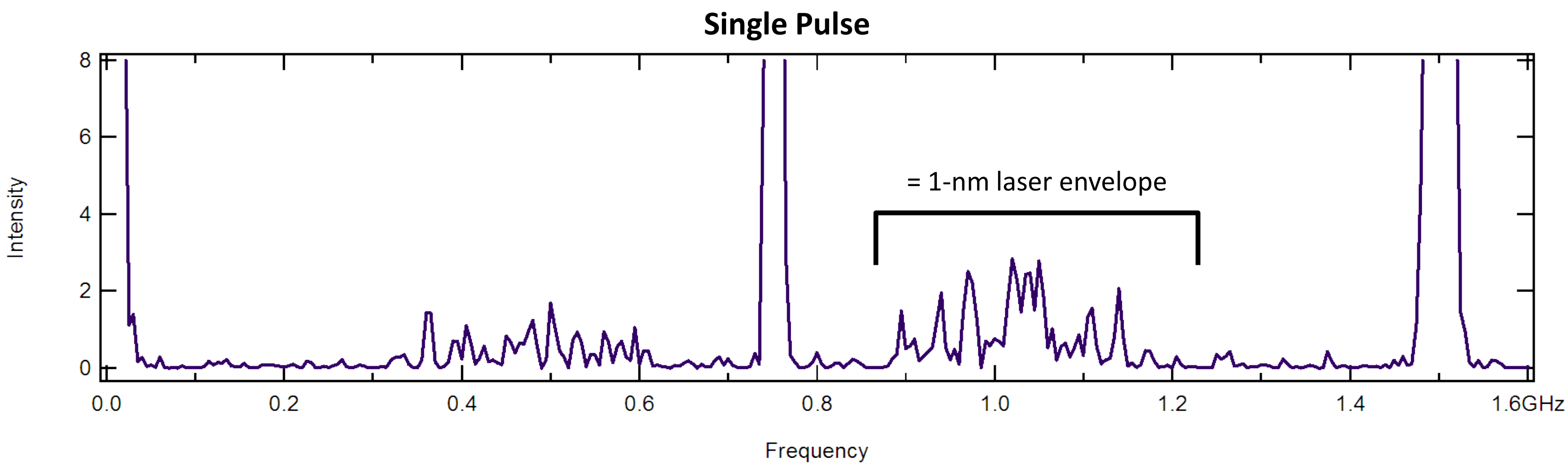


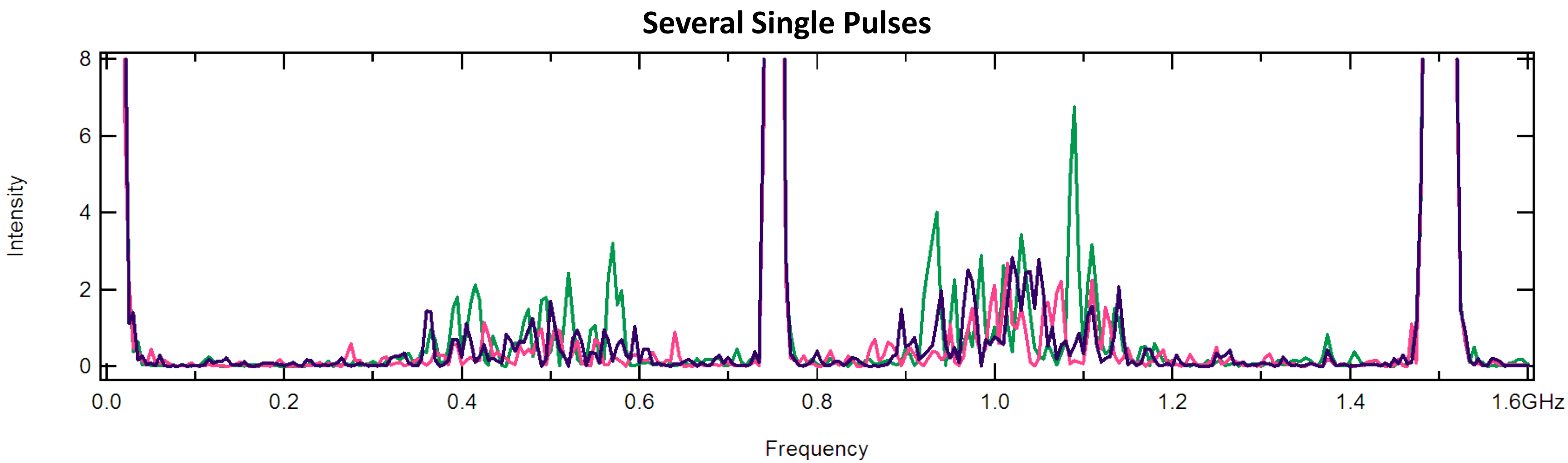
ΔFSR: 700 kHz

N_{BF} in non-overlapped region: 1,070

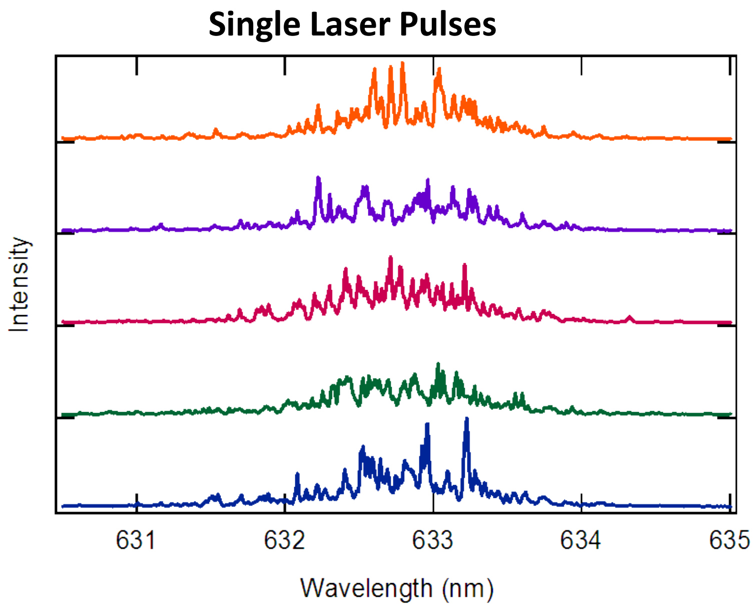
Non-overlapped spectral width: 53.6 cm^{-1} (2.15 nm)

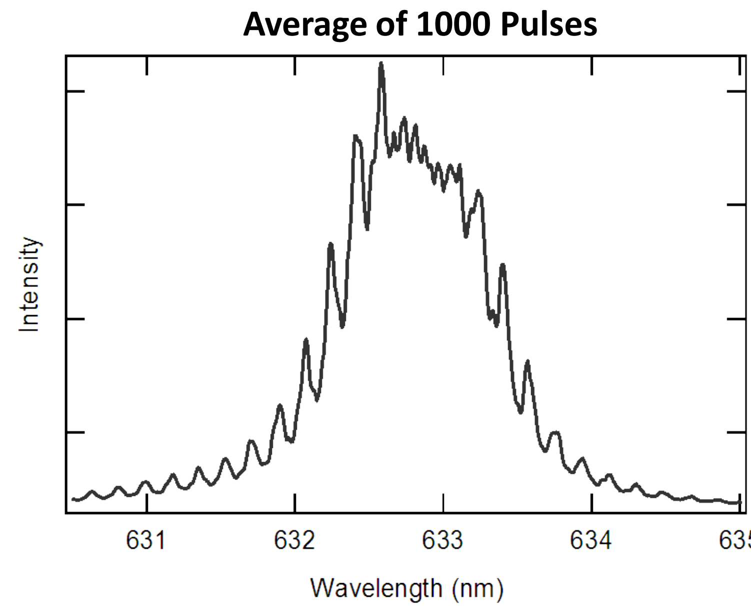
Variable, Structured Laser Intensity Profile





