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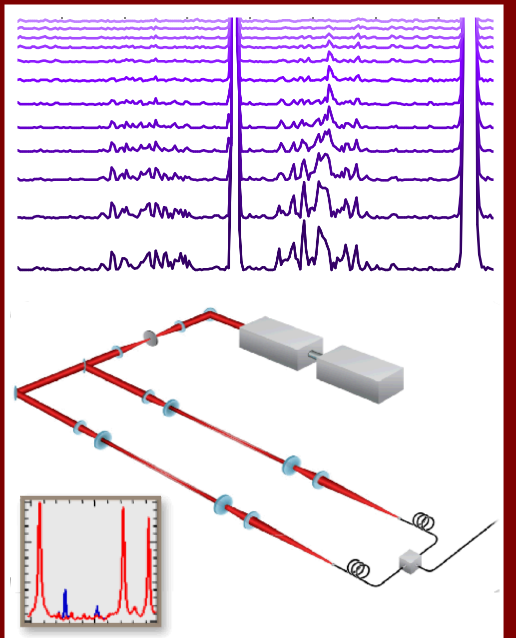
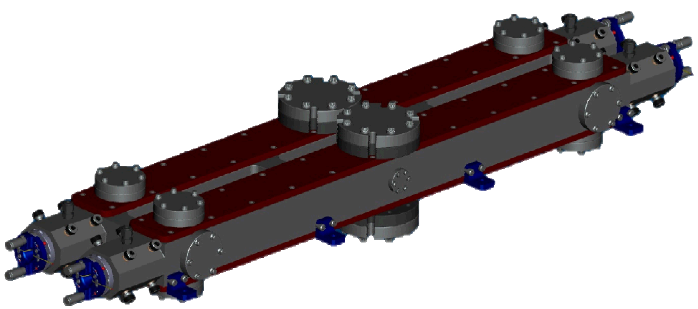


Laser-Based Detection of Trace-Level Contaminants

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

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



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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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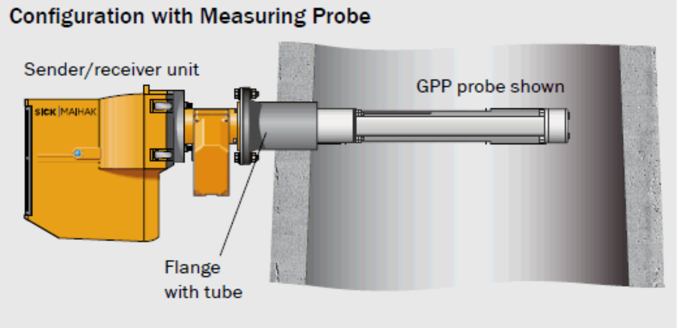
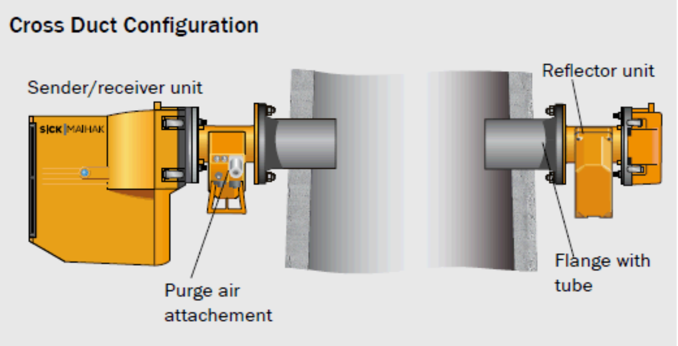
Motivation

- 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)

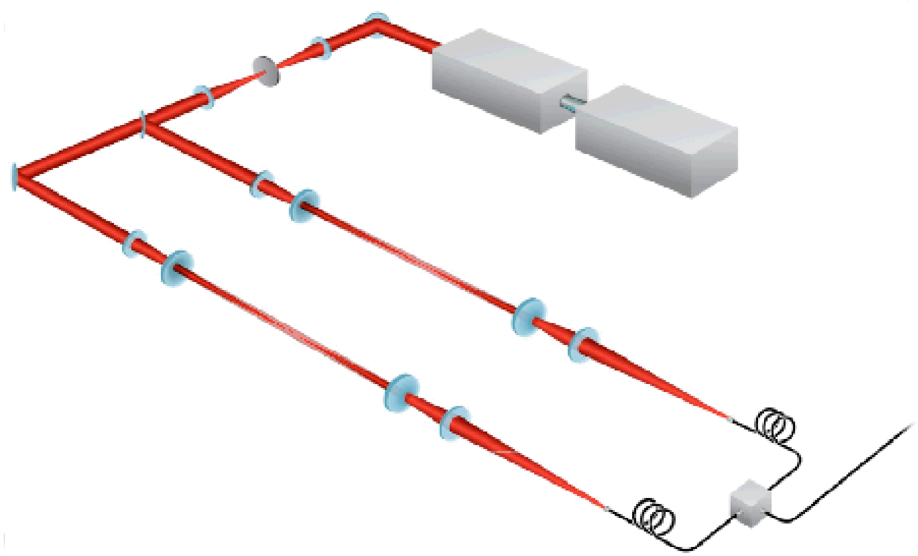
- Principles of operation:
  - Laser pulse is injected into a high finesse cavity and the decay of light intensity, I(t), leaked out of the cavity is monitored:

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

  - 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

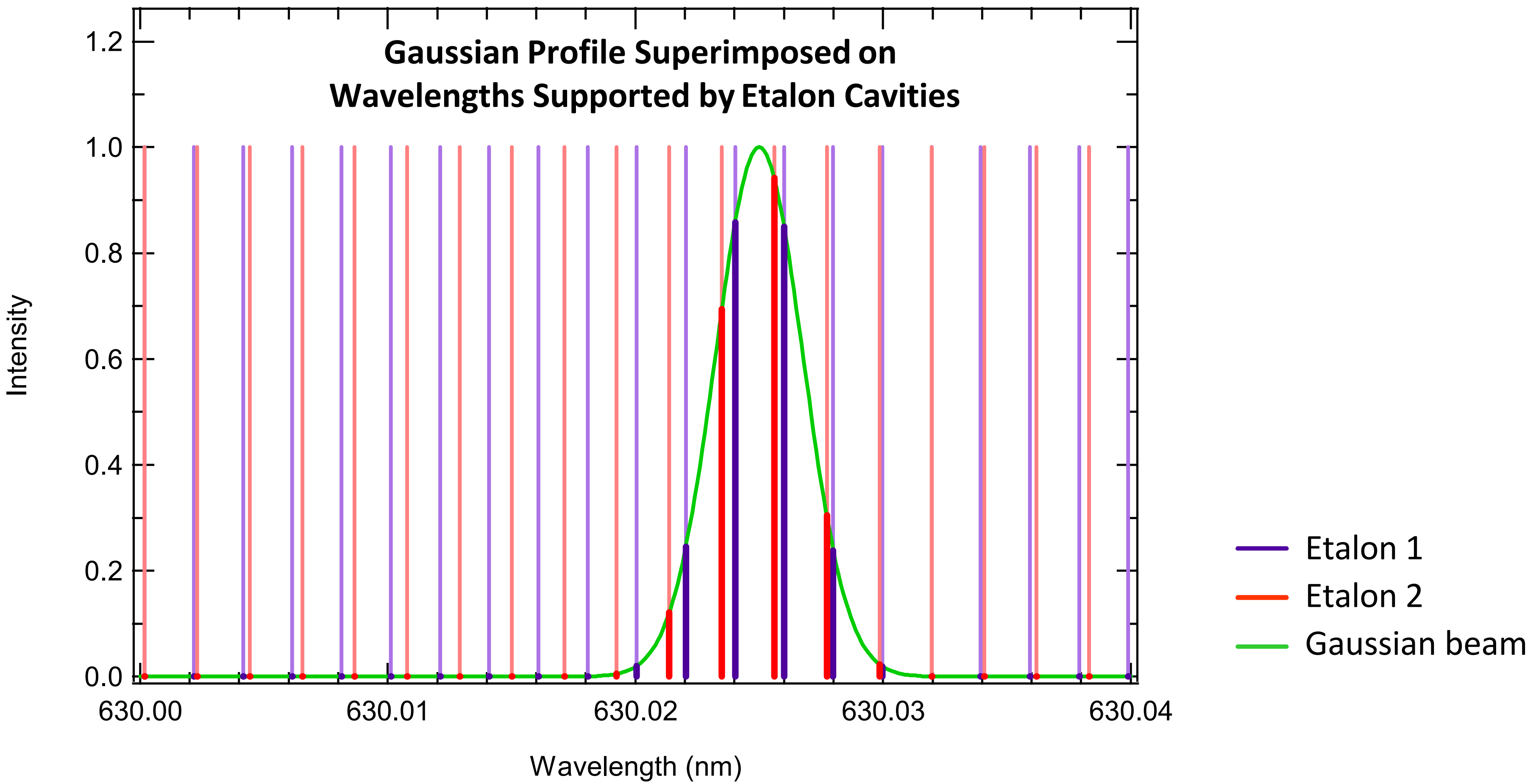
- New technique* recently developed at Sandia to generate a broad-bandwidth, high-resolution spectrum with the sensitivity of CRDS in a single laser pulse
- Broad bandwidth laser beam directed through two etalon cavities of slightly different lengths
- Output beams are two frequency combs with spacings 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

