



PICARRO AMMONIA SUMMIT

20-21 March 2024 - Aarhus, Denmark

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CRDS Theory

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G2509 Hands-on Training

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Q&A Customer Support



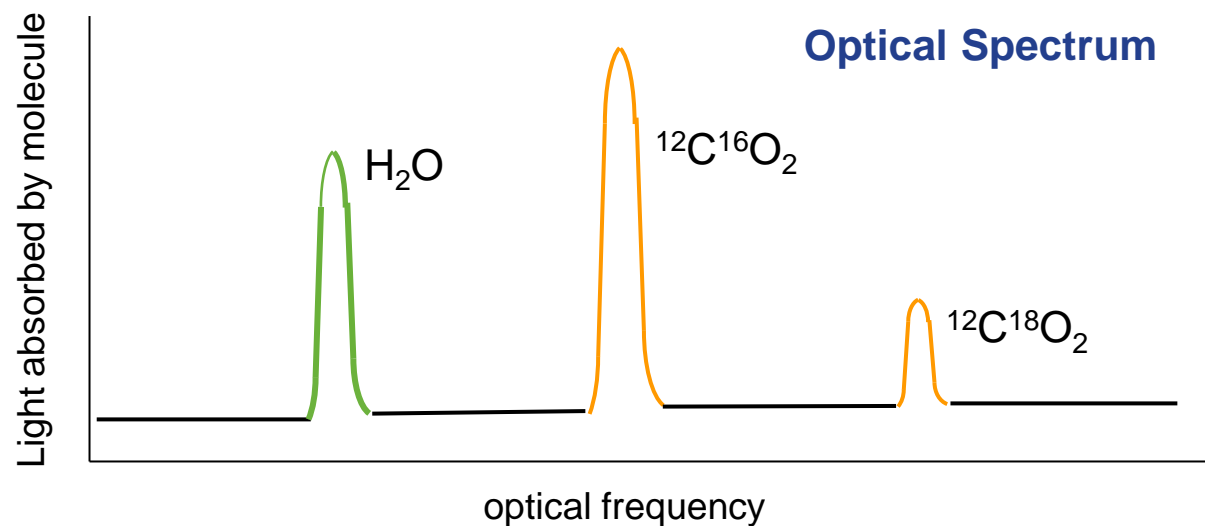
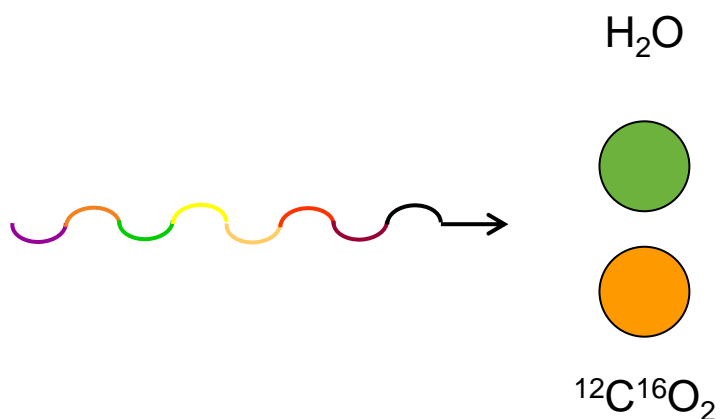
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CRDS Theory

Jan Woźniak
Application Scientist

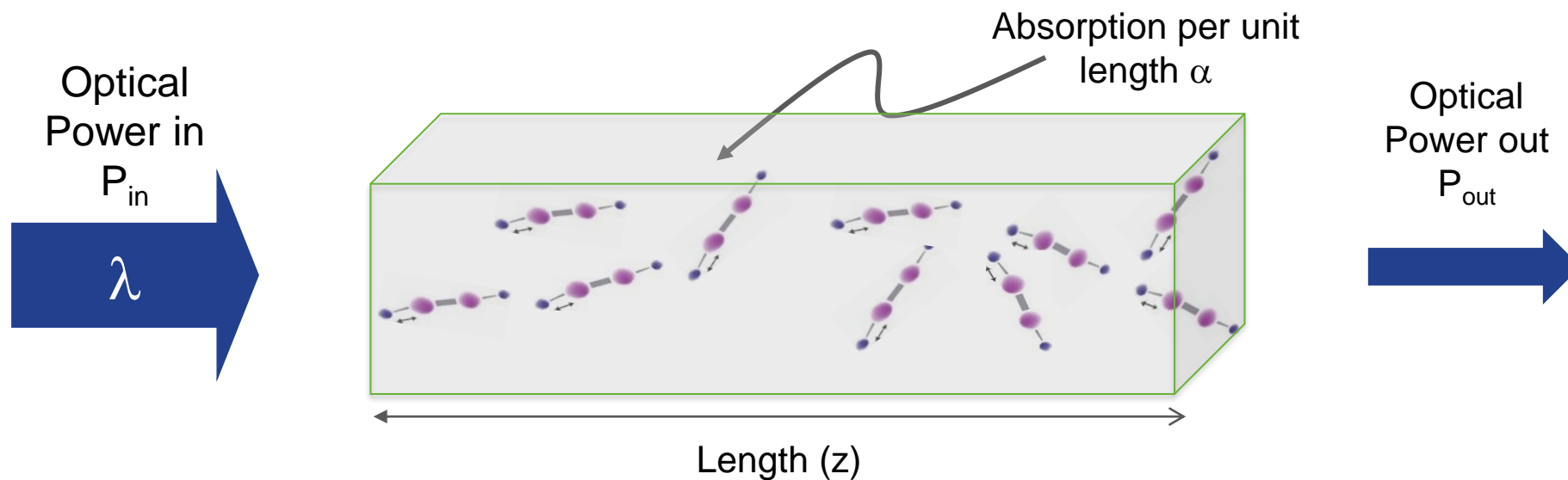
Resonant Optical Spectroscopy



Each type of molecule has a unique optical absorption

1. Molecules absorb at optical frequencies where they resonate mechanically
2. A spectrum is measured by changing the frequency of light passing through a sample and measuring the amount of light absorbed
3. A spectrum of a given species of molecule usually consists of a number of absorption features
4. By measuring an isolated absorption feature of a species, its concentration can be determined