Laser Profile

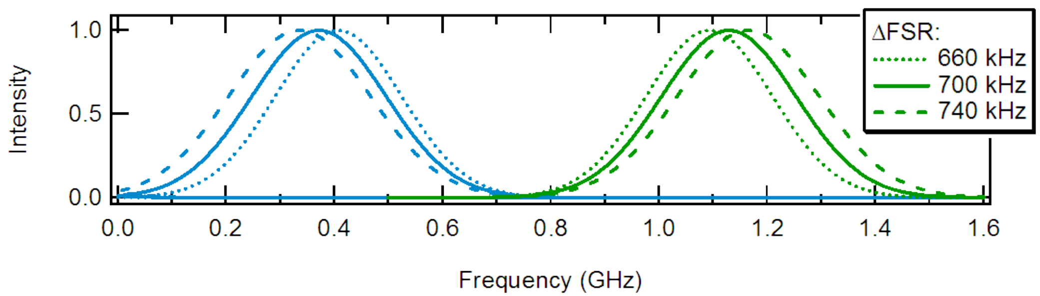




- Independently measure laser profile with 1-m spectrometer
- Confirmation that laser output has considerable structure and pulse-to-pulse variations
- Filtered laser profile:
  - Center λ: 632.8 nm
  - FWHM: 0.98 nm
  - $1/e^2$ full width: 2.0 nm

Data Analysis with Structured Laser Profile: 2 Approaches

- Signal averaging
  - With a sufficient number of averages, gaps in laser spectral profile are minimized
  - However, an observed drift in signal due to thermal fluctuations impedes simple signal averaging:
    - Simulated Gaussian profile, 1.5-GHz FSR:

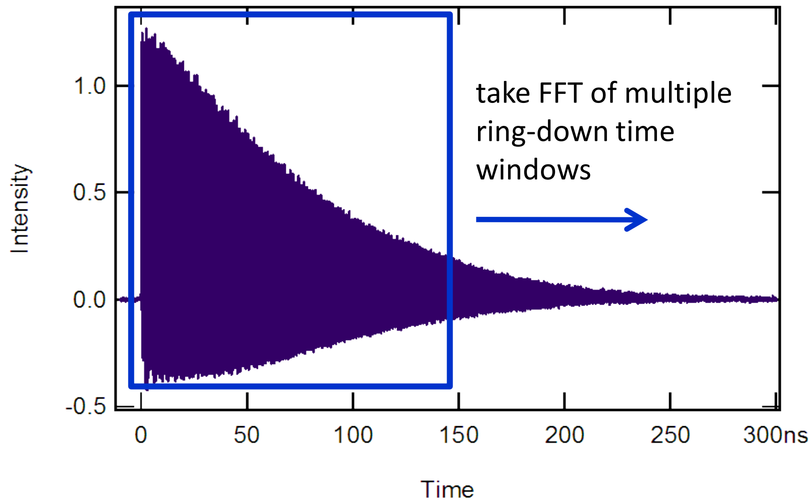


    - ±40 kHz in ΔFSR (±2.7 μm change in cavity length) causes shift of 36 MHz in Fourier transform (2.5 cm^{-1} shift in wavelength spectrum)

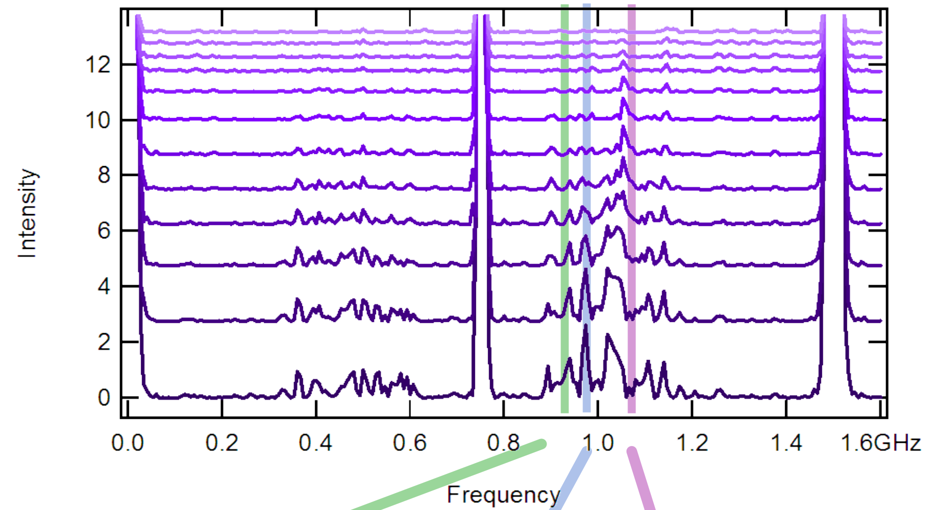
- Measure decay of individual beat frequencies in Fourier transform
  - Cavity ring-down signals independent of laser intensity
  - However, peaks may be missed if the laser power is too low

Examine Decay of Individual Beat Frequencies

Combined Ring-Down Signal



FFT of Ring-Down Sections



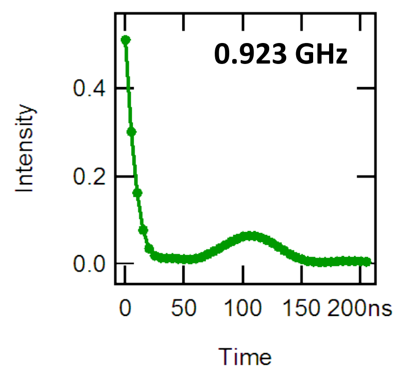
Decay of Individual Beat Frequencies

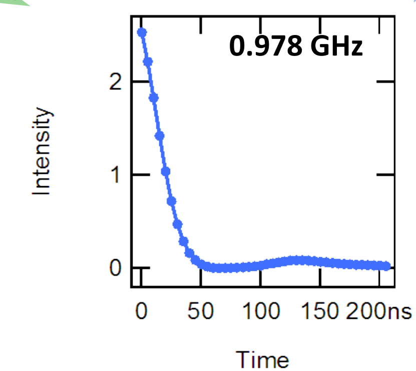
Fit decay signal to:

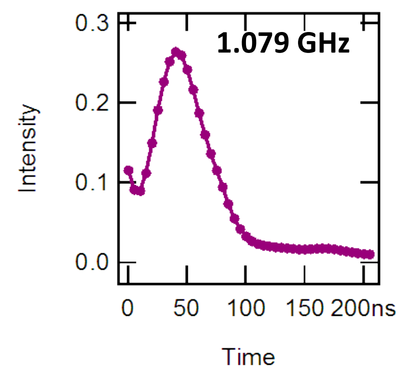
$I(t) = I_0 \exp[-t\,(1/\tau + \alpha c)]$