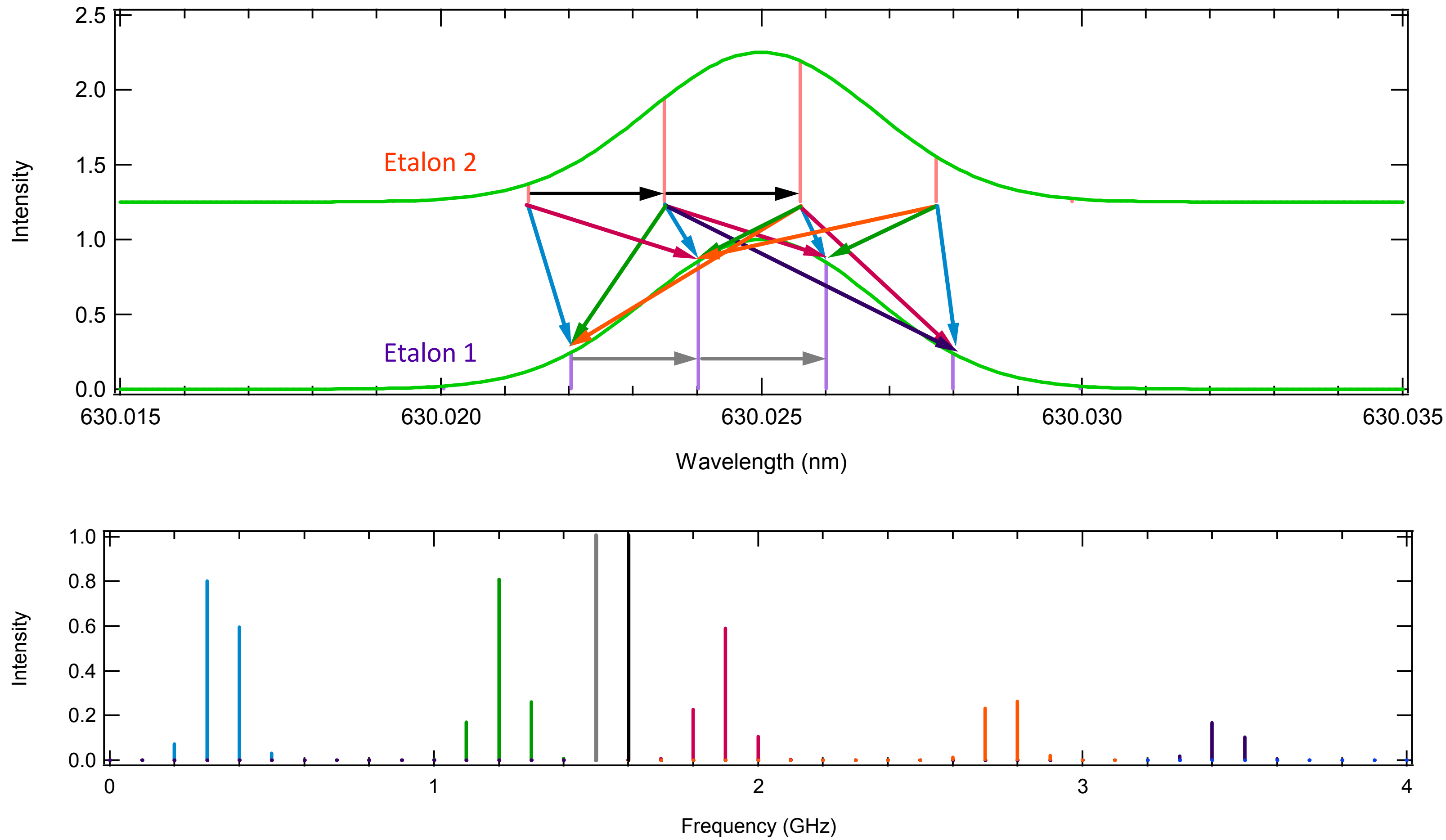
Simulated Etalon Output

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



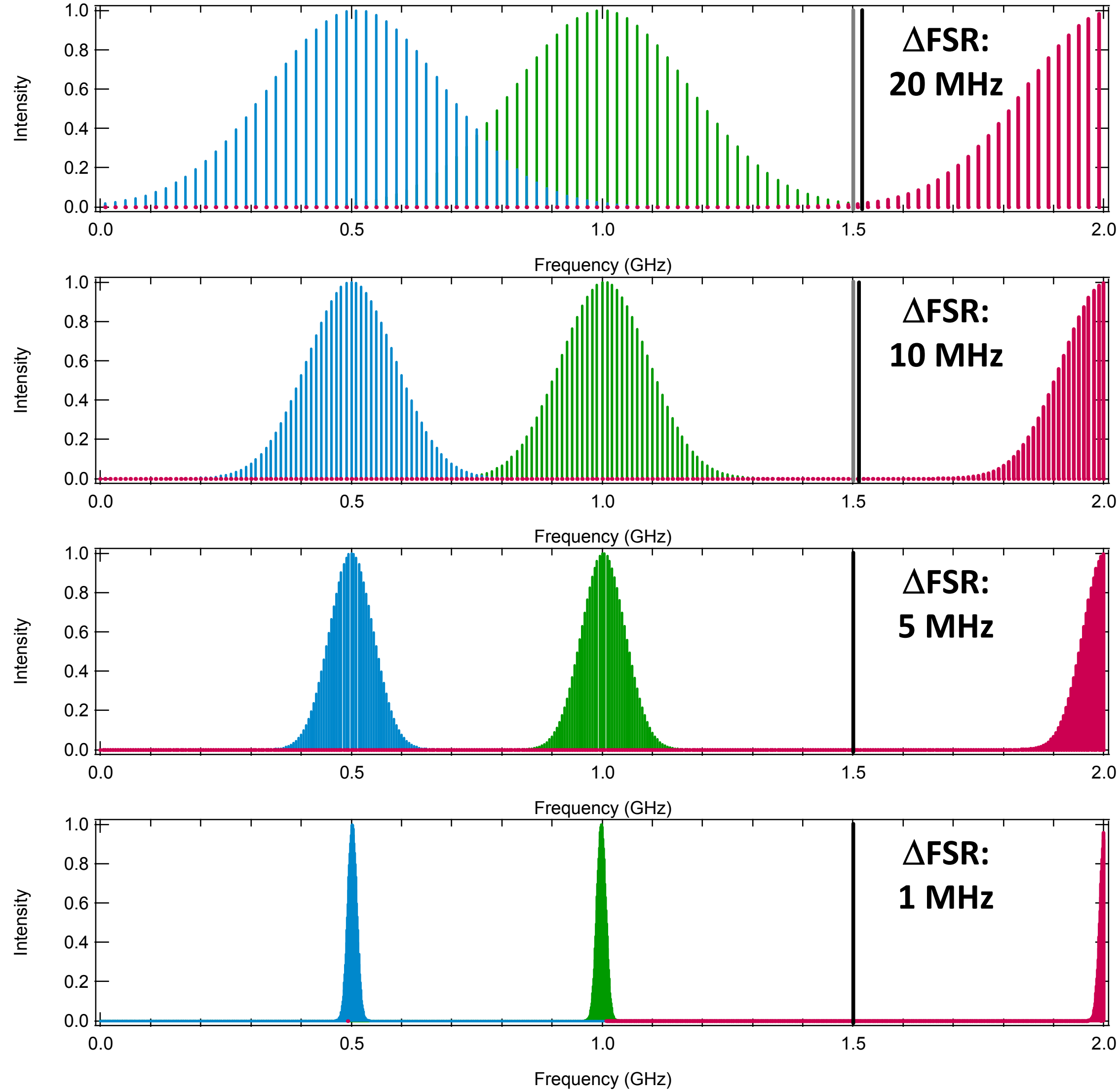
Generation of Beat Frequencies

- 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



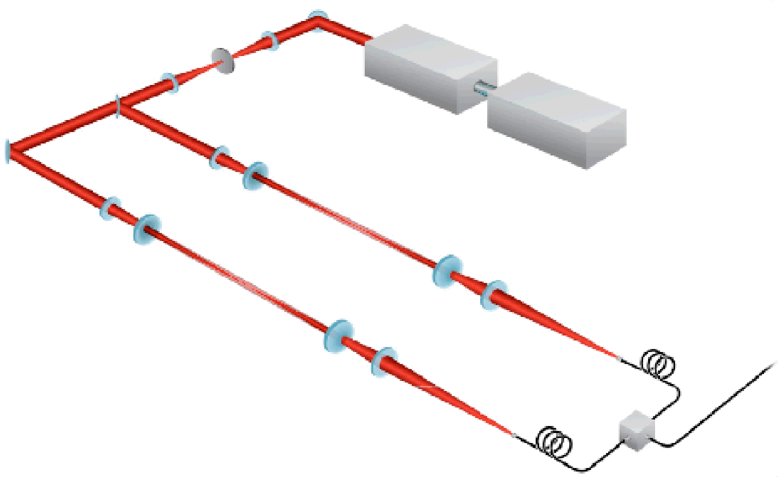
Impact of Etalon FSR Offset

- 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: $FSR \times N_{BF}$
  - N_{BF} : number of beat frequencies in non-overlapped region ($N_{BF} = 0.5\ FSR / \Delta FSR$)
- 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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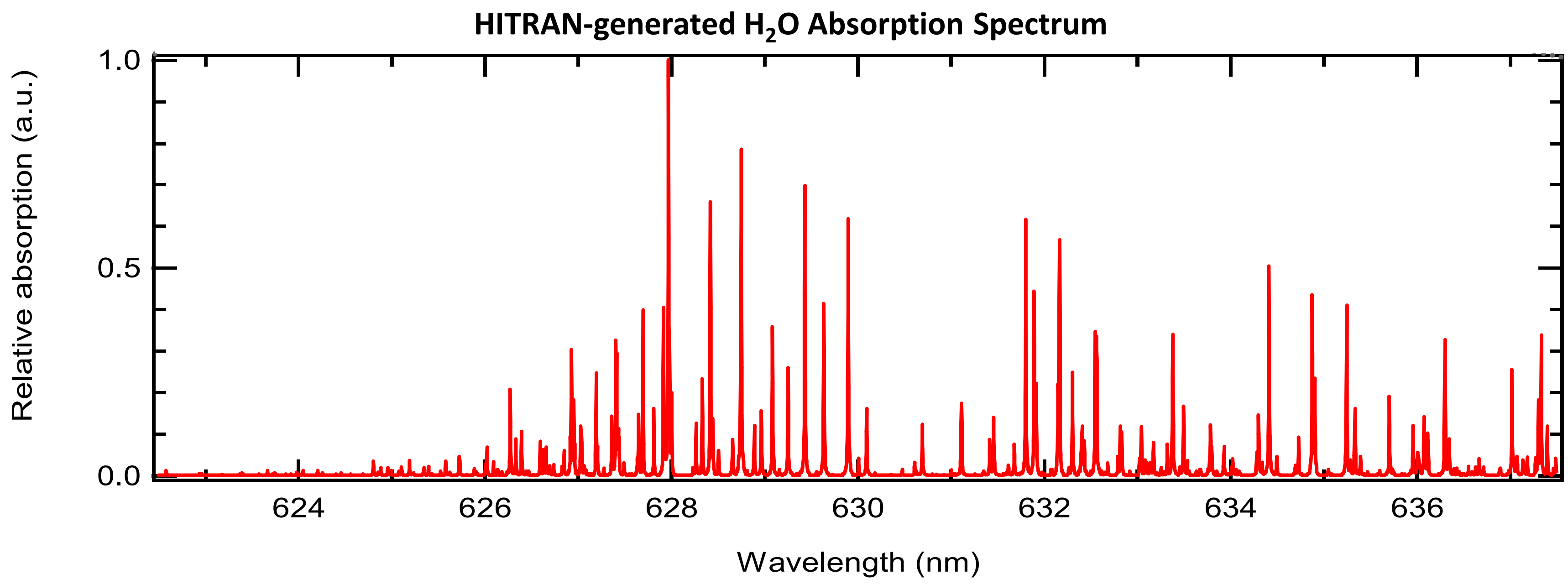
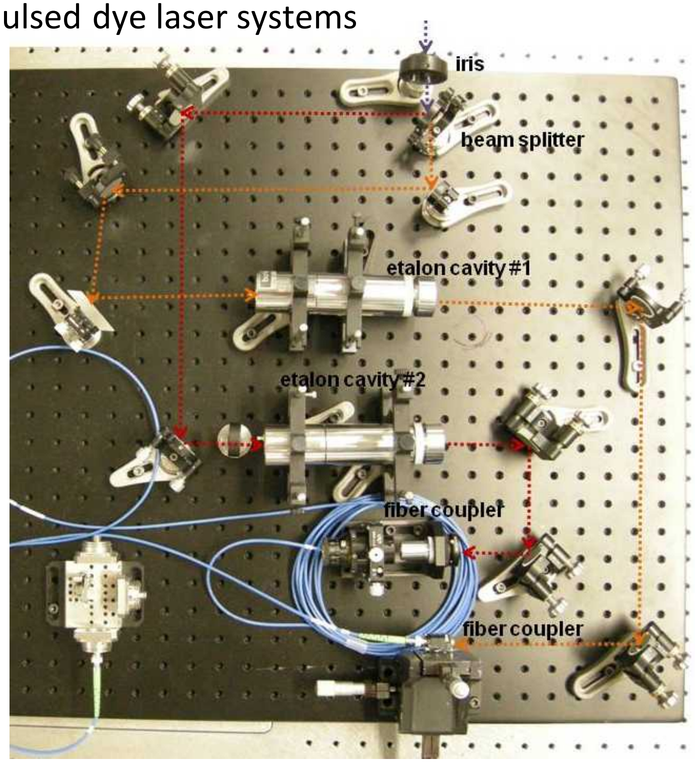
Proof-of-Principle Experiments