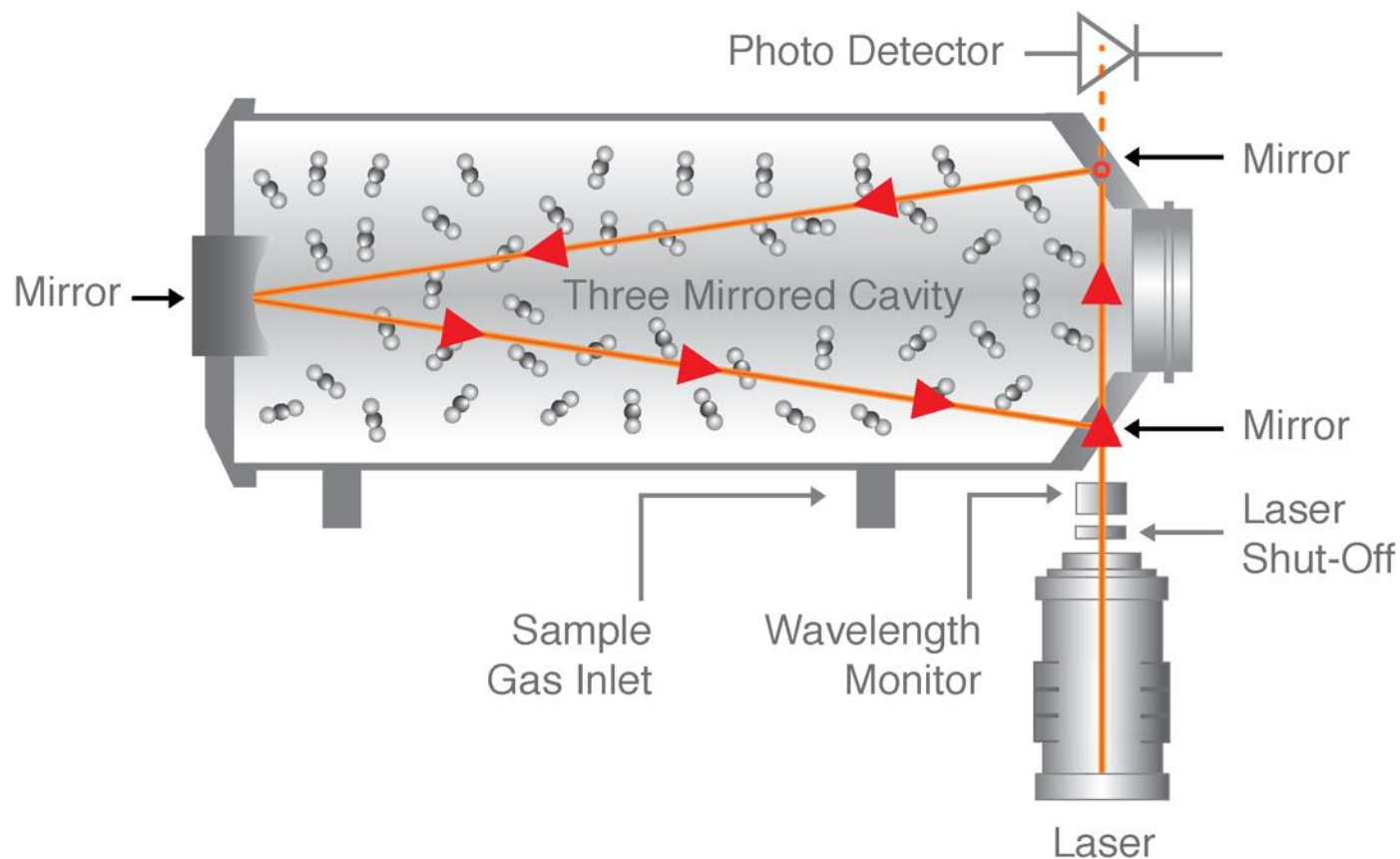
Beer-Lambert Law for Optical Absorption



$$P_{out} = P_{in} e^{-(\alpha_{molecule} + \alpha_{everything\ else})z}$$

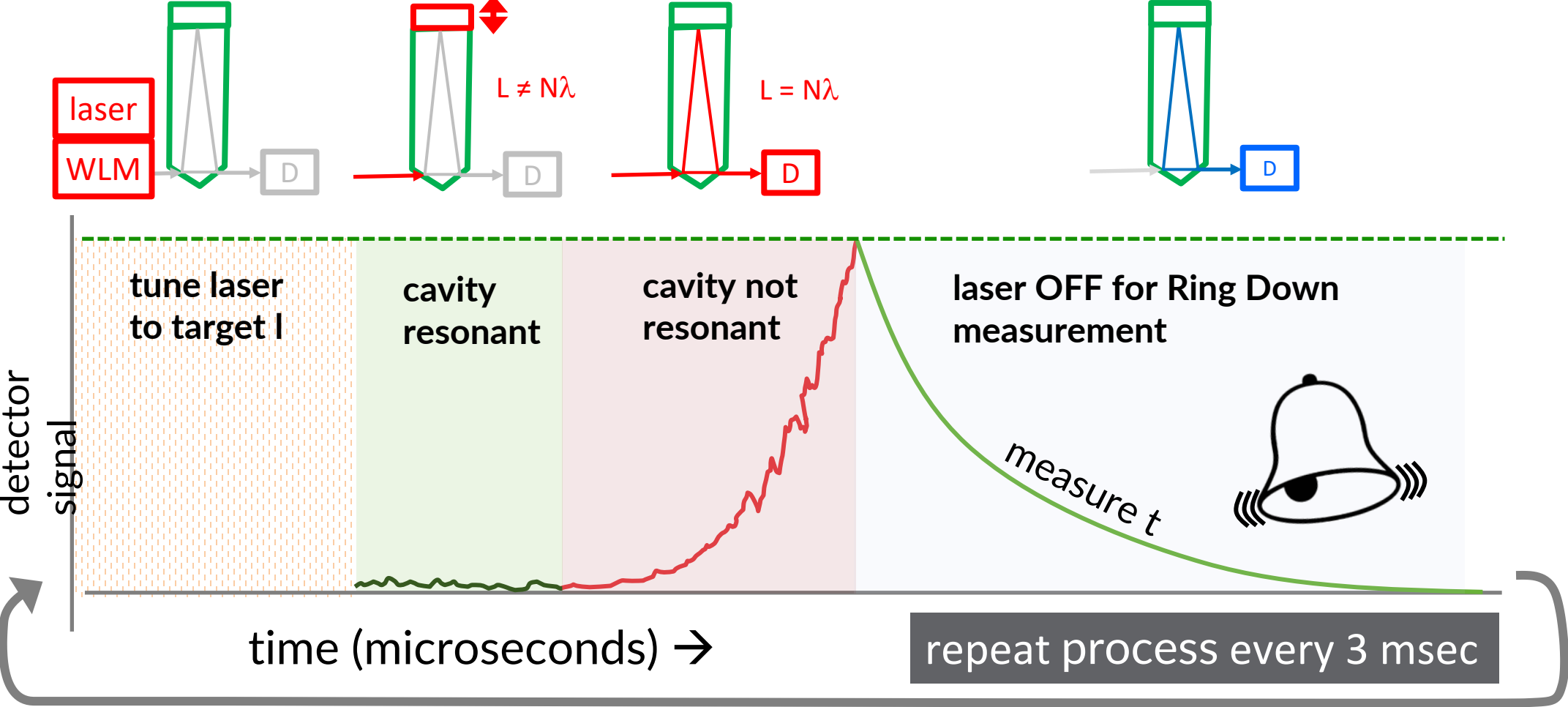
- **Maximize** $\alpha_{molecule}$: Pick λ where the target molecule absorbs strongly
- **Minimize** $\alpha_{everything\ else}$: Pick λ where all the other molecules don't absorb, and take care so that there is no loss of signal in your optics
- **Maximize** z : Get the longest path length you possibly can