α: absorbance

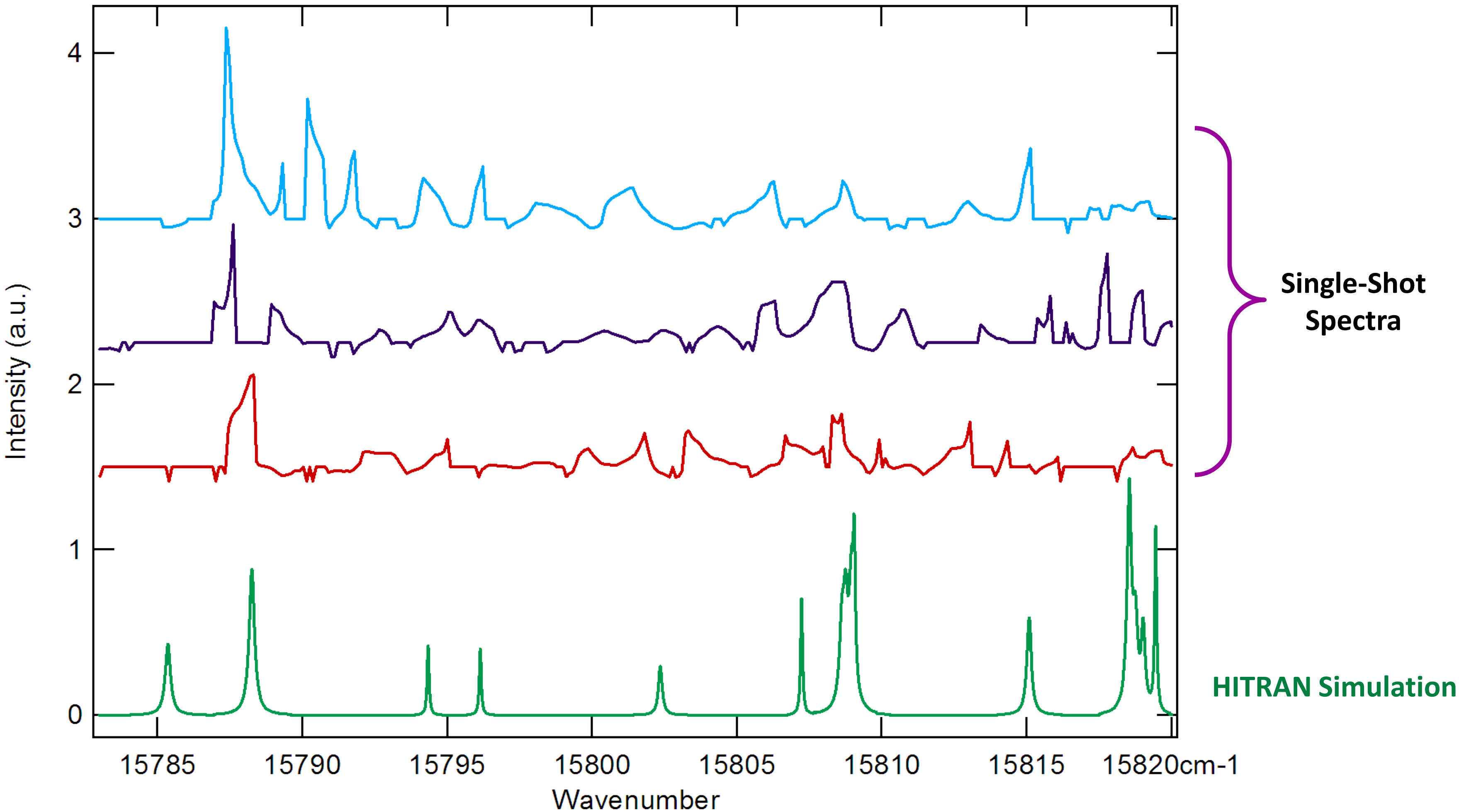
c: speed of light







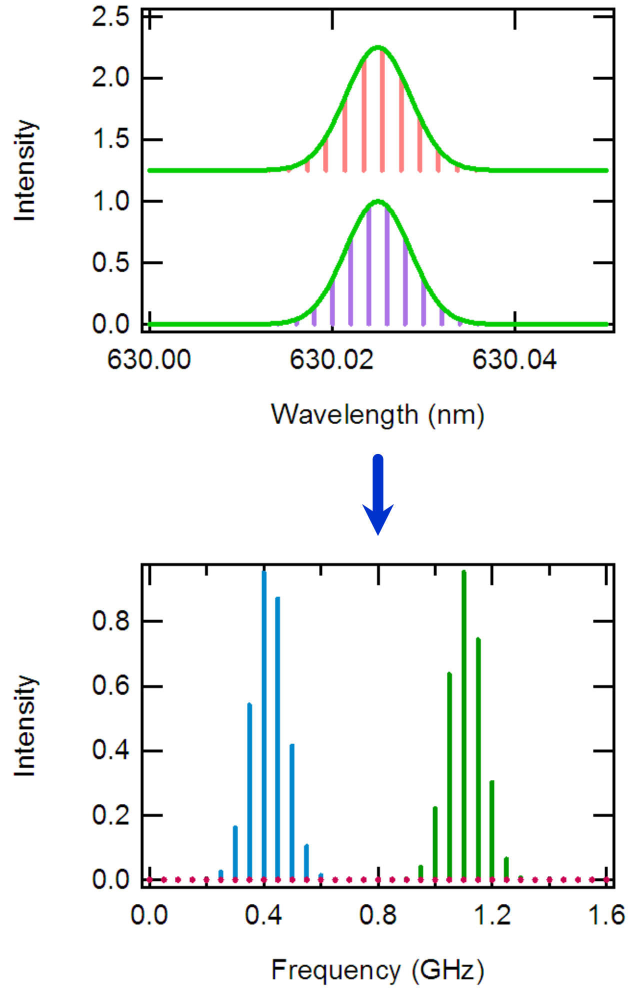
Absorption Spectra of Air



* Resolution limited by cavity decay constant

Spectral Resolution

- Ultimate spectral resolution limit determined by etalon FSR
- However, ability to resolve beat frequencies is limited by ring-down times (Fourier transform resolution determined by time window)
- Assuming cavity decay constant sets resolution, for τ = 75 ns:
  - Fourier transform resolution: 13 MHz
  - Corresponding spectral resolution: 0.95 cm^{-1}



Experimental Setup II

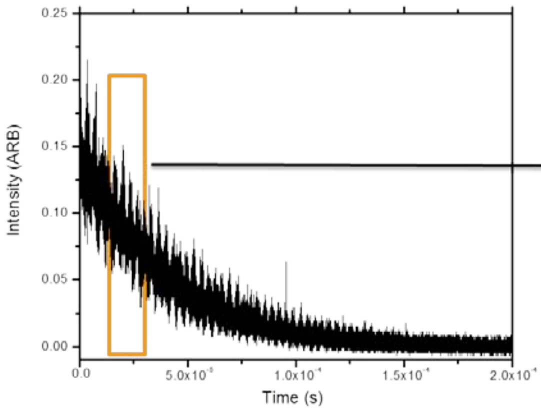
Setup Comparison

		Setup I	Setup II
Laser	Wavelength	633 nm	629 nm
	Pulse energy	10 mJ	3 mJ
	Pulse width	65 ps	6 ns
	Linewidth	25 cm^{-1}	0.15 cm^{-1}
Cavities	Length	10 cm	50 cm
	FSR	1.5 GHz	300 MHz
	ΔFSR	700 kHz	240 kHz
	Mirror reflectivity	>99.5%	>99.99%
	Cavity decay constant, τ	75 ns	50 μs
Detector		1.2-GHz photodiode	PMT

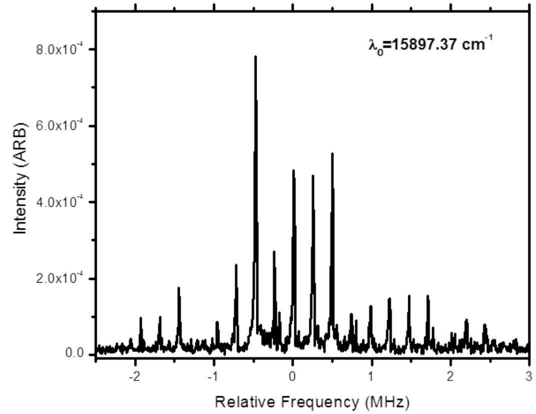
- Considerably smaller spectral region captured with single pulse
- Higher mirror reflectivity and longer cavity length results in longer decay constant, increased sensitivity, and higher spectral resolution