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



Experimental Setup I

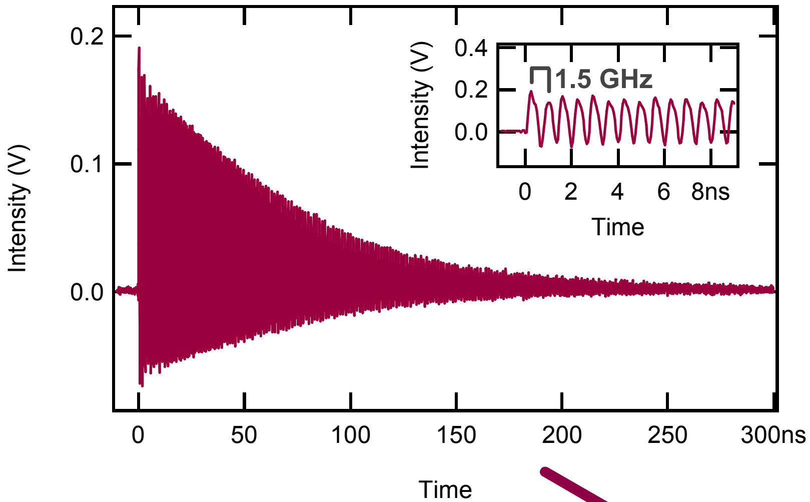
- Laser: amplified broadband dye laser w/DCM
  - Laser thought to lack longitudinal mode structure common in pulsed dye laser systems
  - Pulse energy: 10 mJ
  - Pulse width: 65 ps
  - Repetition rate: 20 Hz
  - Bandwidth: 15 nm



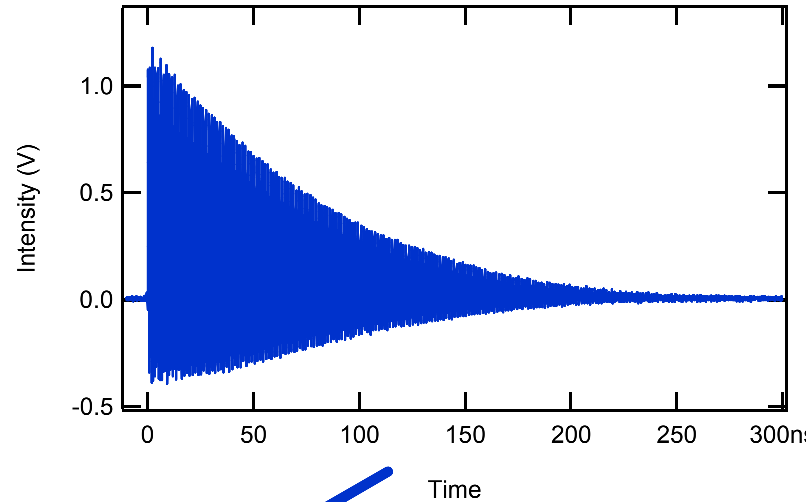
- Bandpass filter to prevent spectral overlap
  - 1 ± 0.2 nm FWHM
  - Center λ: 632.8 nm
  - Peak transmission: 50%
  - Out-of-band transmission (200-1100 nm): <0.01%
- Etalon cavities:
  - Length: 10 cm (1.5-GHz FSR)
  - Mirror reflectivity: >99.5%
  - Confocal configuration: beam collimated in forward 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

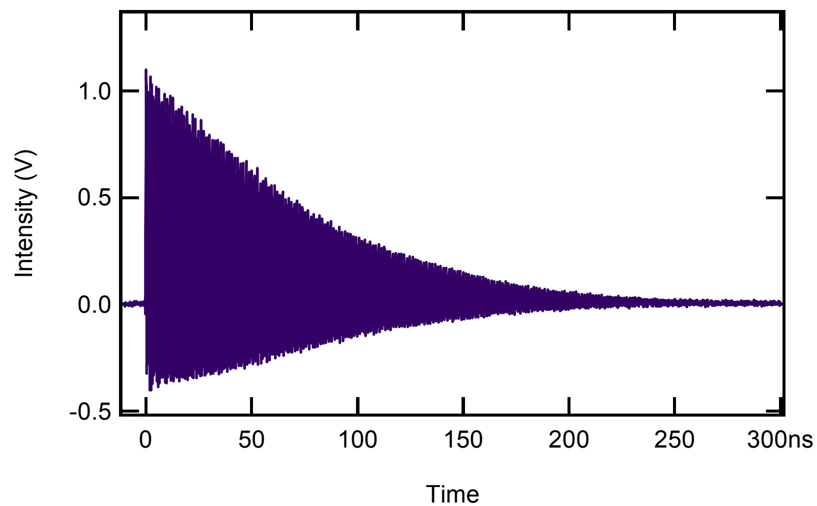
Cavity 1



Cavity 2



Both Cavities



FSR: 1.5 GHz

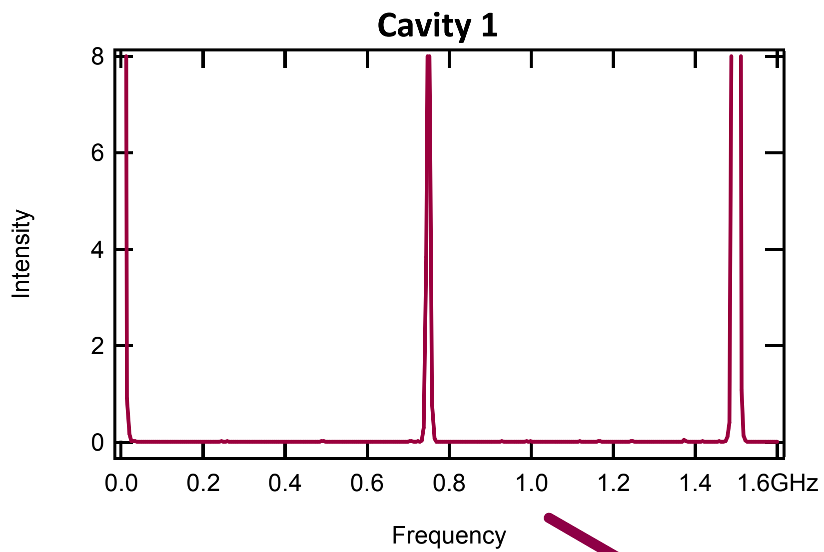
Fit ring-down decay to:

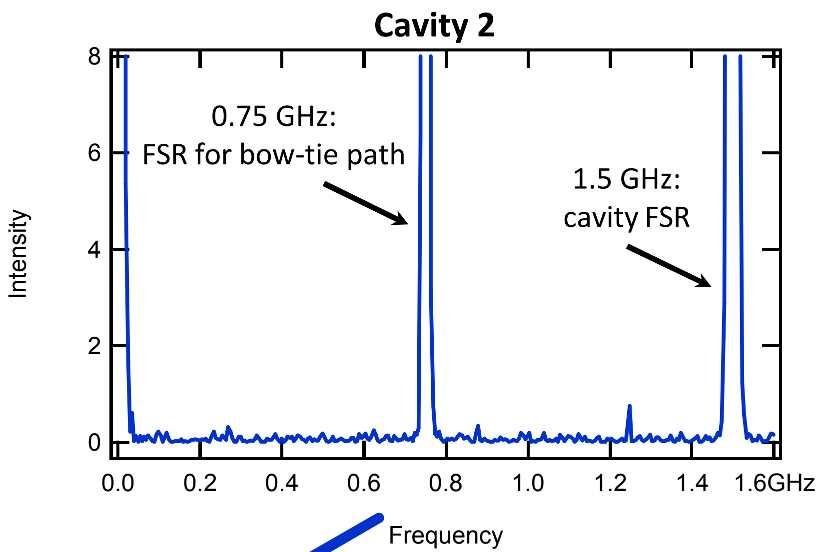
$I(t) = I_0 e^{-t/\tau}$

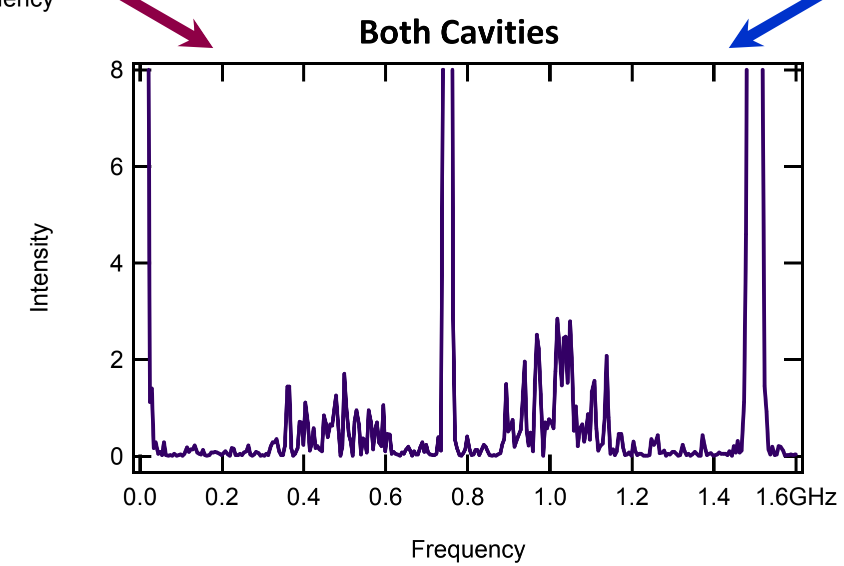
Cavity decay constant:

τ = 75 ns

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





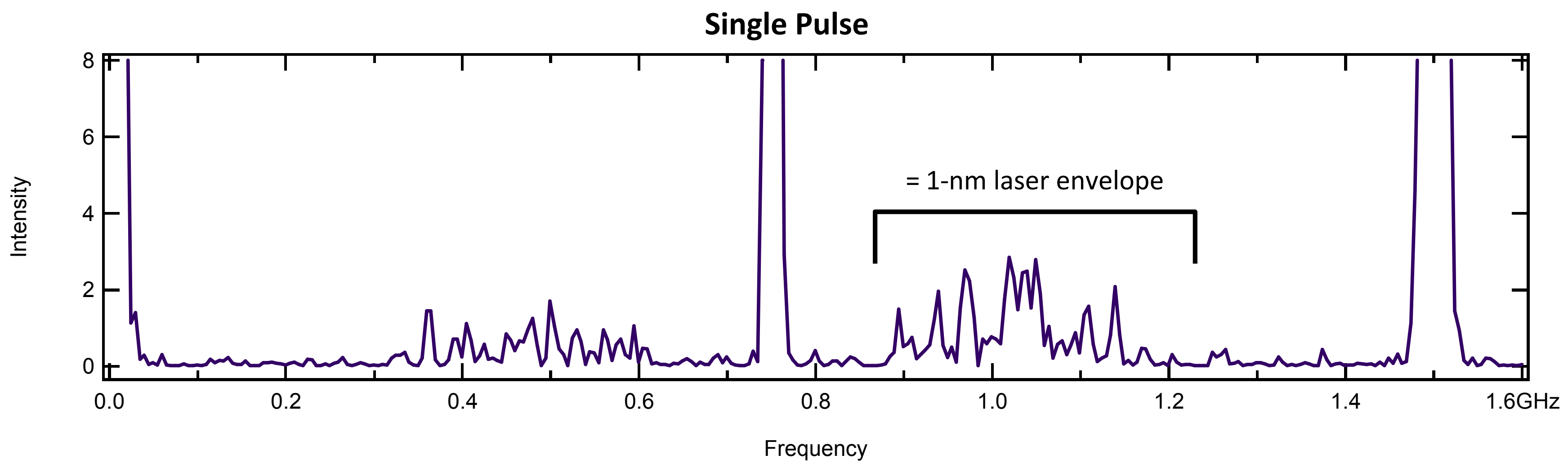


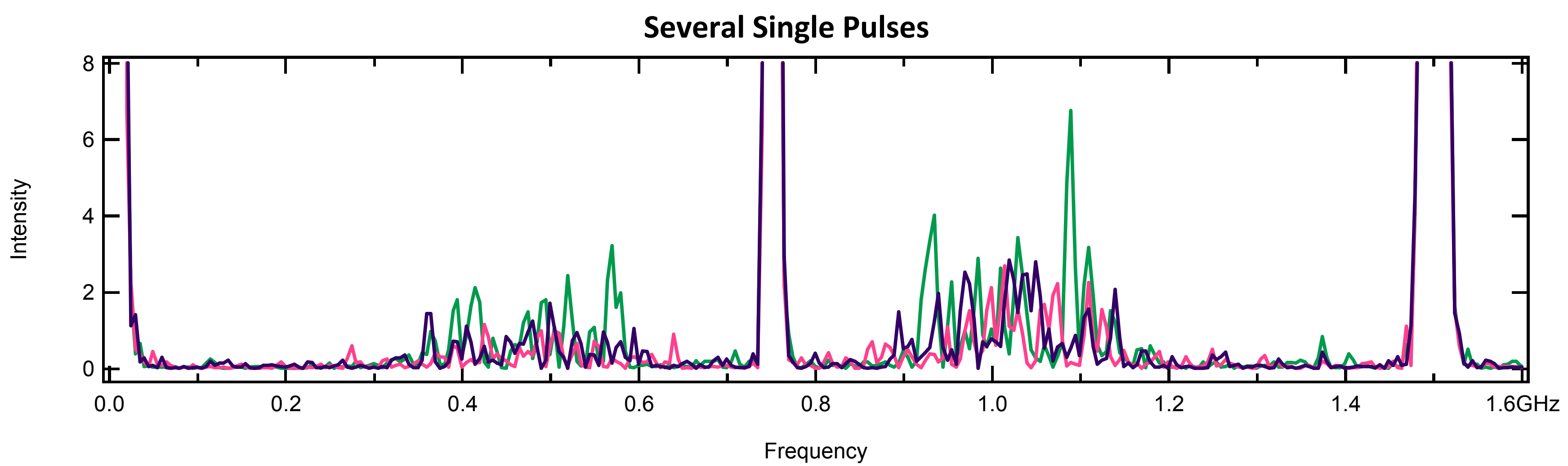
ΔFSR: 700 kHz

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

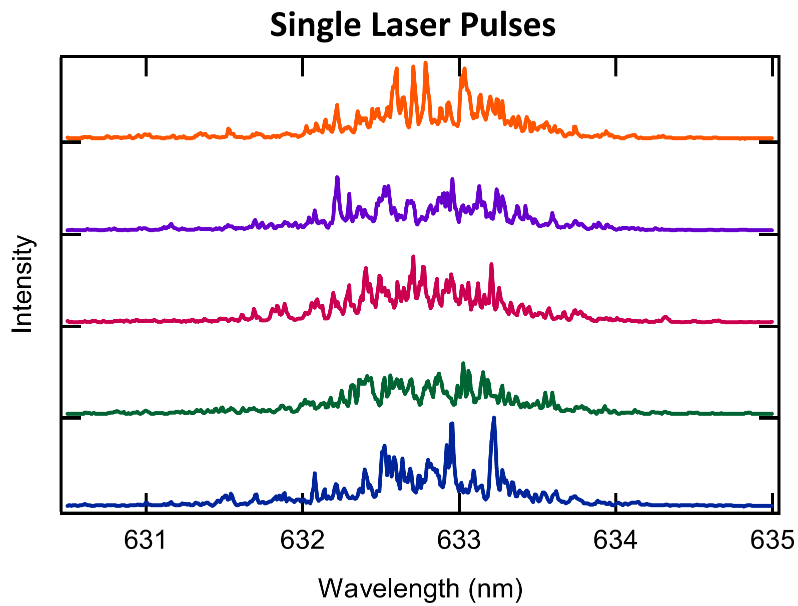
Non-overlapped spectral width: 53.6 cm^{-1} (2.15 nm)

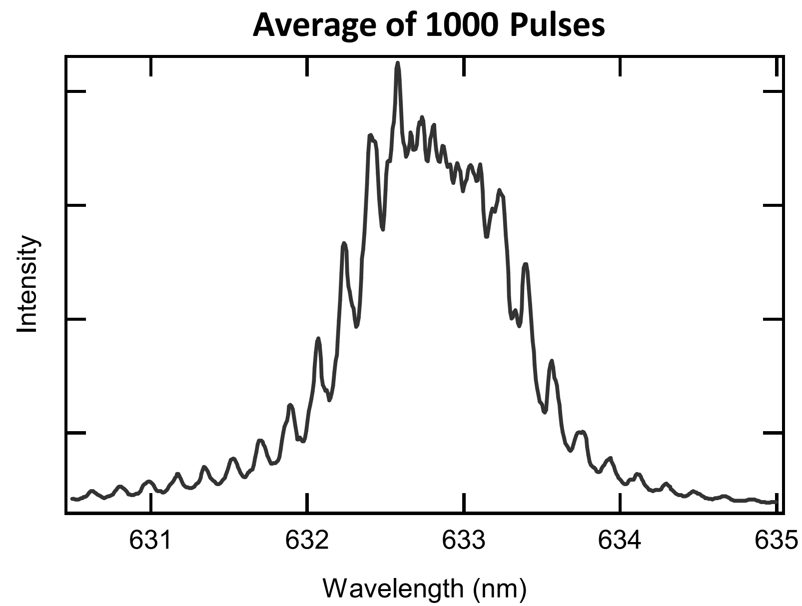
Variable, Structured Laser Intensity Profile





Laser Profile

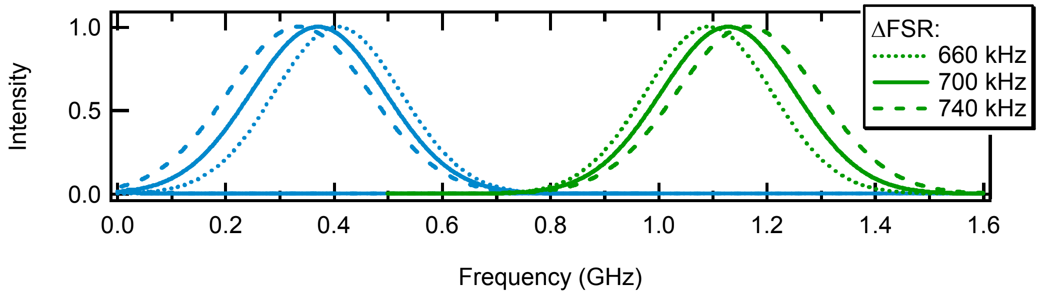




- Independently measure laser profile with 1-m spectrometer
- Confirmation that laser output has considerable structure and pulse-to-pulse variations
- Filtered laser profile:
  - Center λ: 632.8 nm
  - FWHM: 0.98 nm
  - $1/e^2$ full width: 2.0 nm

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:

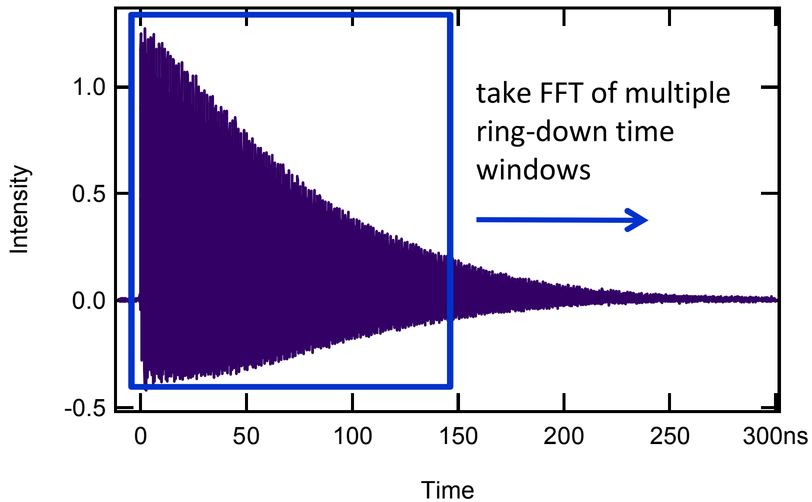


    - ±40 kHz in ΔFSR (±2.7 μm change in cavity length) causes shift of 36 MHz in Fourier transform (2.5 cm^{-1} shift in wavelength spectrum)

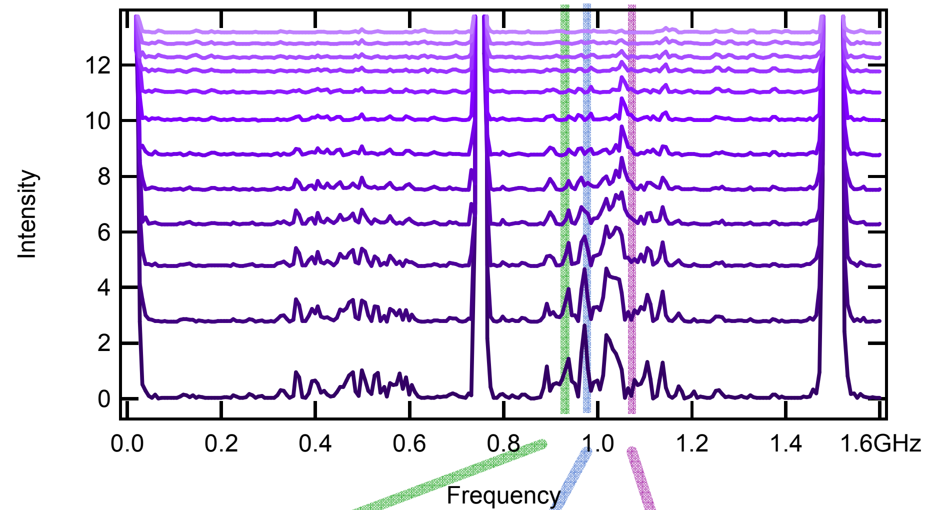
- Measure decay of individual beat frequencies in Fourier transform
  - Cavity ring-down signals independent of laser intensity
  - However, peaks may be missed if the laser power is too low