CRDS: Time, not Absorbance



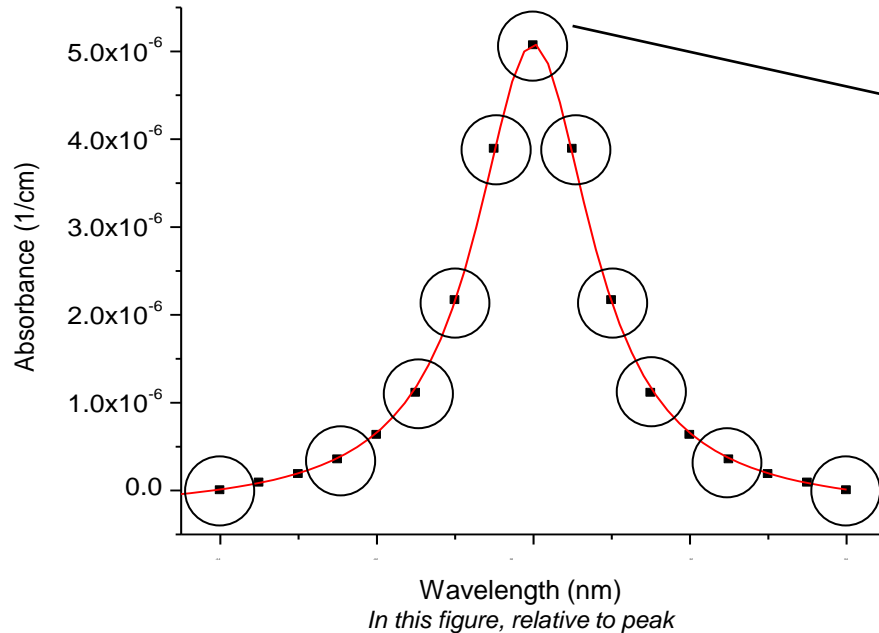
- CRDS utilizes the unique infrared absorption spectrum of gas-phase molecules to quantify the concentration of (and sometimes isotopes of) H_2O , CO_2 , CH_4 , N_2O , CH_2O , NH_3 , etc.
- Measure decay rate, rather than absolute absorbance
- Small 3-mirrored cavity ~ 35 cc
- Long effective path-length (> 10 km)
- Time-based measurement
- Laser is switched on and off, and scanned across wavelengths

CRDS: Principle of Operation

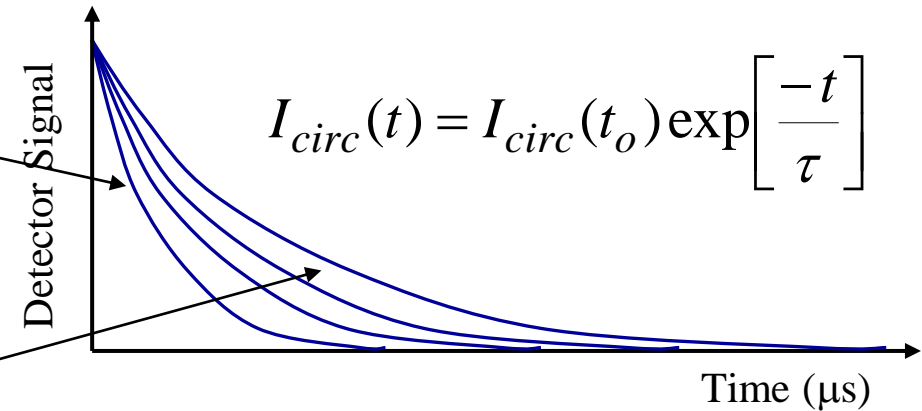


Turning Ring-Down Times into Concentrations

1. Select wavelength using λ -monitor



2. Measure decay time using CRDS



3. Calculate loss (a)

$$\alpha = 1/c\tau$$

I = light intensity in cavity

c = speed of light

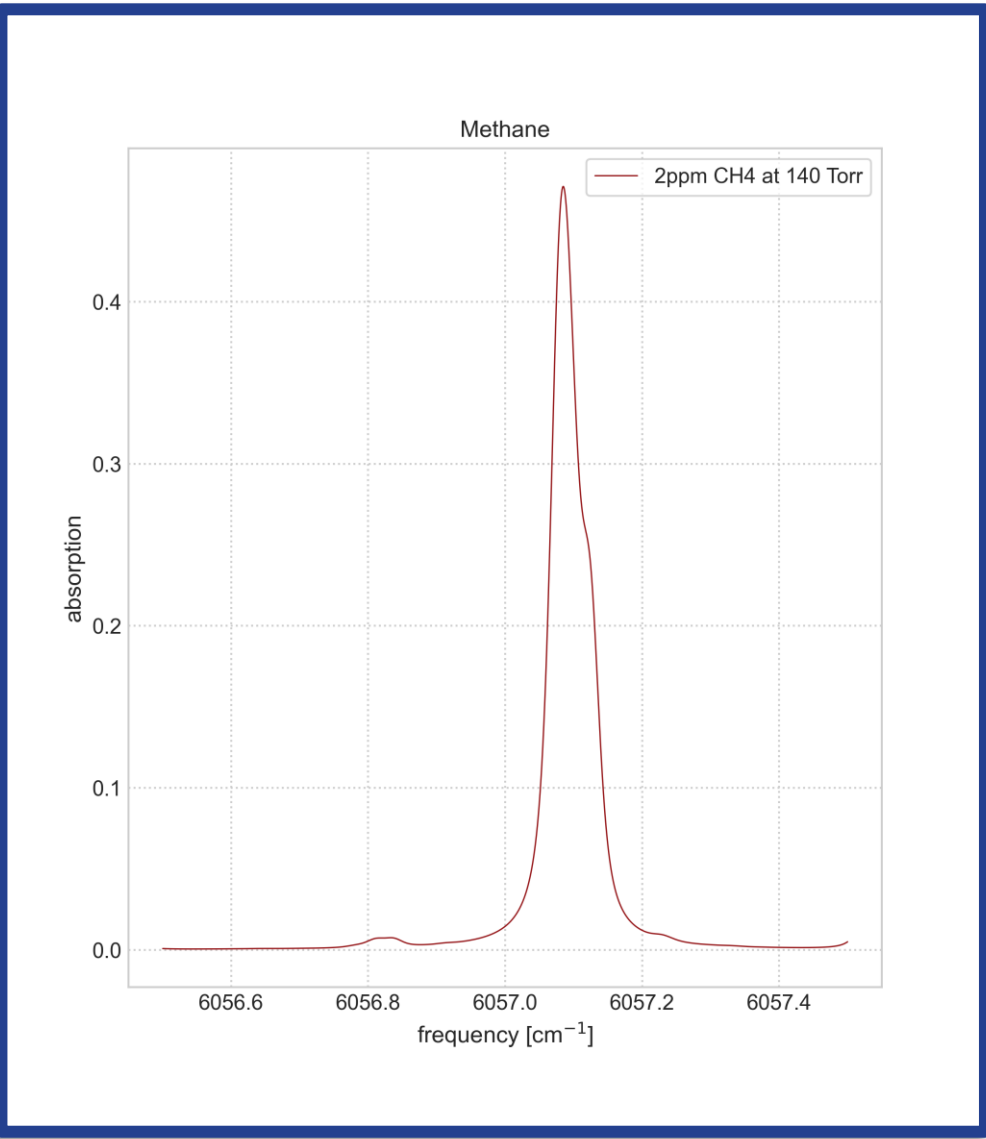
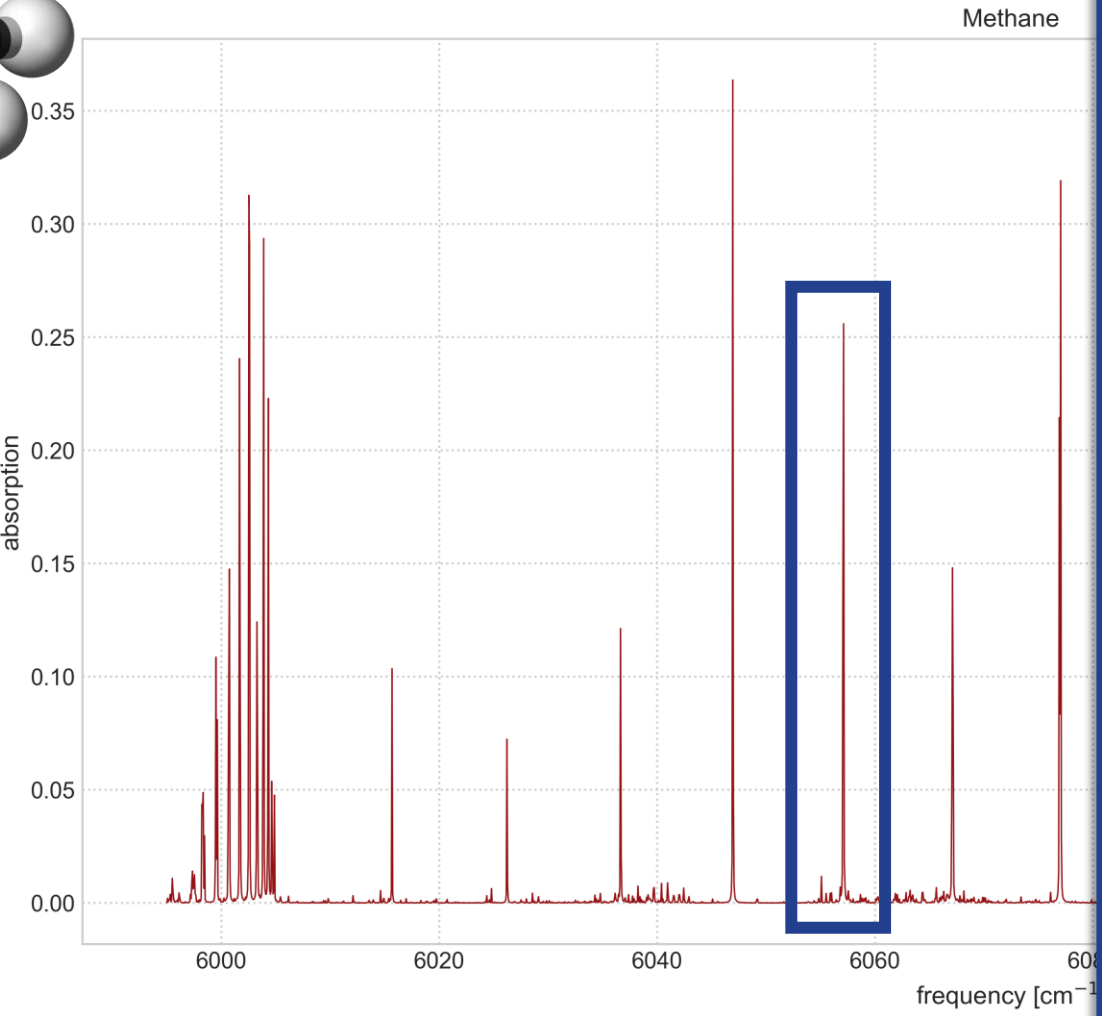
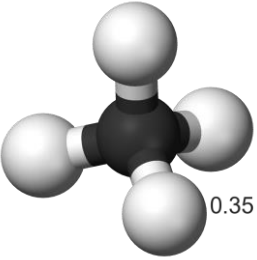
t = cavity ring-down time