Results and Analysis

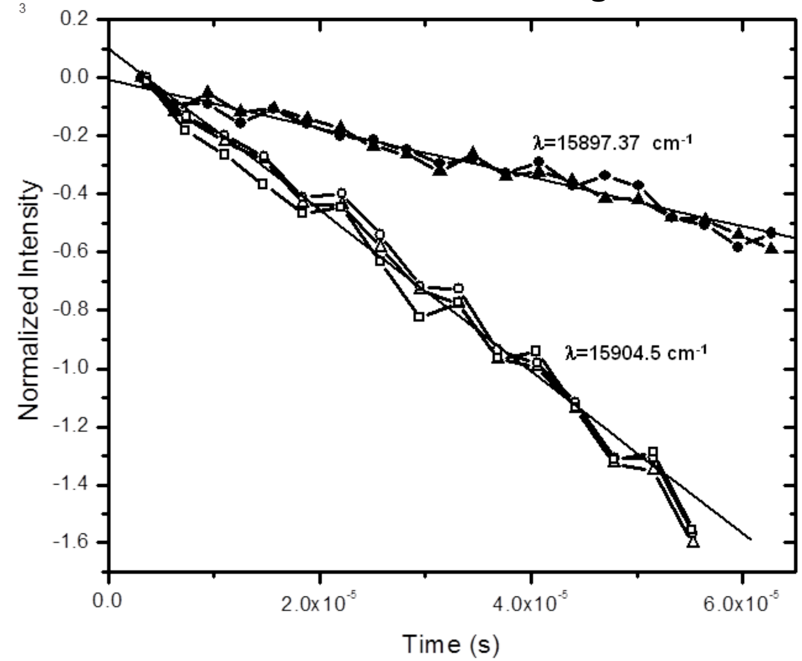
Combined Ring-Down Signal



FFT of Ring-Down Section



Decay of Several Beat Frequencies for Two Laser Wavelengths



FSR: 300 MHz

ΔFSR: 240 kHz

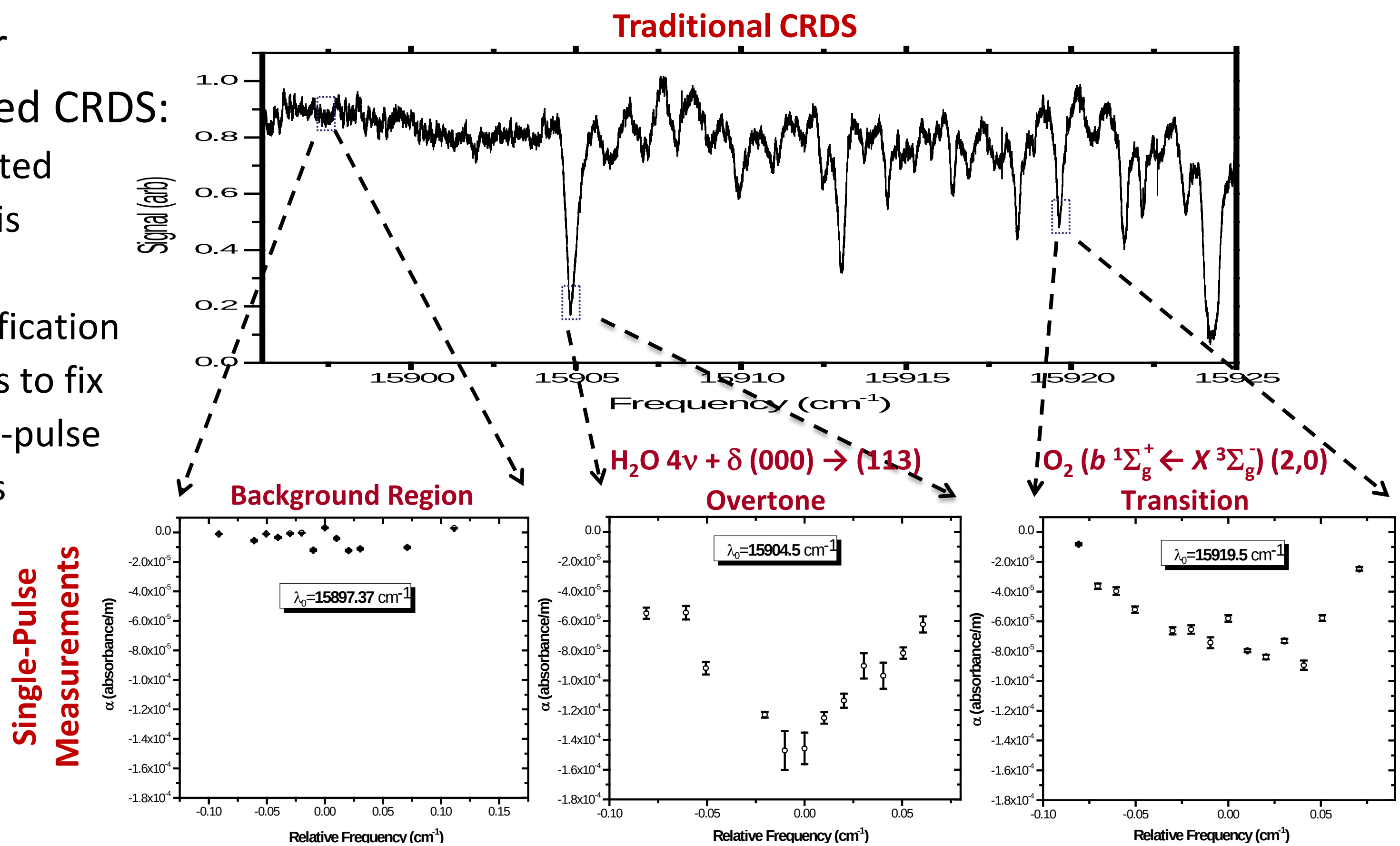
N_{BF} in non-overlapped region: 625

Non-overlapped spectral width: 6.25 cm^{-1} (0.25 nm)

Fit decay signal to: $I(t) = I_0 \exp[-t\,(1/\tau + \alpha c)]$

Absorption Spectra

- Traditional, laser bandwidth-limited CRDS:
  - Collect integrated signal as laser is scanned
  - Enabled identification of wavelengths to fix laser for single-pulse measurements



- Excellent agreement between observed spectra taken w/dual-etalon, frequency-comb spectrometer and that from the lower-resolution conventional CRDS method

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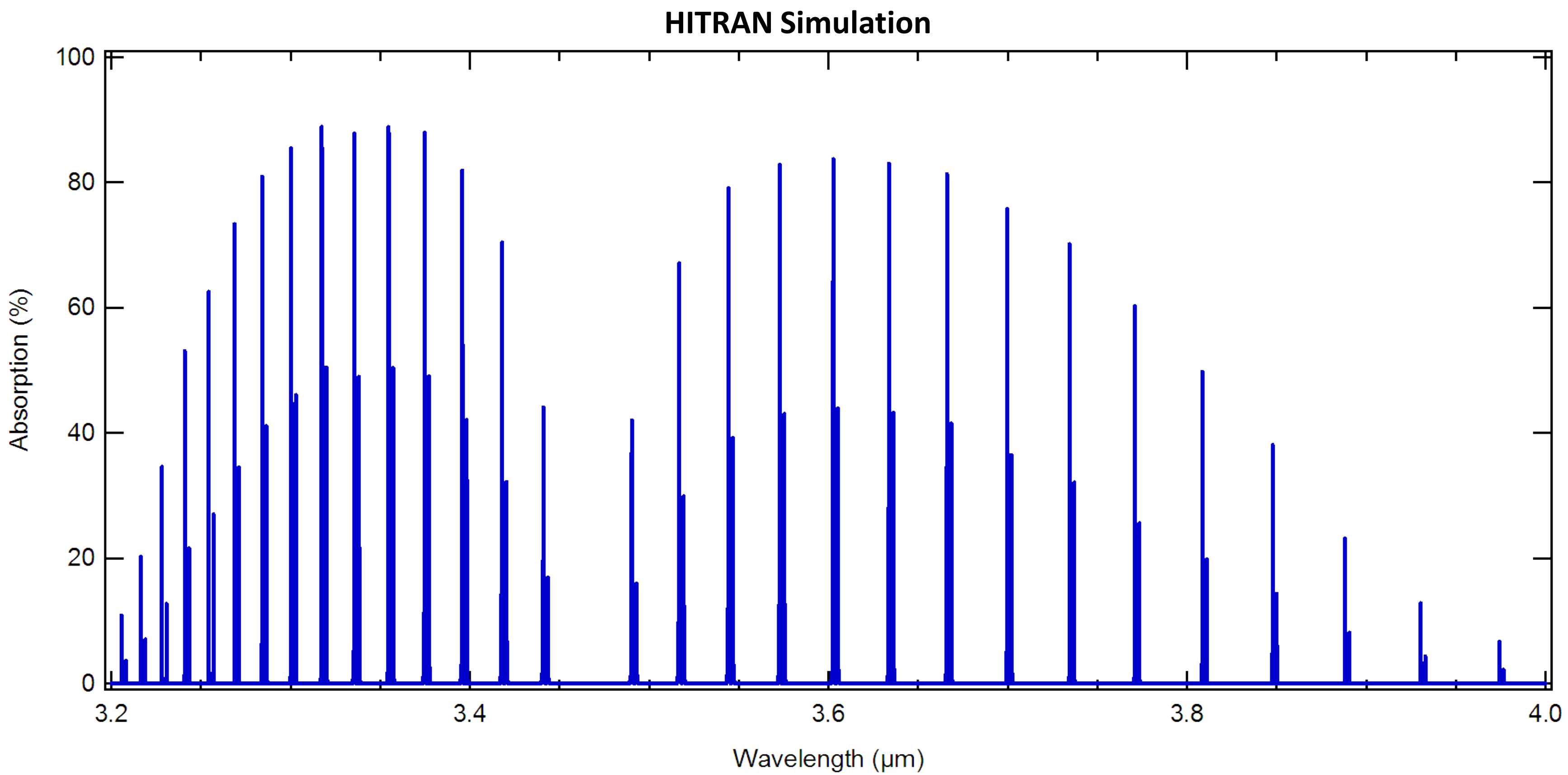
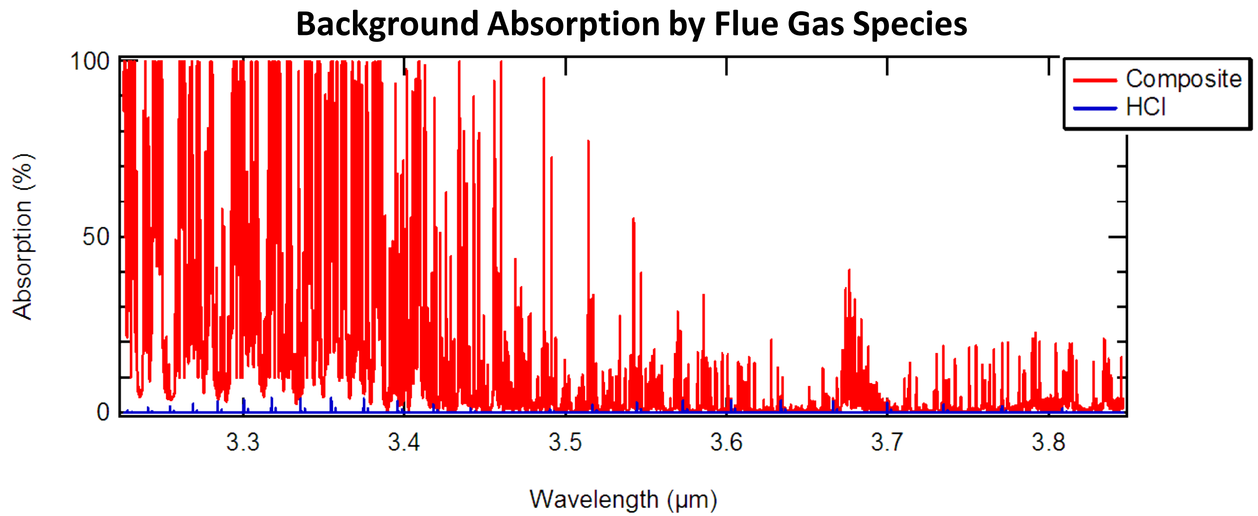
HCl Spectroscopy