Examine Decay of Individual Beat Frequencies

Combined Ring-Down Signal



FFT of Ring-Down Sections



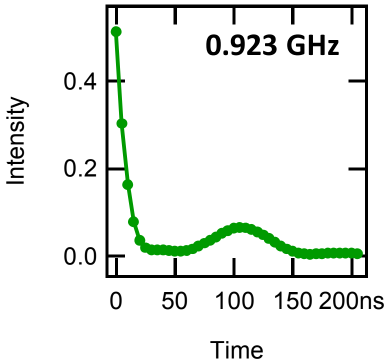
Decay of Individual Beat Frequencies

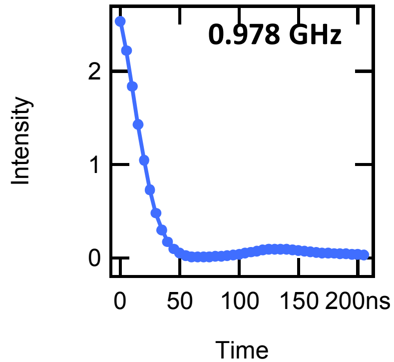
Fit decay signal to:

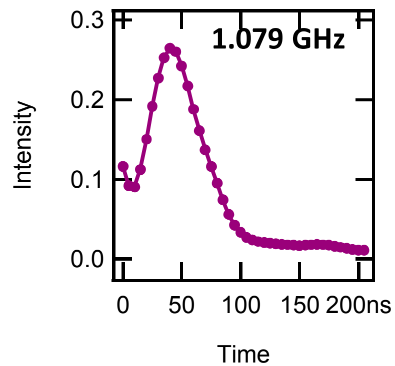
$$I(t) = I_0 \exp[-t\,(1/\tau + \alpha c)]$$

α: absorbance

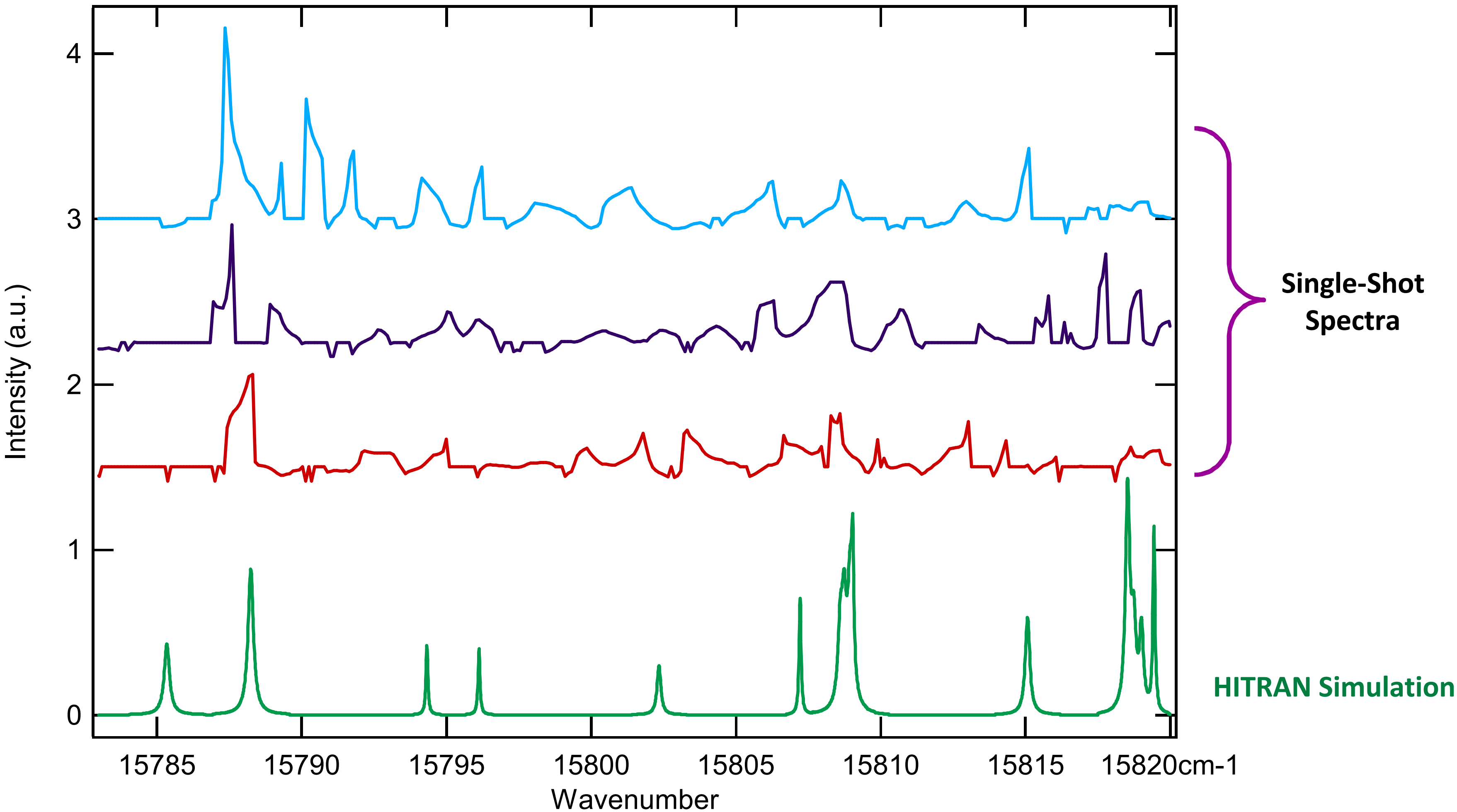
c: speed of light







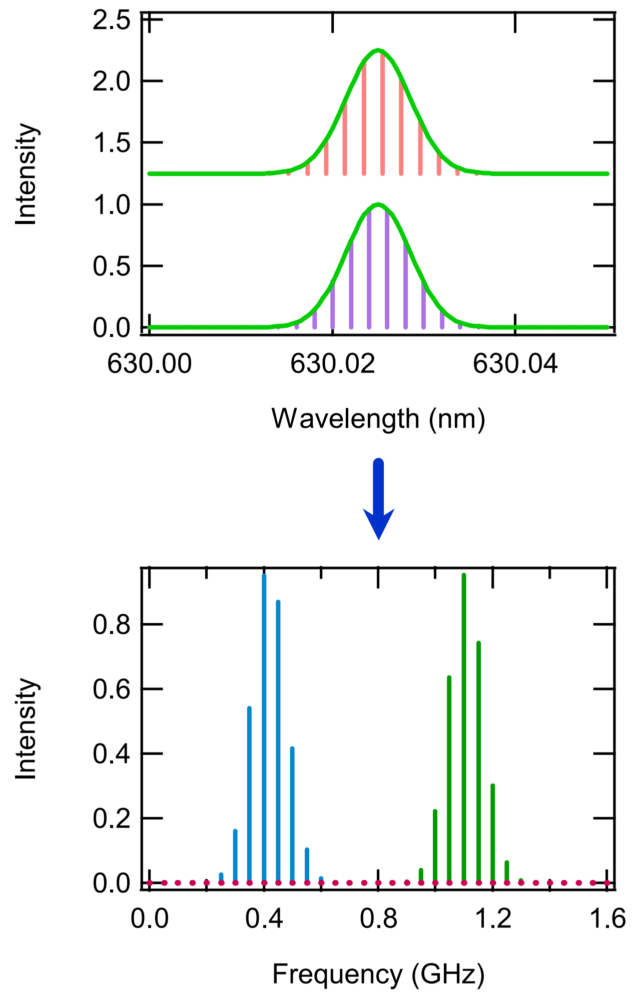
Absorption Spectra of Air



* 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

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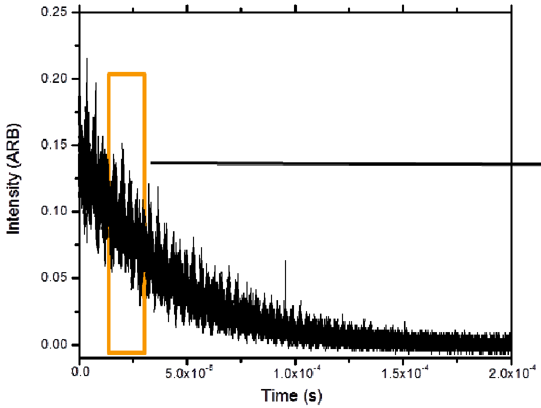
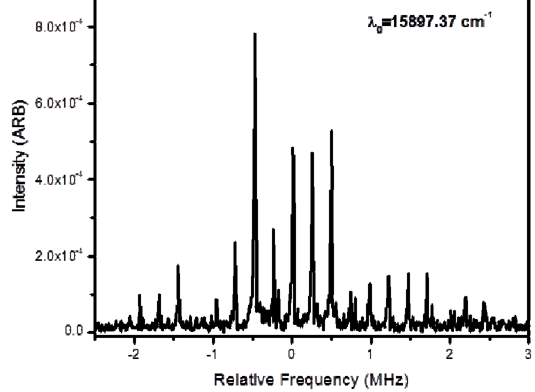
Combined Ring-Down Signal