a = cavity loss per unit length (ppm/cm)

Repeat

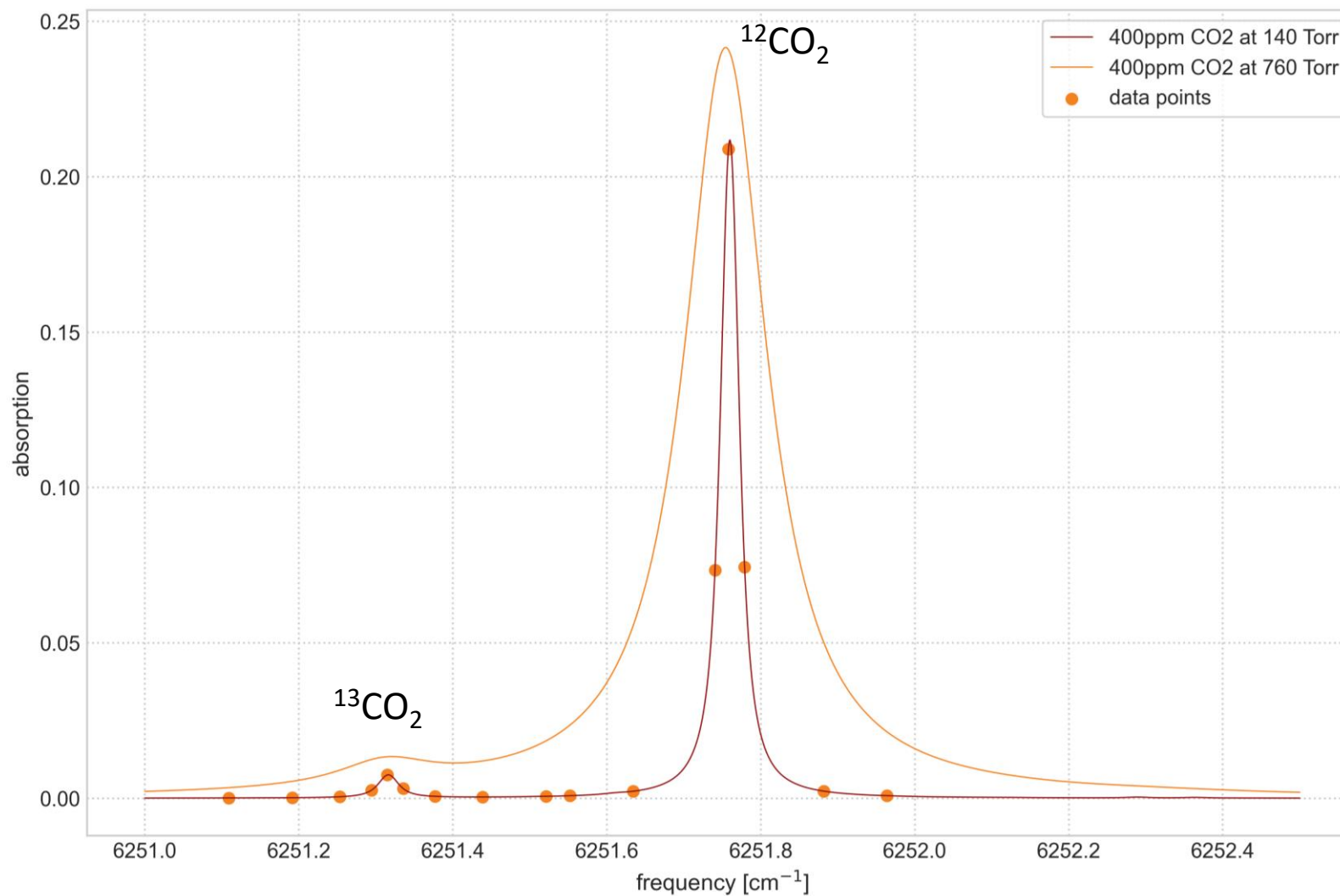
Gas concentration is proportional to the area under the curve, given constant T and P