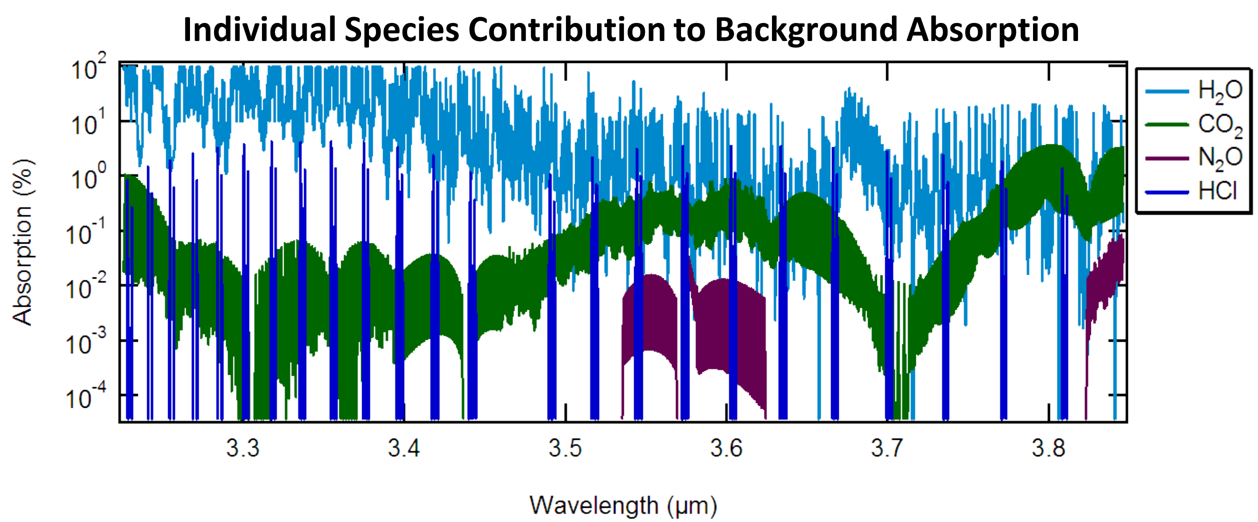
- Strong absorption features spanning 3.2-3.8 μm
- Simple, well-resolved spectrum