FFT of Ring-Down Section



FSR: 300 MHz

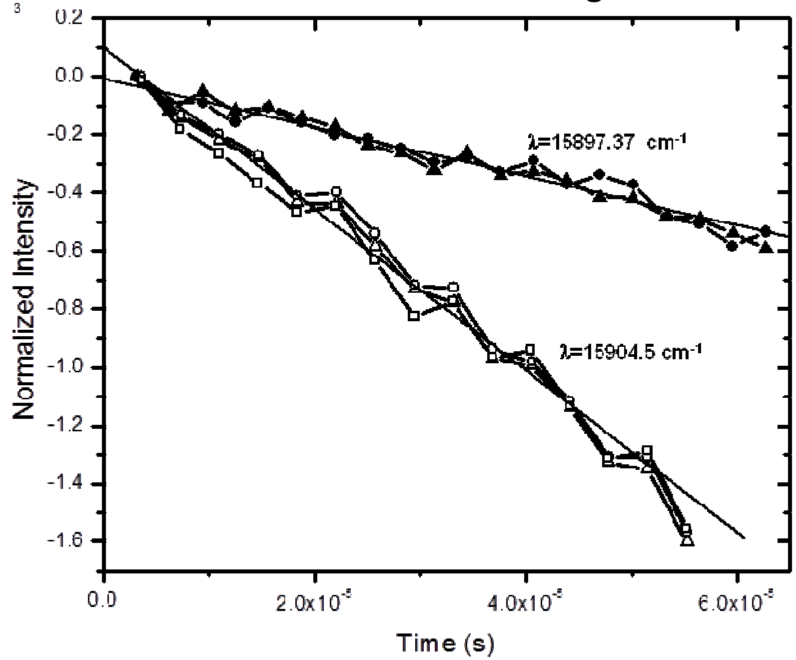
ΔFSR: 240 kHz

N_{BF} in non-overlapped region: 625

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

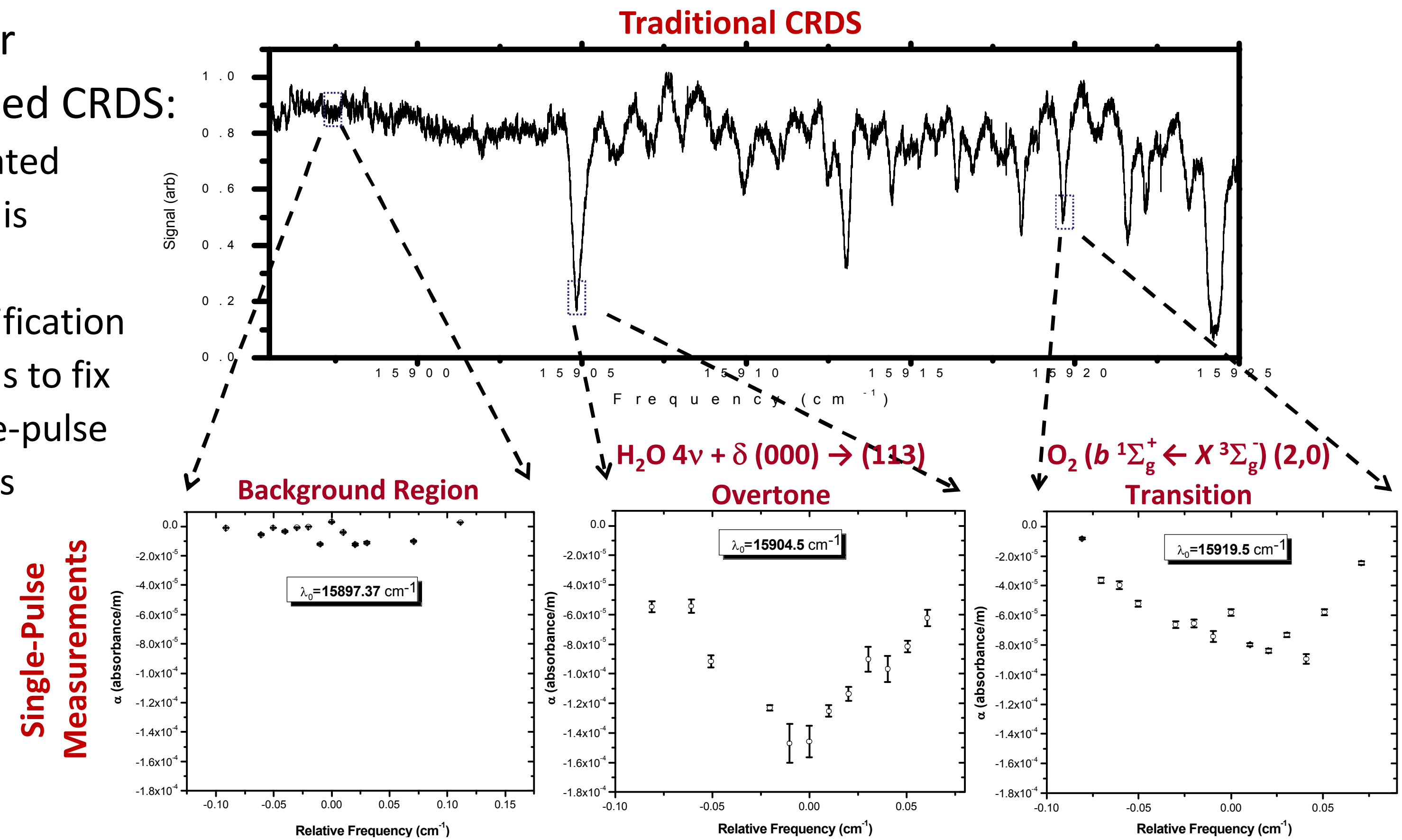
Fit decay signal to: $I(t) = I_0 \exp[-t\,(1/\tau + \alpha c)]$

Decay of Several Beat Frequencies for Two Laser Wavelengths



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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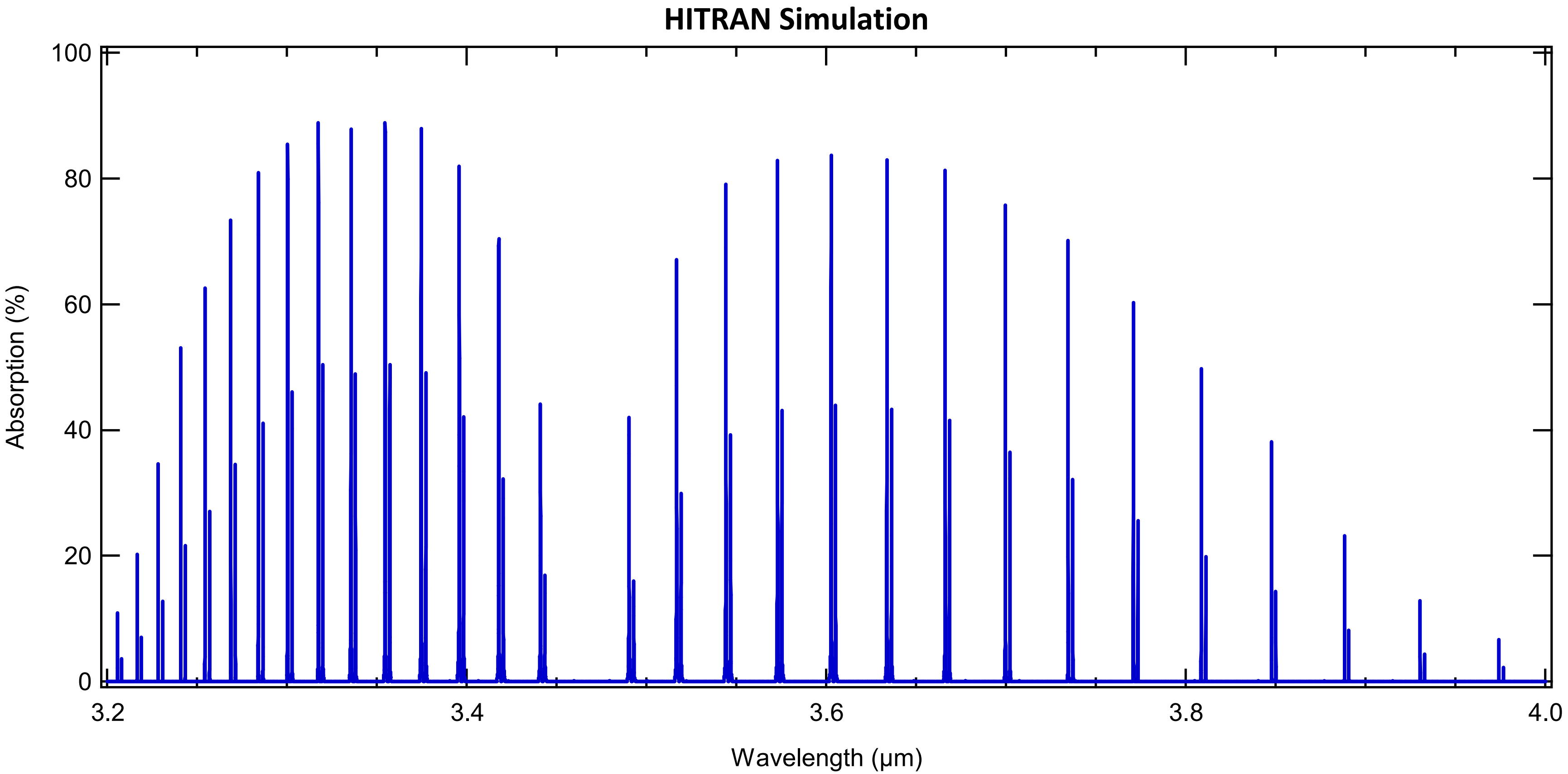
HCl Spectroscopy

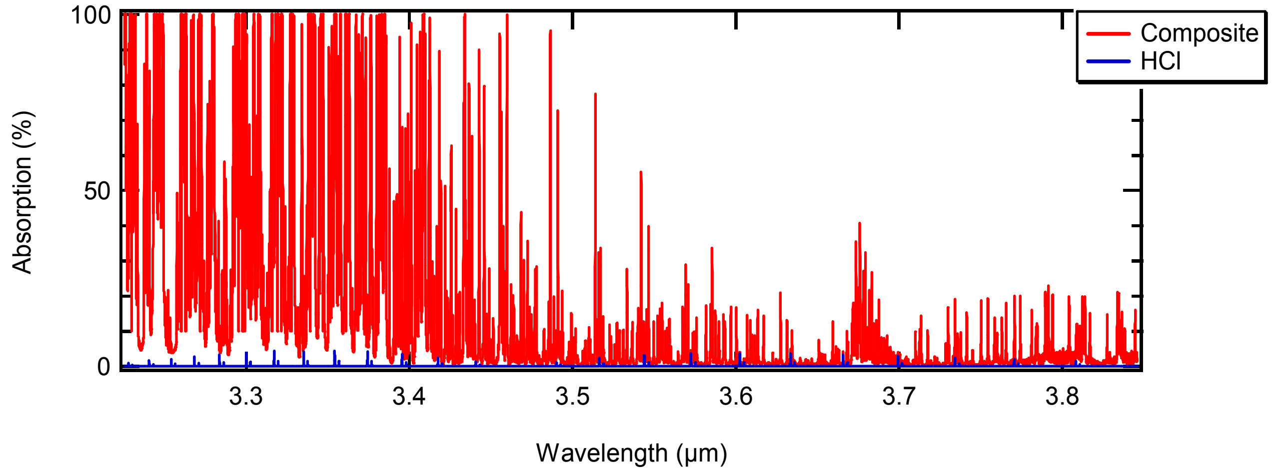
- Strong absorption features spanning 3.2-3.8 μm
- Simple, well-resolved spectrum