Methane Spectrum



Pressure Reduction

- Pressure reduction allows clear discrimination between absorbing species



Generating Stable Spectrograms

1. A high-quality **absorption measurement**

- CRDS delivers a precise and accurate measurement of the optical loss

2. A clean stable **frequency axis**

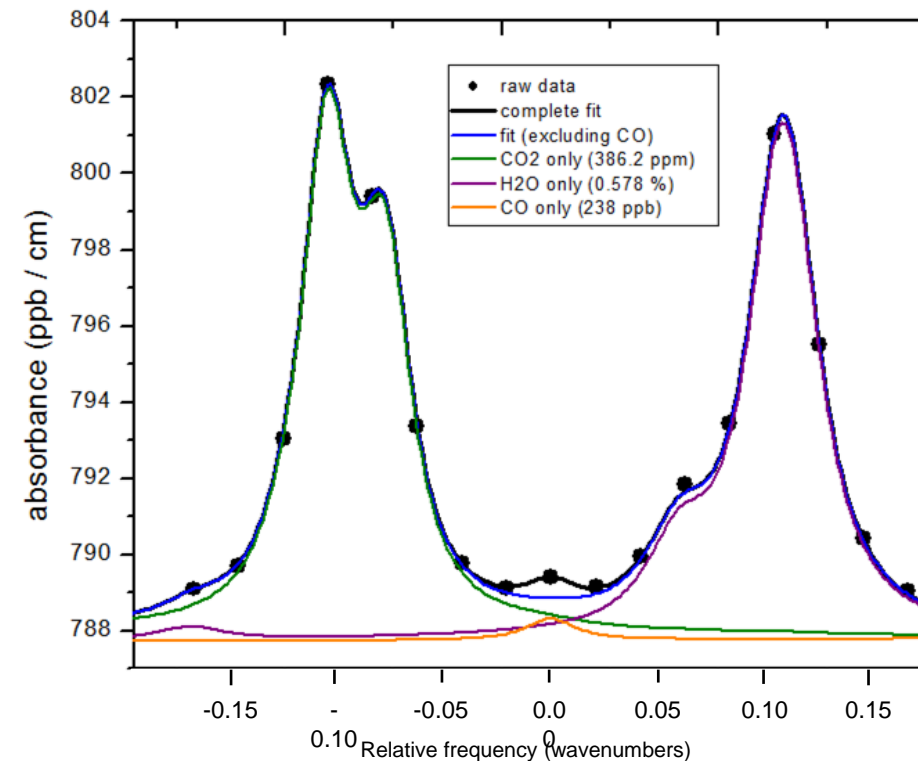
- An accurate and precise tool for determining the laser wavelength