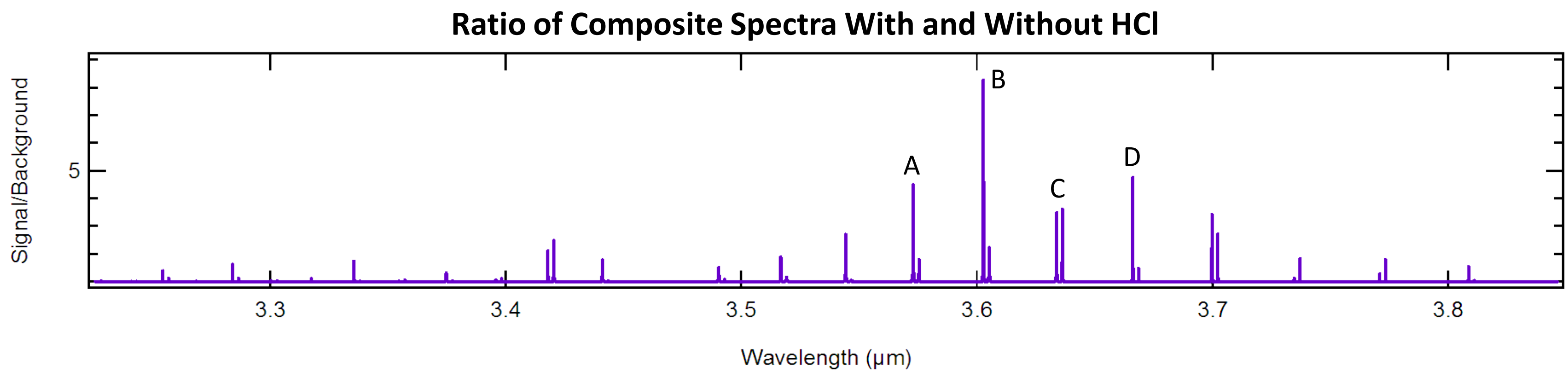
Non-Negligible Background Absorption

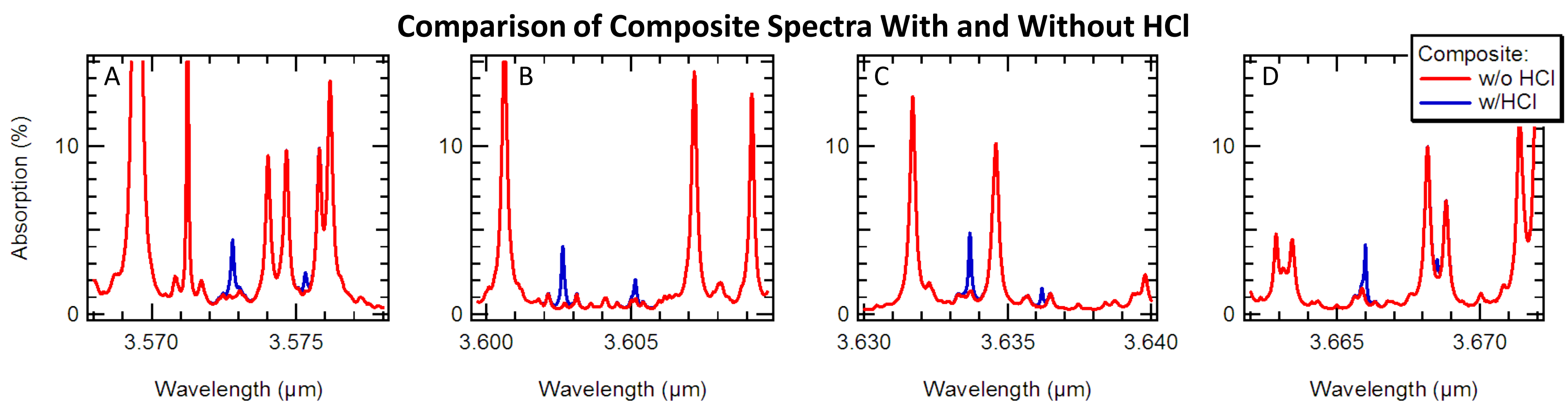
- HITRAN simulation assumptions:
  - Primary gas components: 6% H_2O, 4% O_2, 14% CO_2, 76% N_2
  - HCl concentration: 0.1 ppm
  - Additional species included (ex. SO_2, NO, NO_2)
  - Temperature: 200 °C
  - Path length: 100 m
- Primary background absorption from H_2O, and to a lesser extent CO_2





Discernible HCl Features Above Background





- With high-resolution spectrometer expect to be able to discern HCl above background

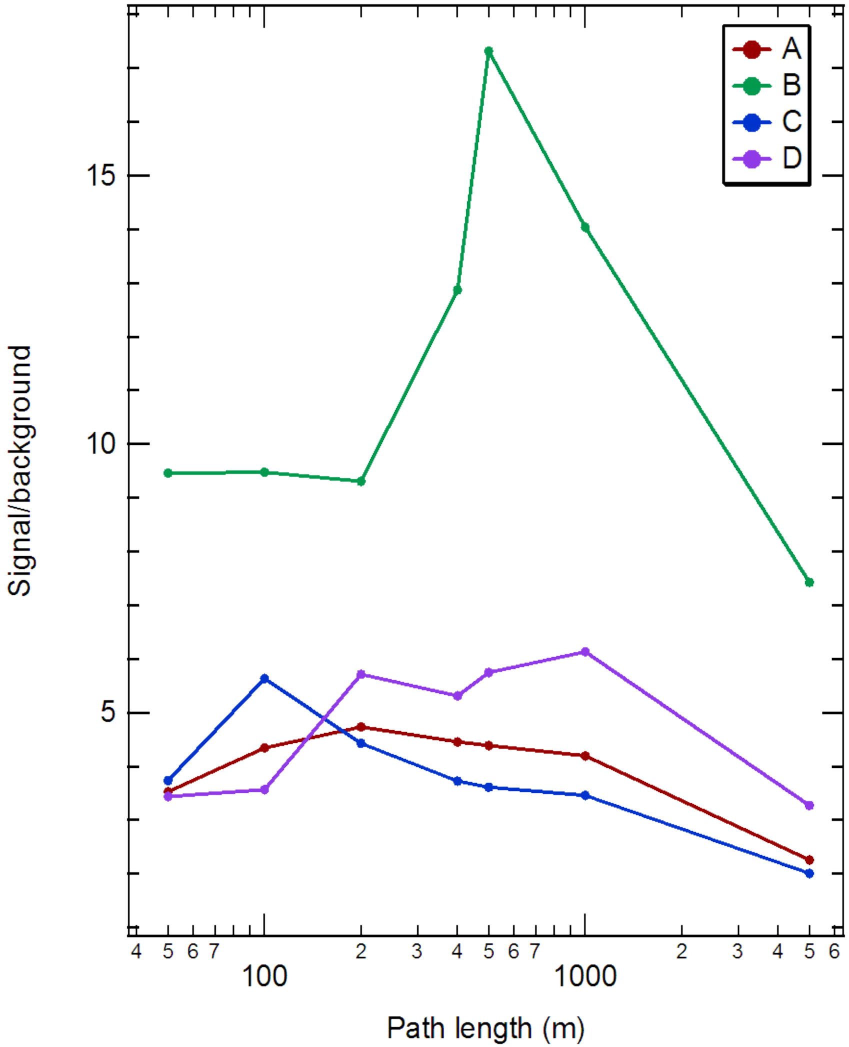
Absorption Path Length and Spectral Resolution

- Increased path length → greater absorption
- Increased ring-down time/cavity decay constant associated with a longer path length → higher resolving power in FFT
- Calculate spectral resolution assuming:
  - FSR: 150 MHz → maximum spectral resolution: 0.005 cm^{-1}
  - ΔFSR: 100 kHz
  - Path length-limited spectral resolution = (FFT resolution) x $\underbrace{(FSR / \Delta FSR)}_{\text{rf frequency} \rightarrow \text{wavelength conversion}}$

Path Length (m)	Ring-down time (μs)	FFT Resolution (MHz)	Spectral Resolution (cm^{-1})	Spectral Resolution Limitation
50	0.17	6.0	0.3	path length
500	1.7	0.6	0.03	path length
5000	17	0.06	0.005	etalon FSR

Absorption Path Length vs. HCl Signal/Background

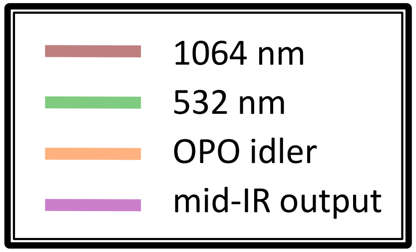
- Simulate absorption spectra with and without HCl for calculated spectral resolutions
- Increasing path length/increasing spectral resolution:
  - Initially improves ability to distinguish HCl features above background
  - At longer path lengths, background absorption dominates the spectra, lowering the signal/background ratio
- Feature B optimum path length
  - ~500 m (1.7-µs ring-down time)
  - Signal/background: ~17

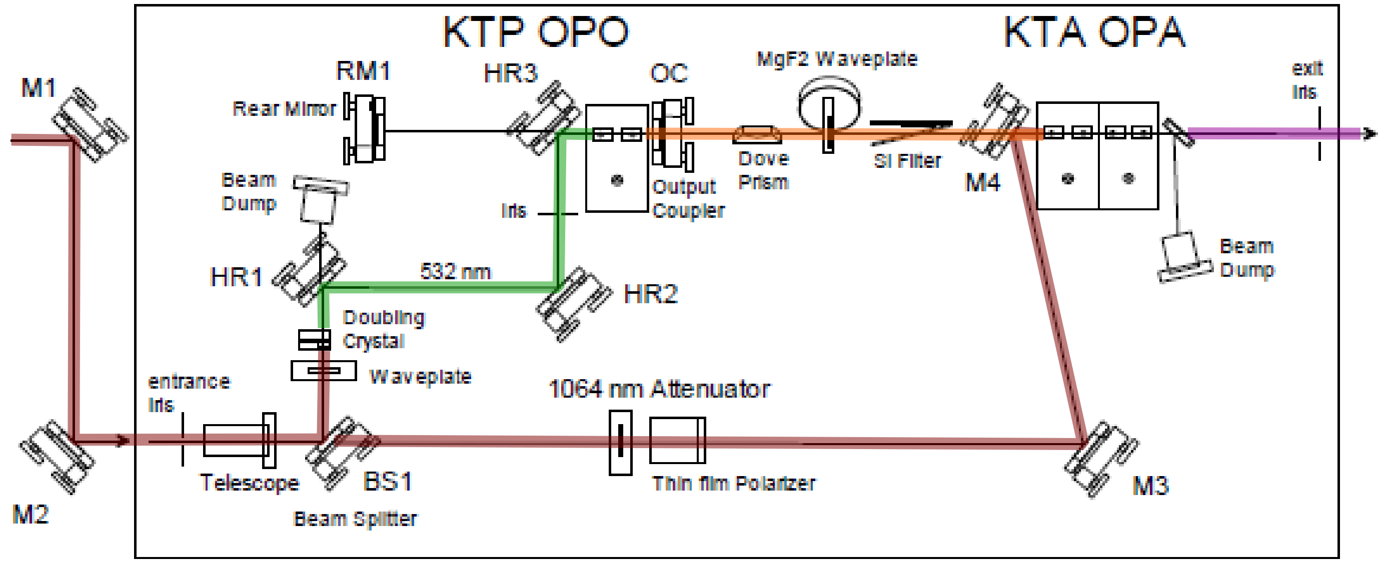


Experimental Setup – Laser Source

- Custom-built Nd:YAG-pumped OPO/OPA
- Pump laser: Continuum Surelite
  - Pulse energy: 500 mJ
  - Pulse width: 9 ns
  - Repetition rate: 10 Hz
- OPO/OPA
  - Measured pulse energy at 3.6 μm: 15 mJ
  - Bandwidth: estimate based on phase matching conditions
    - Seeded pump: 2 cm^{-1}
    - Unseeded pump: 19 cm^{-1}