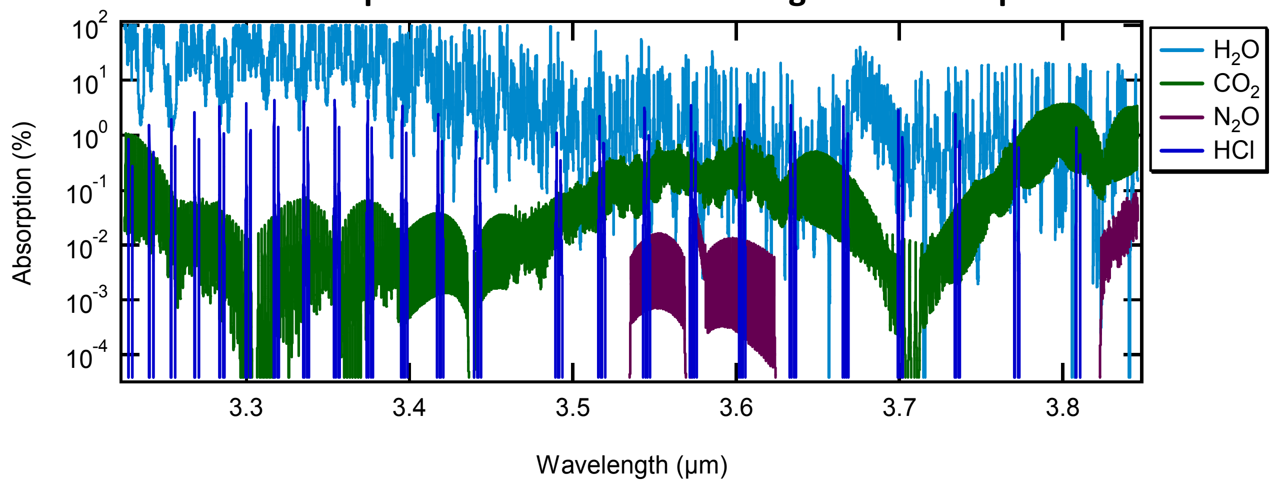
Non-Negligible Background Absorption

- 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

Background Absorption by Flue Gas Species

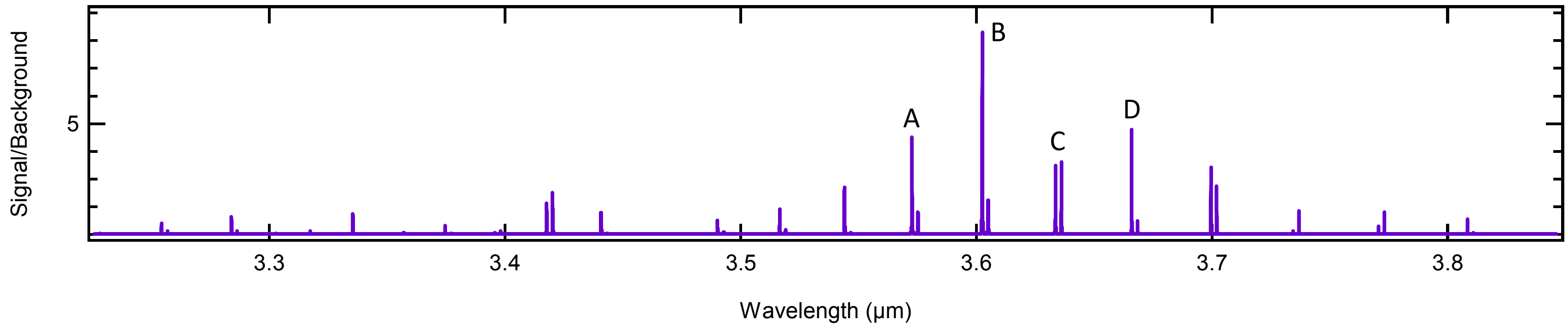


Individual Species Contribution to Background Absorption

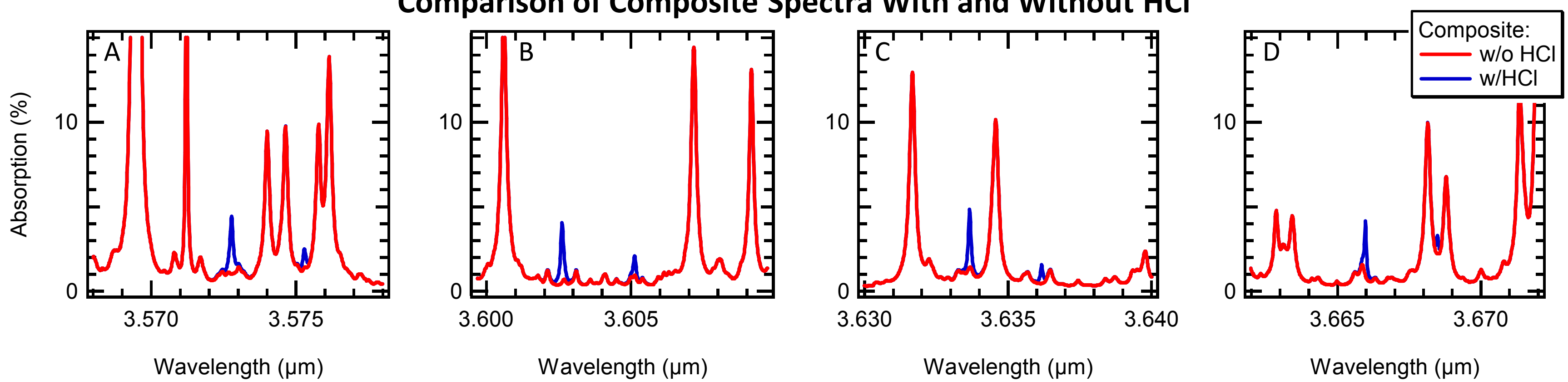


Discernible HCl Features Above Background

Ratio of Composite Spectra With and Without HCl



Comparison of Composite Spectra With and Without HCl



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

Absorption Path Length and Spectral Resolution

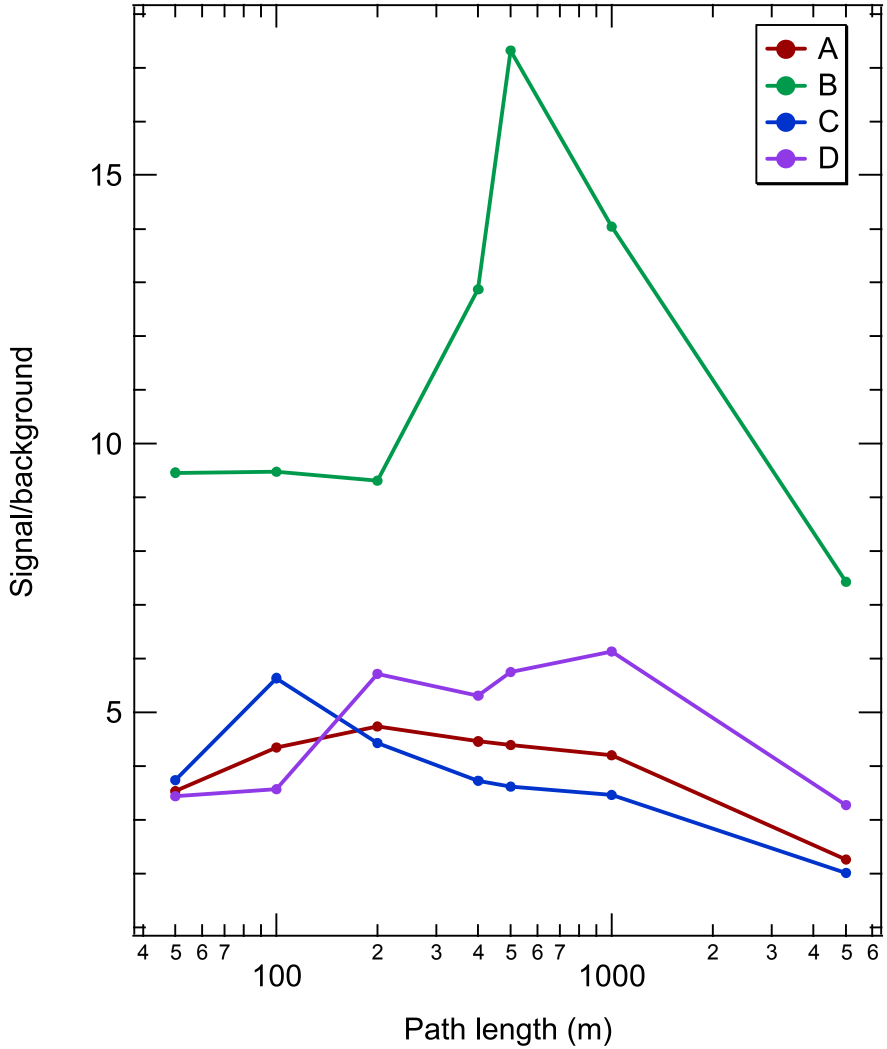
- Increased path length → greater absorption
- Increased ring-down time/cavity decay constant associated with a longer path length → higher resolving power in FFT
- Calculate spectral resolution assuming:
  - FSR: 150 MHz → maximum spectral resolution: 0.005 cm^{-1}
  - ΔFSR: 100 kHz
  - Path length-limited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

rf frequency → 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

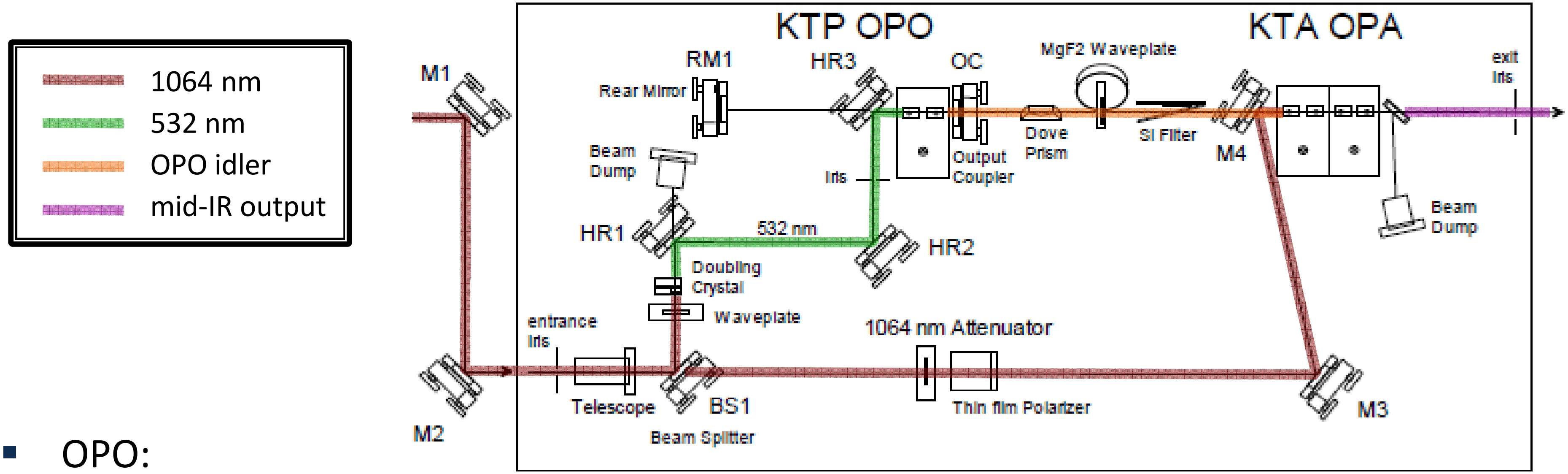
- Simulate absorption spectra with and without HCl for calculated spectral resolutions
- Increasing path length/increasing spectral resolution:
  - Initially improves ability to distinguish HCl features above background
  - At longer path lengths, background absorption dominates the spectra, lowering 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