3. Precise **temperature control**

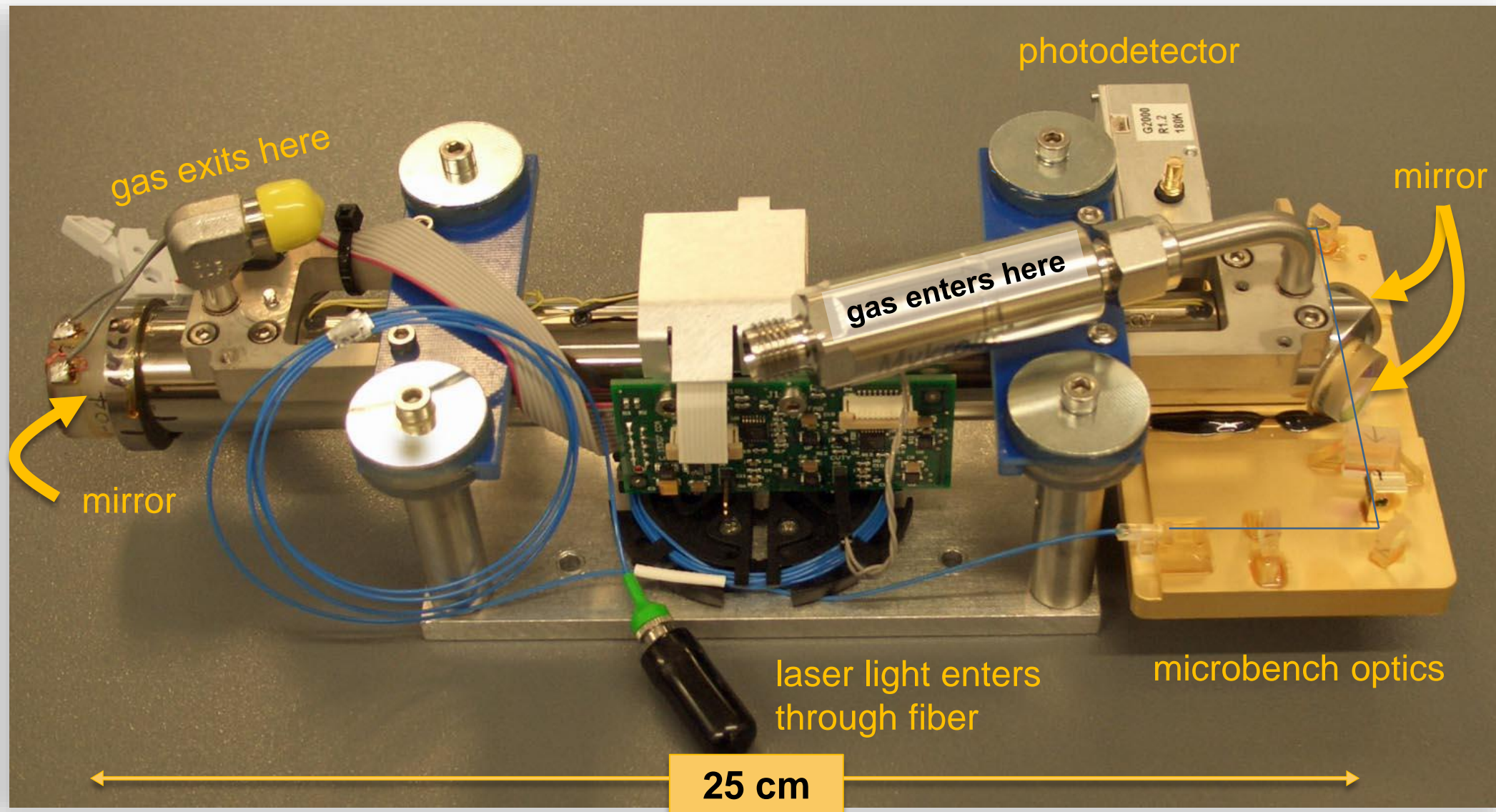
- Engineered control loops

4. Precise **pressure control**

- Engineered control loops



Nuts and Bolts



Inside the Box

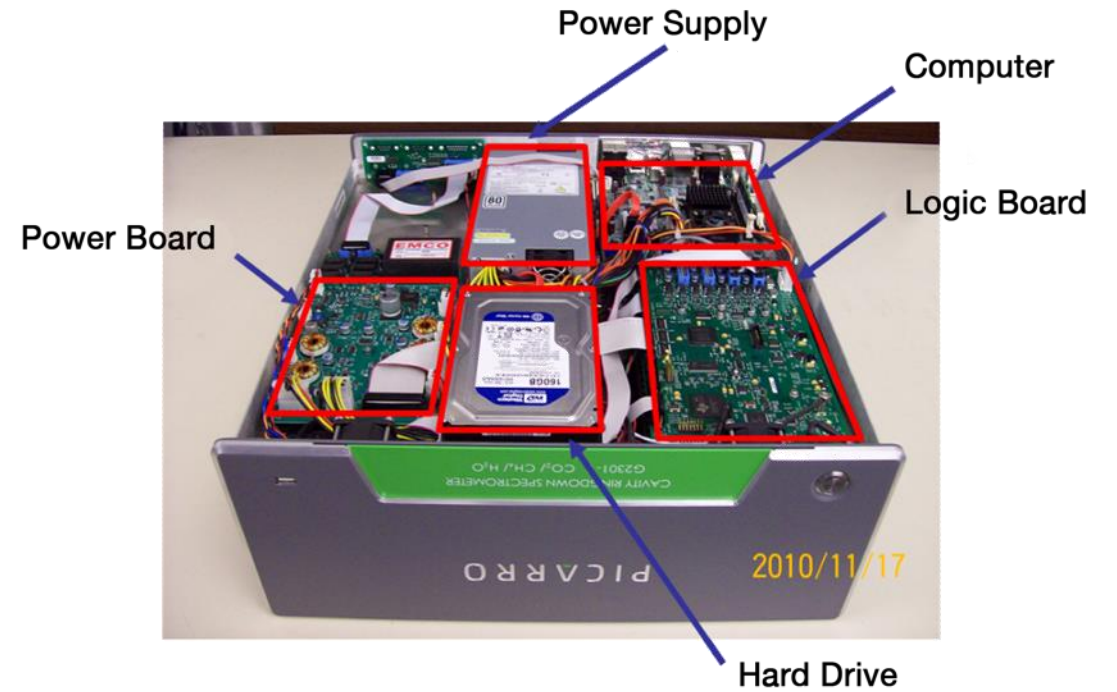
Warm Box
(Wavelength Monitor)

Laser
Cards



Hot Box
(Cavity and
Sample Handling)

Optical
Amplifier





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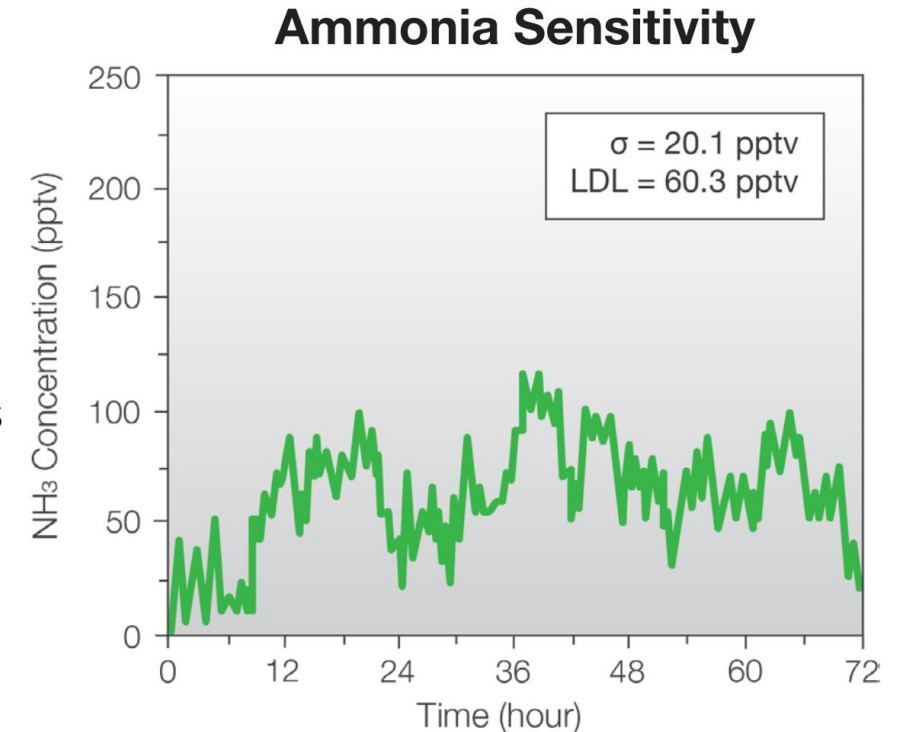
Application Considerations

Magdalena Hofmann
Senior Application Scientist

Surrogate Gas Validation

G/SI2103 and G2509

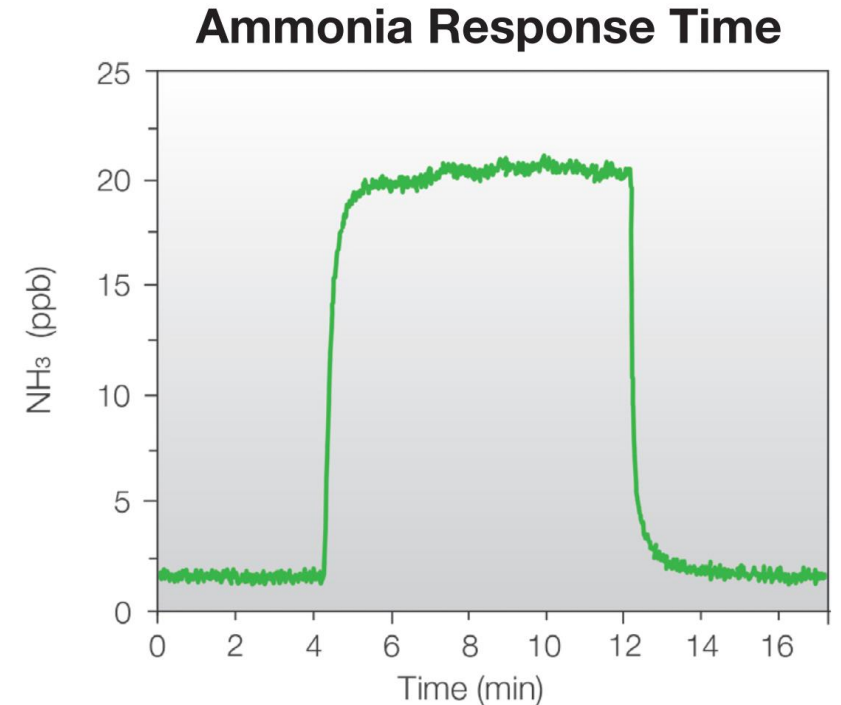
- Wavelength monitor constantly corrects drift (water vapor is measured as reference line)
- Surrogate gas validation (monthly to yearly)
 - Carbon dioxide acts as surrogate gas: non-reactive, easily commercially available, adsorption spectrum adjacent to ammonia
 - Avoids common accuracy issues of ammonia calibration standards (adsorption and stability)
 - Verify zero-drift with zero-air measurement (Phosphoric Acid Impregnated Charcoal (PAIAC) as NH_3 scrubber)
- [Surrogate Gas Validation Tech Document](#)



Typical noise zero drift of the SI2103 analyzer over 72 hours.