Generation of 3.6 μm



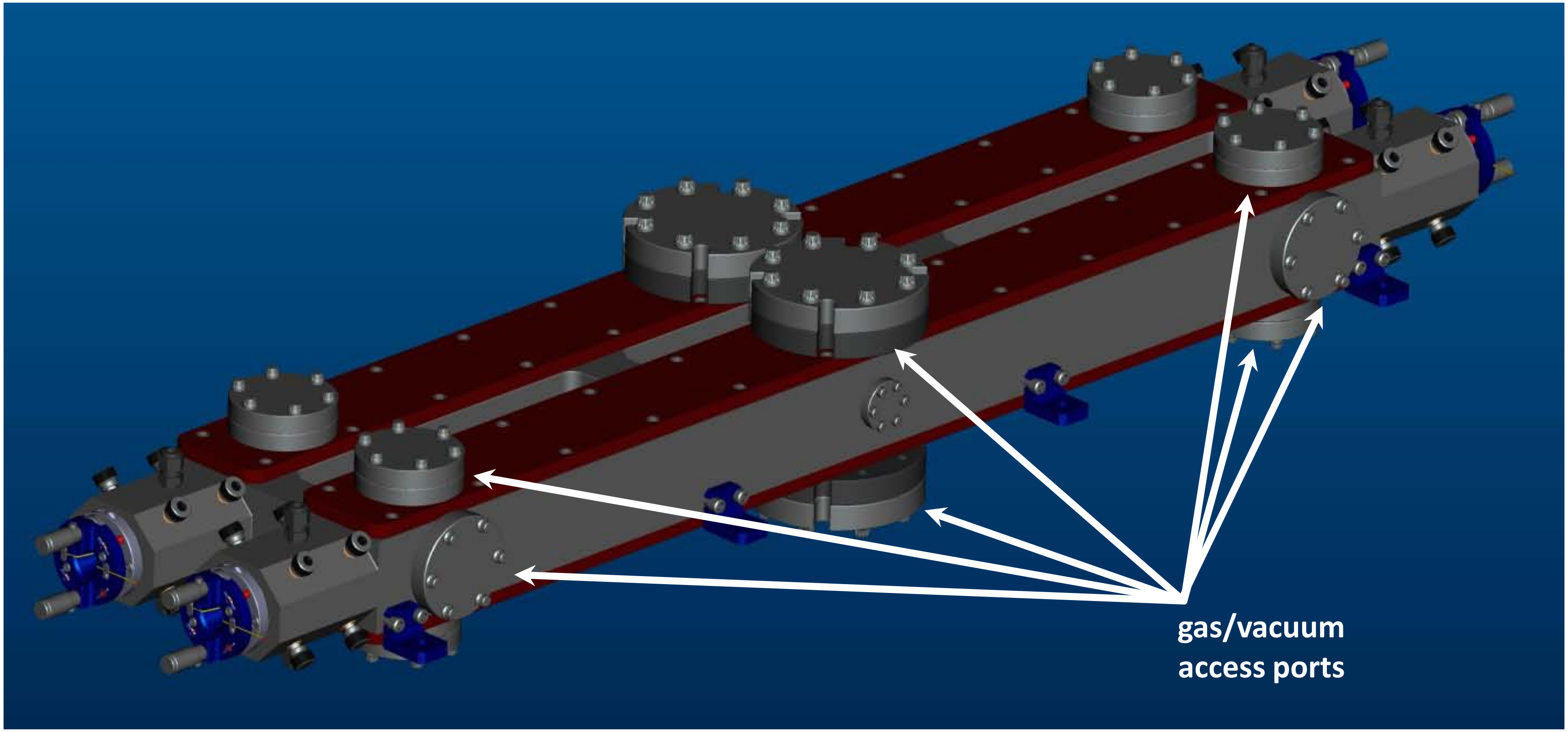


- OPO:
  - Pump λ: 532 nm
  - Crystal: KTP, type II phase matching
  - Output: tunable signal light over 710-885 nm
- OPA:
  - Pump λ: 1064 nm
  - Seed: idler from OPO
  - Crystals: KTA, type II phase matching, walk-off compensating geometry
  - Output: tunable mid-IR light over 1.35-5 μm via difference-frequency mixing

Experimental Setup – Monolithic Dual-Etalon Assembly

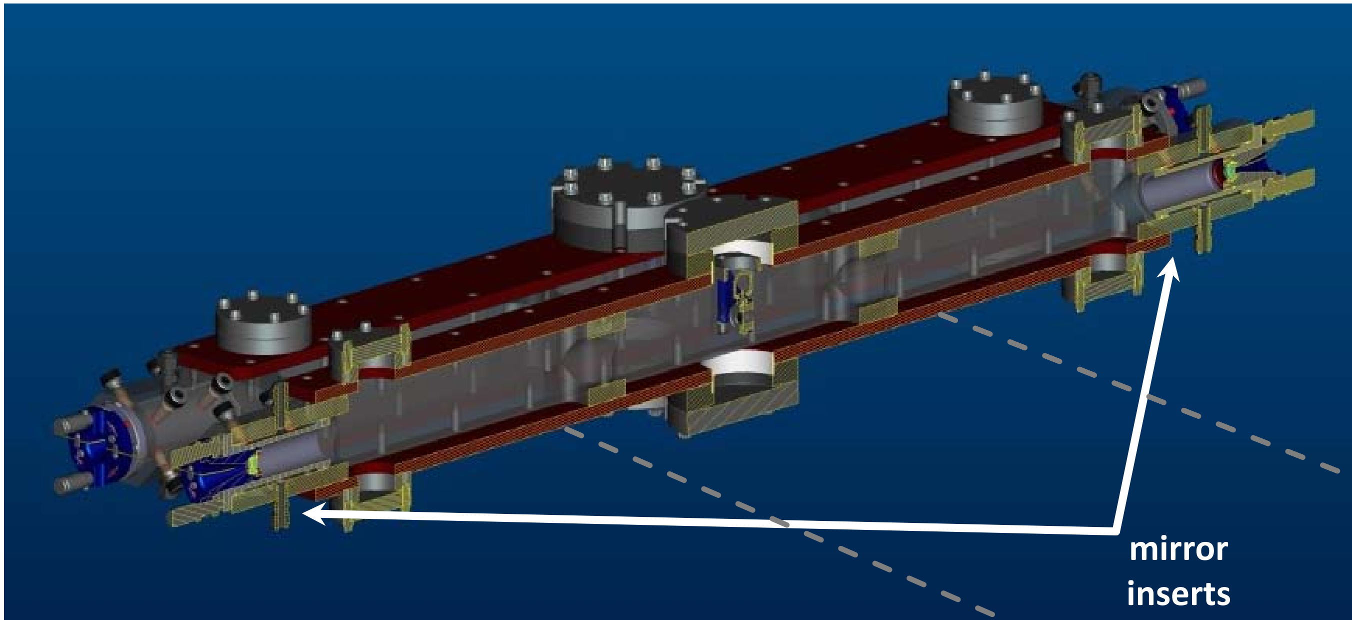
- Primary goals:
  - Minimize thermal variations between two cavities, which adds considerable complexity to the data analysis and increases measurement uncertainty
  - Independent adjustment of cavity mirrors to enable precise alignment, ensuring maximum ring-down times
- Additional features:
  - Multiple gas/vacuum access points
  - HCl-resistance
  - Stable, rugged unit
- Cavity length: 1 m
  - FSR: 150 MHz
  - Spectral resolution limit: 0.005 cm^{-1}