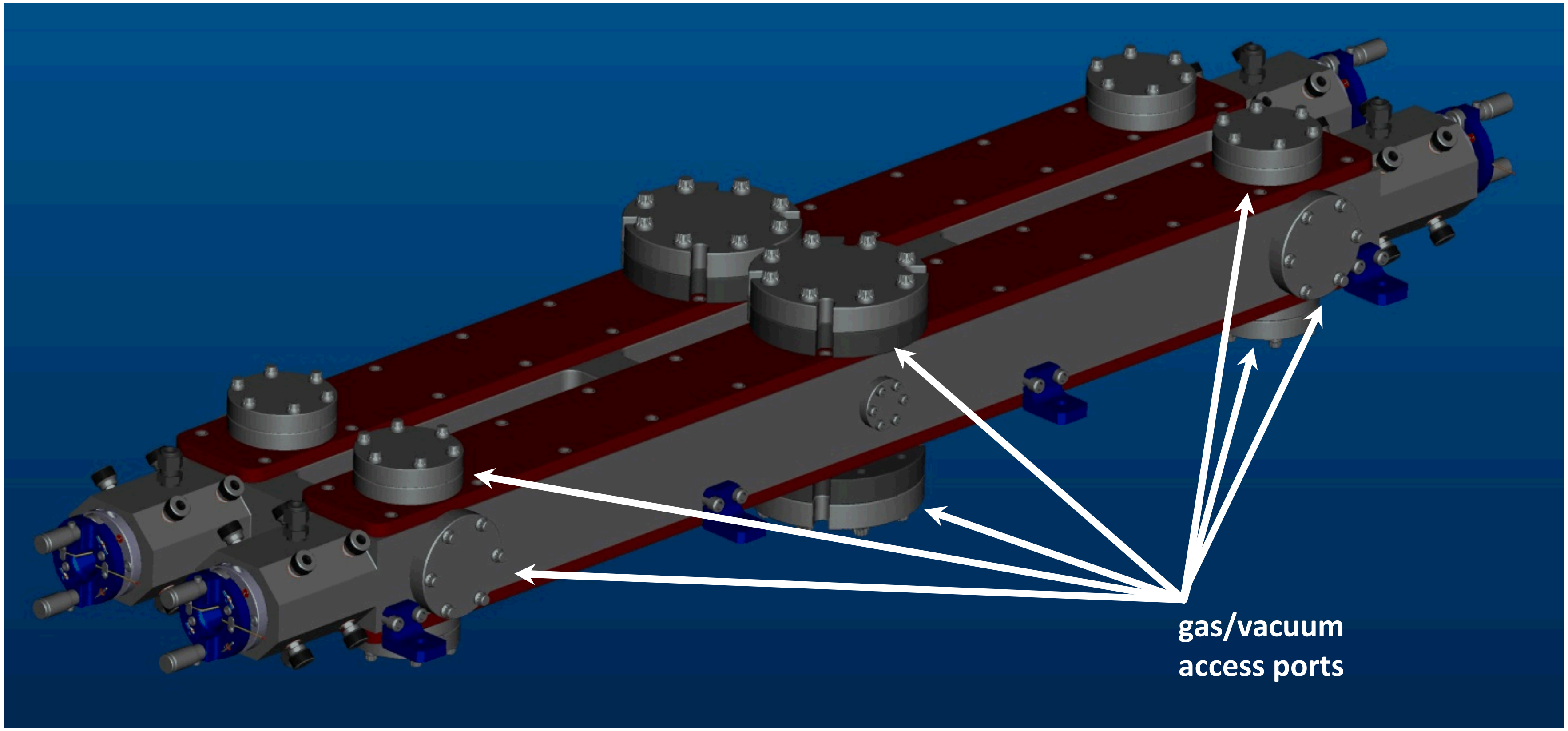
Experimental Setup – Monolithic Dual-Etalon Assembly

- 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

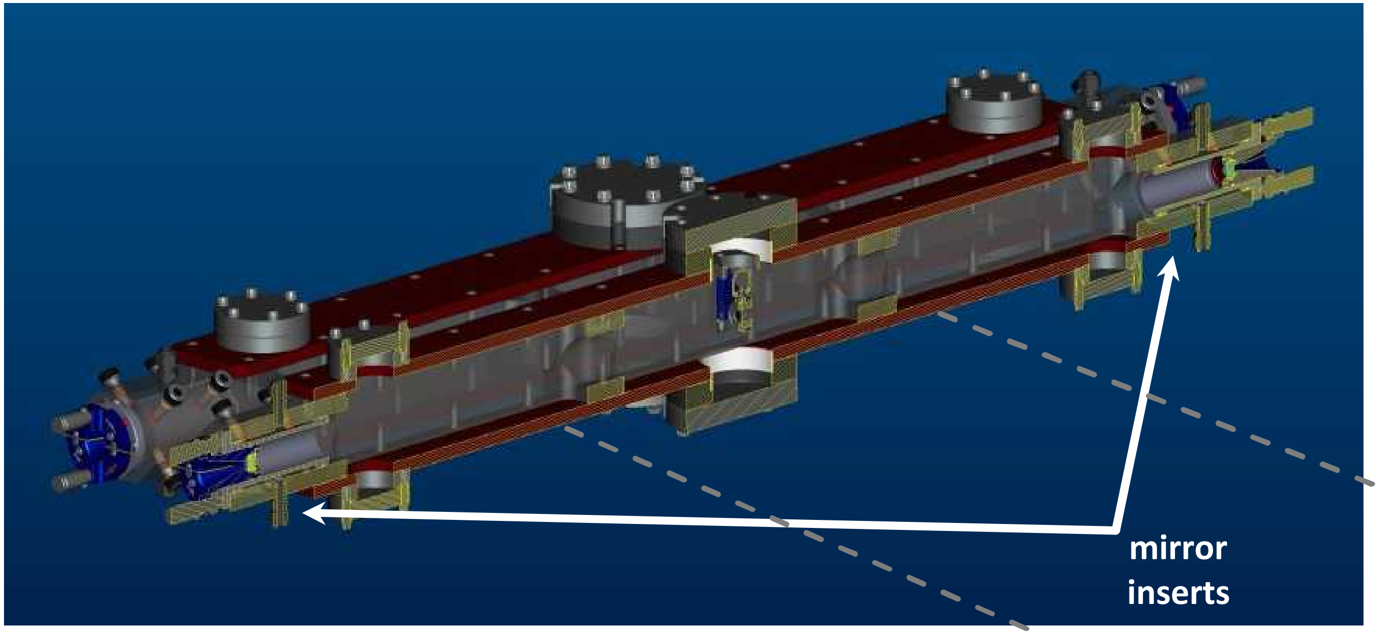
- Cavity length: 1 m
  - FSR: 150 MHz
  - Spectral resolution limit: 0.005 cm^{-1}

Design

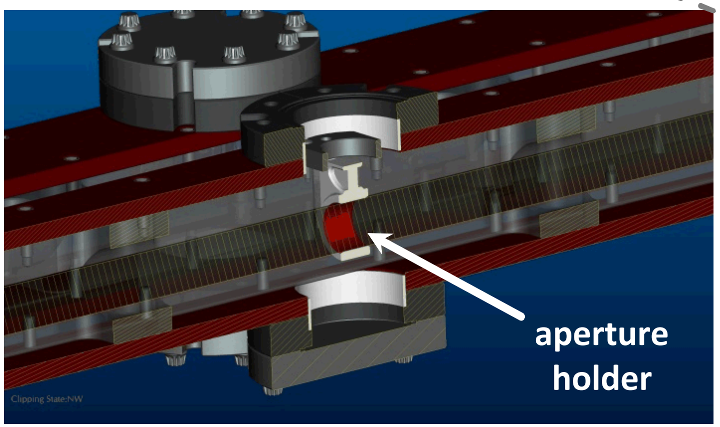


- Two etalon cavities thermally coupled
- Multiple conflat flanges for gas/vacuum line access
- 0.5”-diameter cavity mirrors contained within an adjustable insert

Design – Cut-Away Views

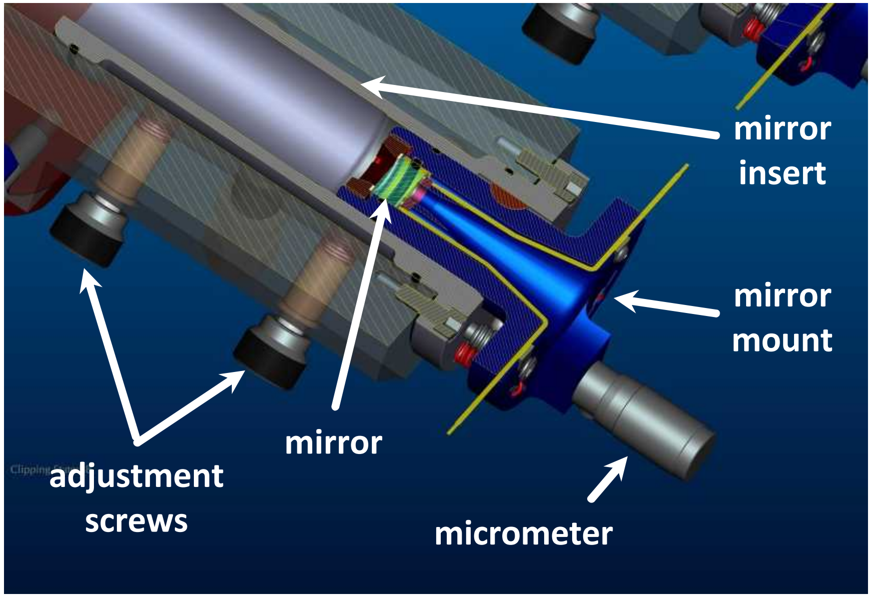


- Concentric cavity arrangement:
  - Fundamental mode of the cavity focuses tightly at the cavity center for both path directions
  - Aperture incorporated at this focus will reduce contribution of higher order modes to the observed signal → reduction in data uncertainty

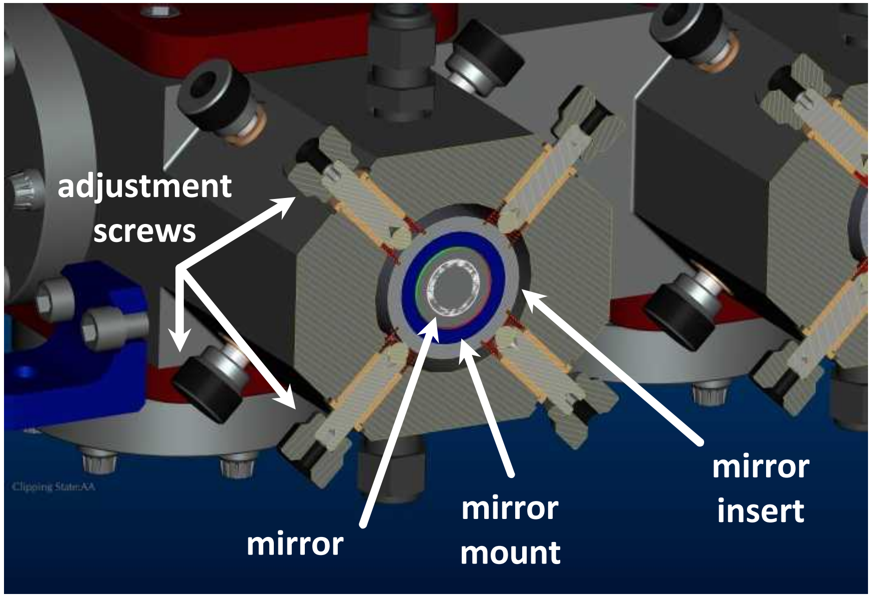


Design – Mirror Insert

Top View



End View

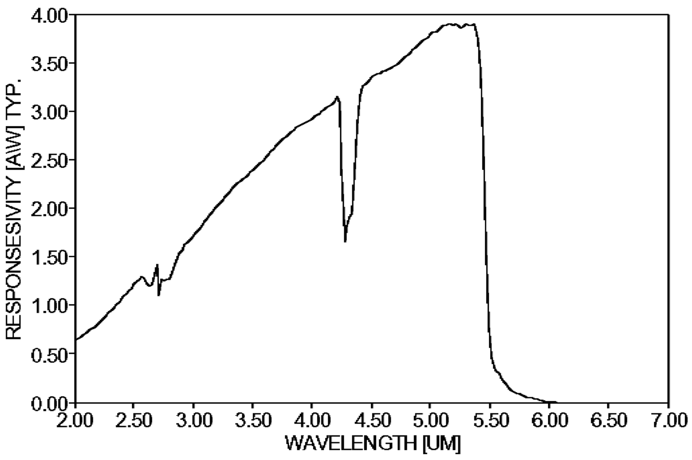


- Mirrors mount housed within an insert
- Mirror insert can be translated and angled slightly within cavity bore via adjustment screws
- Micrometer provides additional tip/tilt control of the mirror mount within the insert

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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