Analyzer Response Time

- Minimizing dead volumes
 - Compact measurement cavity of 30mL
- Use of material with low adsorption of NH_3
 - Teflon/PTFE for tubing and connectors
 - Coatings for stainless steel components
- Increased flow rate (>1.5L/min)
- Response time (0-20ppb), 10-90%, 90%-10 rise/fall time: <2min
- Every analyzer is tested to guarantee the specified response time



Typical response time for a 10-90% and 90-10% 20 ppb ammonia challenge

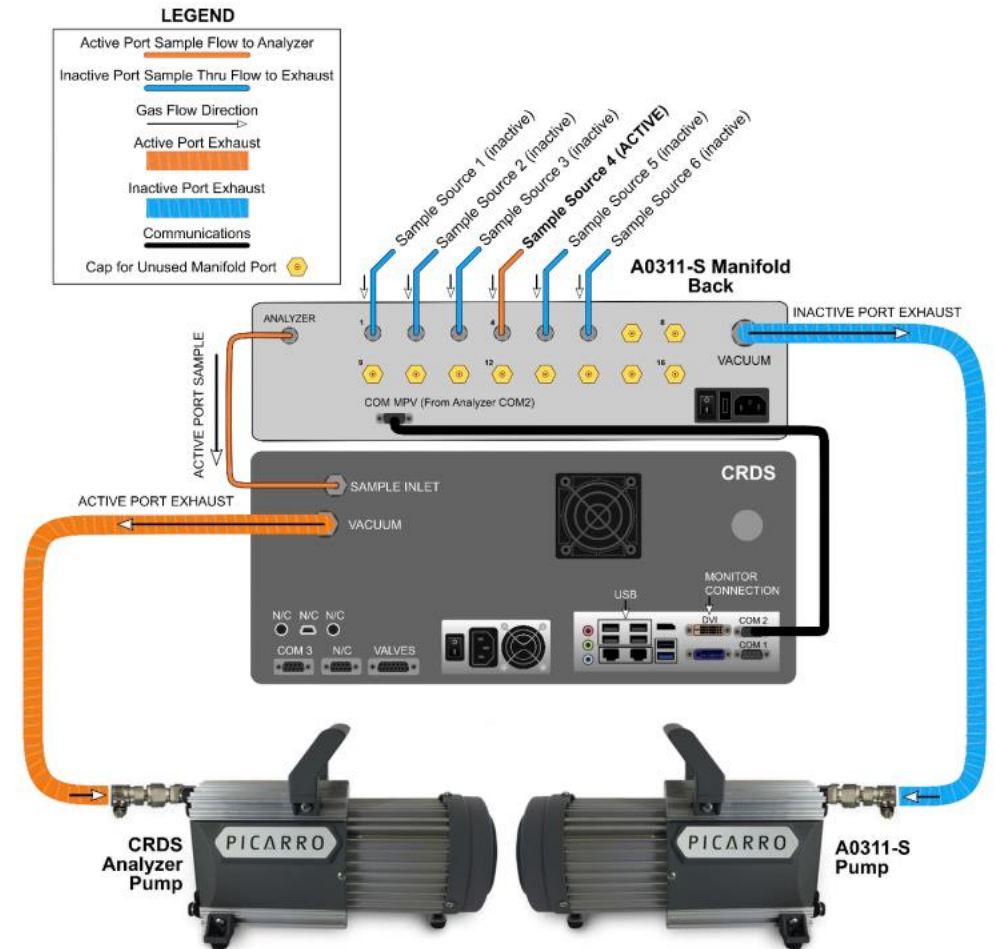
Sample Gas Handling for Ammonia Measurements

- Use appropriate material: PTFE (Teflon), PFA, Silconert 2000 coated, PFTE coated
- Keep inlet tubing as short as possible
- Consider heating sample line tube to $\sim 45^{\circ}\text{C}$ if tubing $> 10\text{m}$
- An additional assist pump may be required when working with long tubing
- Note: Ammonia dissolves in condensed water!

Silconert Coated Multiplexer

- Silconert™ coated multiplexer
 - Continuous flow
 - 16 channels

A0311-S1 coated Multiplexer



Field Deployment

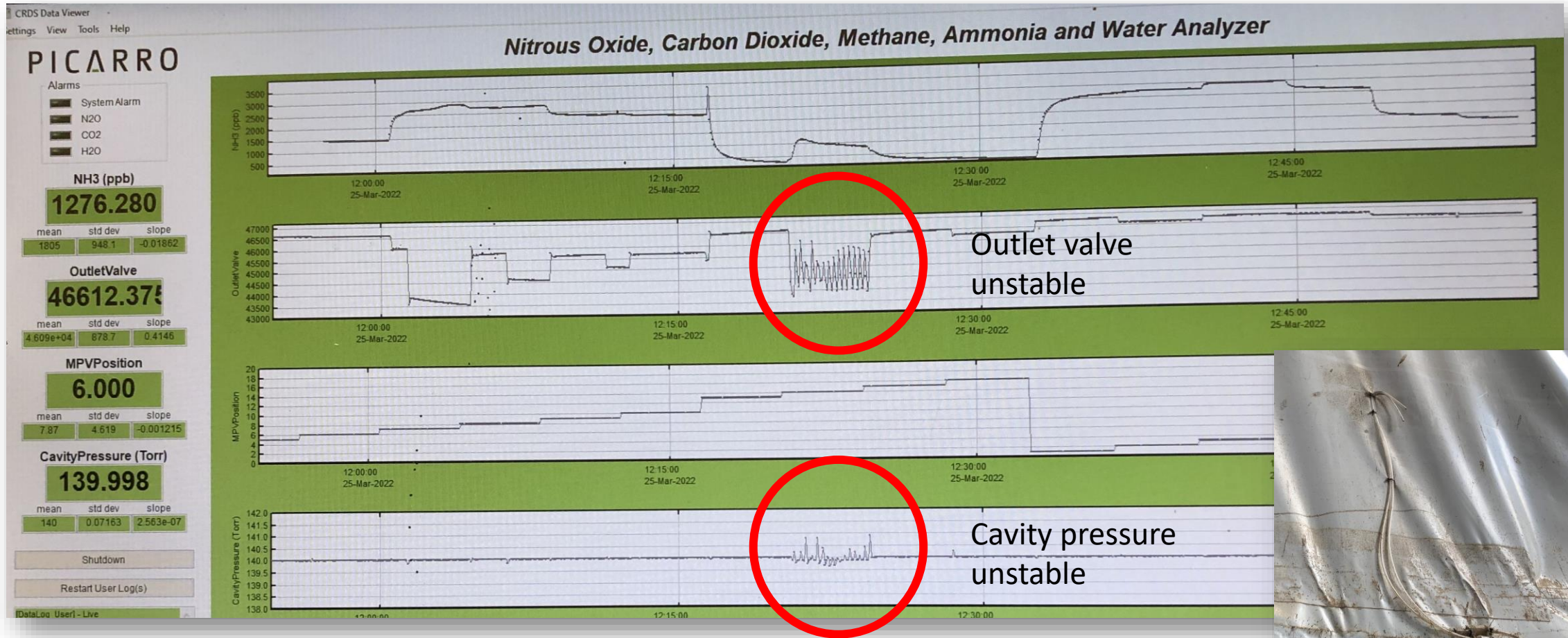
- Transportation
 - Horizontal position
- Protection against harsh weather conditions
 - Shelter for instrument, e.g., enclosures
- Battery: Deep cycle battery
- External filter recommended
 - Recommended pore size and frequency of filter replacement varies for applications



[UGT](#) ClimBox



Example of Filter Clogging



Interference Detection (ChemDetect)

- Interference detection is available on G2509 (not on G/SI2103)
- ChemDetect flags data points when the spectroscopic fitting model for NH_3 , CO_2 , CH_4 , or N_2O deviates from the observation (large residual values)
 - ChemDetect is either 0 (no contamination) or 1 (potential contamination)
 - Positive flagging may be an indication of an interference (affecting at least one of the four gases)
 - False positive flagging can occur, e.g., due to sudden pressure changes (-> valve switching)
- RDF files can be analyzed by Picarro for the source of contamination (by evaluating the residual data)
- Note: RDF files are large (on average 1GB/day) and are deleted frequently from the analyzer (usually after ~2 weeks)