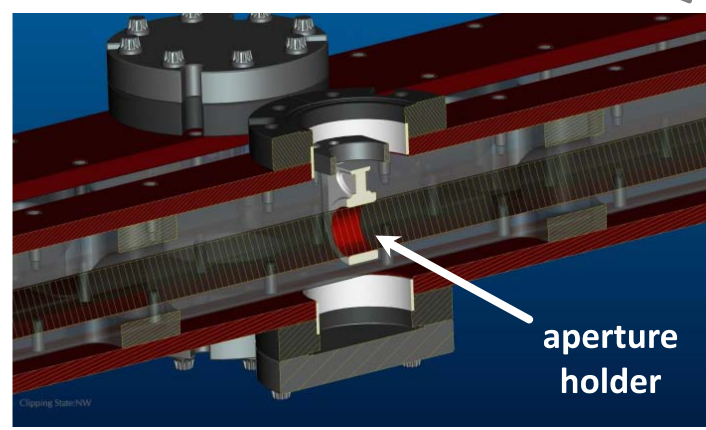
Design



- Two etalon cavities thermally coupled
- Multiple conflat flanges for gas/vacuum line access
- 0.5”-diameter cavity mirrors contained within an adjustable insert

Design – Cut-Away Views

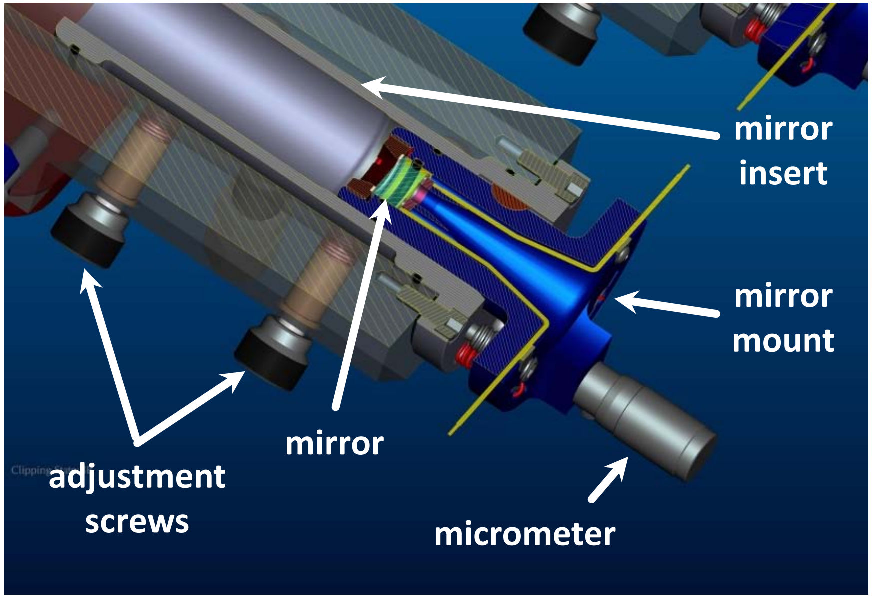




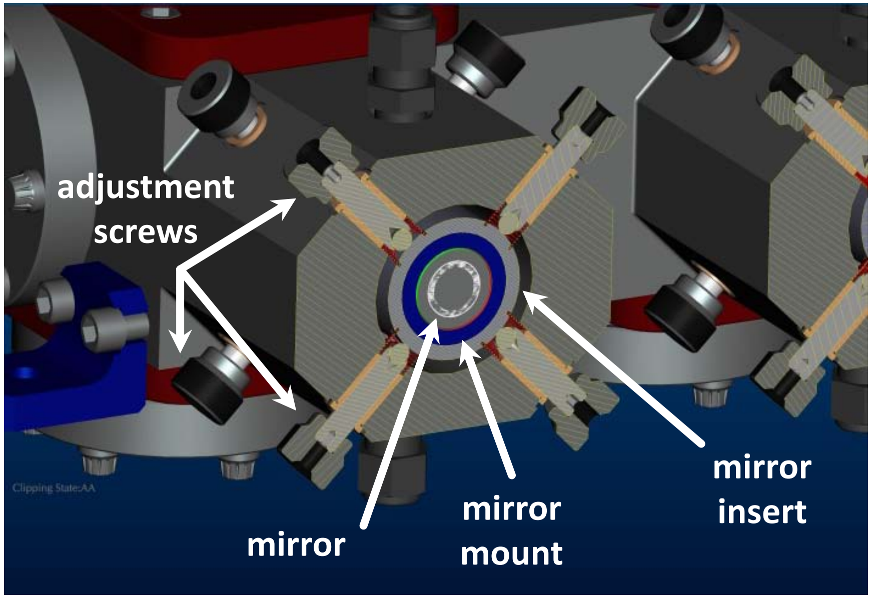
- Concentric cavity arrangement:
  - Fundamental mode of the cavity focuses tightly at the cavity center for both path directions
  - Aperture incorporated at this focus will reduce contribution of higher order modes to the observed signal → reduction in data uncertainty

Design – Mirror Insert

Top View



End View

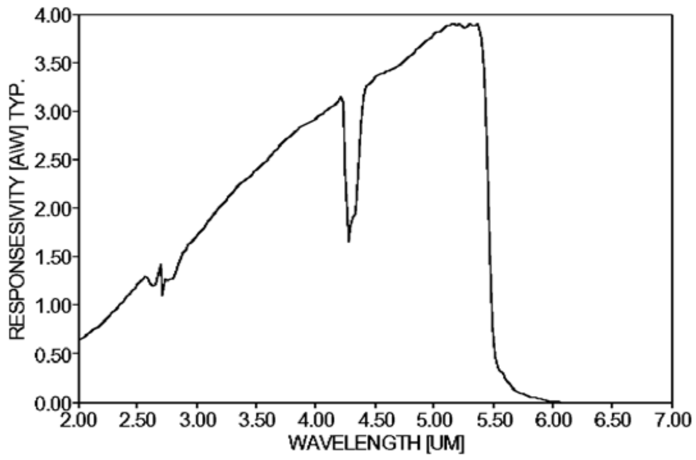


- Mirrors mount housed within an insert
- Mirror insert can be translated and angled slightly within cavity bore via adjustment screws
- Micrometer provides additional tip/tilt control of the mirror mount within the insert

Experimental Setup – Additional Key Components

- Cavity mirrors
  - Concentric configuration: 0.5-m radius of curvature
  - Confocal configuration: 1-m radius of curvature
  - Reflectivity: 99.98%
- Fluoride glass fiber
  - Transmission range: 0.3-4.5 μm
  - Typical loss: <0.2 dB/m at 3.6 μm
- Detector: InSb photodiode
  - Rise time: 3 ns
  - Bandwidth: 120 MHz
  - Requires liquid N_2 cooling

Detector Responsivity Curve



Outline

- Motivation
- Dual-etalon, frequency-comb cavity ring-down spectrometer
- Proof-of-principle experiments: H_2O, O_2
  - Setup I: broadband laser, low-resolution cavity
  - Setup II: narrowband laser, high-resolution cavity
- Application to HCl detection
  - HCl spectroscopy
  - Component selection and next-generation dual-etalon spectrometer design
- Summary and next steps

Summary

- Dual-etalon, frequency-comb cavity ring-down spectrometer is being developed at Sandia to generate a broad-bandwidth, high-resolution spectrum with the sensitivity of CRDS in a single laser pulse
  - Width of single-shot spectrum determined by laser bandwidth
  - Maximum spectral resolution set by etalon FSR, not laser linewidth
- The feasibility of this spectroscopic detection approach has been demonstrated with air
  - Developed data analysis tools
  - Lessons learned from initial proof-of-principle experiments incorporated in design of next-generation dual-etalon assembly
- Components for application to HCl detection at 3.6 μm have been obtained

Next Steps

- FY12
  - Assemble spectrometer for HCl detection
  - Evaluate HCl spectral signature
  - Quantify HCl detection sensitivity
  - Evaluate impact of primary flue gas constituents and potential spectroscopic interference species
- FY13-14
  - Couple dual-etalon, frequency-comb cavity ring-down spectrometer with flue gas from laboratory scale burner
  - Design and assemble a portable system

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