NH₃ Operating Range

G/SI2103

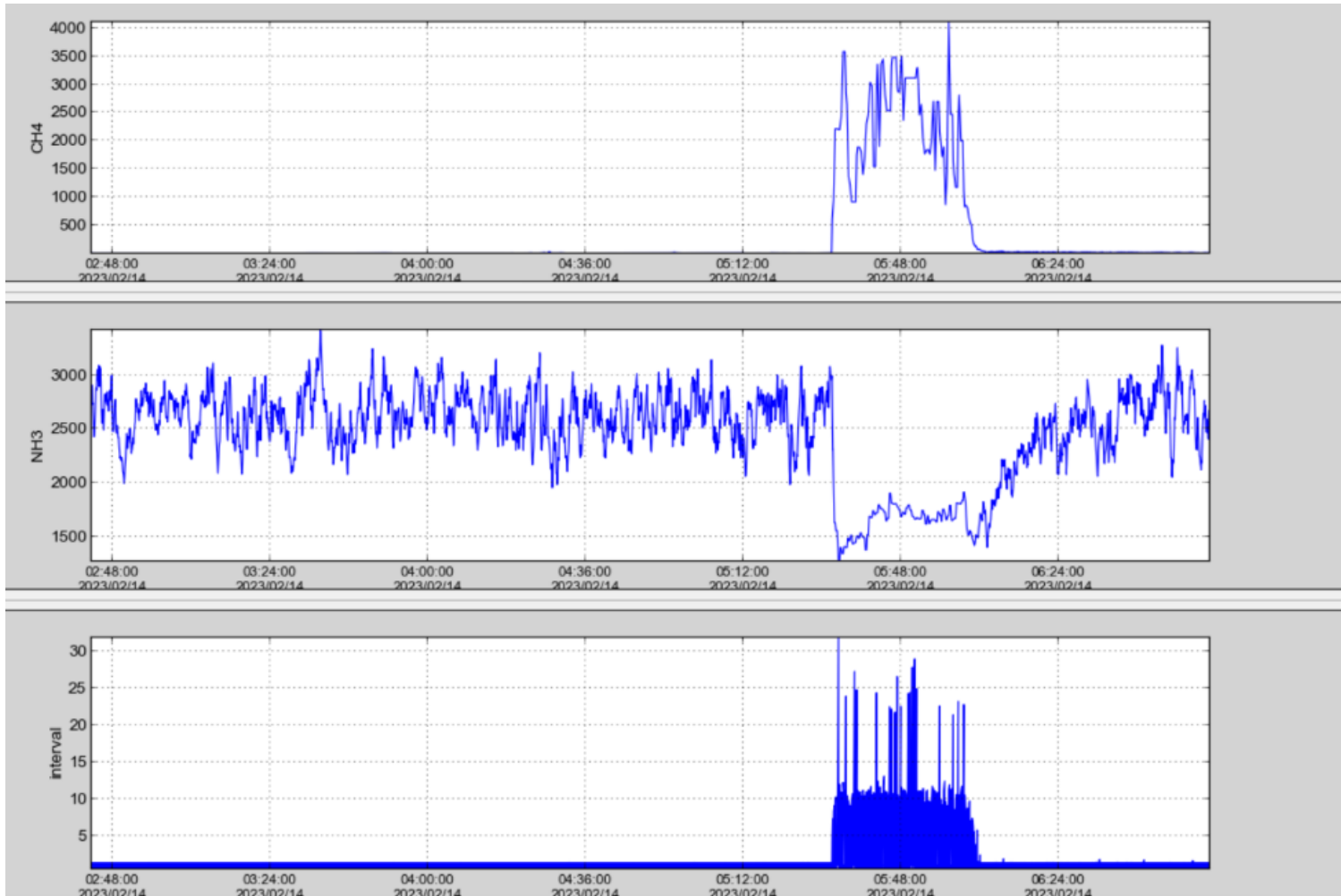
- Guaranteed: 0-10ppm
- Extended range: 0-50ppm

G2509

- Guaranteed: 0-10ppm (for NH₃>2ppm, N₂O will be affected)
- Tested by customers: 50ppm and higher
 - Custom water vapor correction should be applied to elevated ammonia concentrations measured with G2509 analyzers built prior to Dec 2023, software version 1.8.1 (see [Martin et al., 2016](#))

The G/SI2103 and the G2509 use the same spectroscopic line to measure NH₃.

Example of Signal Saturation



- CH₄ absorption line is saturated
 - Concentration exceeding operational range (max. 800ppm CH₄)
 - Ammonia signal affected
 - Measurement interval slows down

G2509/G2103 manual

- [Updated G2509/G2103 manual](#) available
- Chapter on ammonia-specific application considerations





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Hands-On Training

Jan Woźniak
Application Scientist

Topics: Software

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- GUI
- Raw data vs. private data vs. RDF files vs. event logs
 - Instrument Status
 - Outlet valve for troubleshooting
 - Event logs and private data needed for technical support
 - RDF files needed for any interference related issues (archiver.ini)
- Data file viewer
- Setup Tool
- Quick introduction to Controller
- Connecting Picarro 16-port manifold or other valve systems
- Analyzer shutdown options

Instrument Status

Table 2 – The Instrument Status Register

<i>Bit Number (0 = LSB, 15 = MSB)</i>	<i>Decimal Value</i>	<i>Mnemonic</i>	<i>Description of set condition</i>
15	32768	<reserved>	This bit currently has no meaning and should be ignored.
14	16384	System Error	0 = The instrument is not currently in an error state 1 = A system error is present. Use <code>_Instr_GetError</code> for more information.
13	8192	Warming up	0 = The instrument has successfully started up 1 = The instrument is currently warming up from power-off or restart
9	512	Warm box temp locked	0 = The warm box temperature is not stabilized within acceptable bounds 1 = The warm box temperature is within acceptable bounds for measurements
8	256	Cavity temp locked	0 = The cavity temperature is not stabilized within acceptable bounds 1 = The cavity temperature is within acceptable bounds for measurements
7	128	Pressure locked	0 = The gas sample pressure is not stabilized within acceptable bounds 1 = The gas sample pressure is within acceptable bounds for measurements
6	64	Gas Flowing	0 = Valves are closed and no gas is flowing 1 = Valves are open (pressure not necessarily stable)
2	4	Error in buffer	0 = The error queue is empty 1 = There is at least one value in the error queue
1	2	Meas Active	0 = The measurement system is currently inactive 1 = The measurement system is currently active
0	1	Ready	0 = The instrument currently cannot make a gas measurement 1 = The instrument is currently capable of measuring the sample gas

Usually when the instrument is under operational condition and taking measurements, the return value should be 963 (= Bit 0 (ready) AND Bit 1 (measurement active) AND Bit 6 (gas flowing) AND Bit 7 (pressure locked) AND Bit 8 (cavity temperature locked) AND Bit 9 (warm box temperature locked)).

Topics: Inside the Analyzer

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- Opening the Box
- Maintenance (Video tutorials: <https://www.picarro.com/environmental/environmental-video-tutorials>)
 - Filter replacement
 - Fan replacement
 - Replacing Pump diaphragms
- Resetting cables

Consumables G2509/G2103/SI2103

Part number hardware	Short description	Frequency
C0360	Drierite	Before shutdown under high humidity levels
-	External particulate filter (3µm)	Depends on particulate load, for barn measurements every ~2-3 weeks
S1021, S3174	Particulate filter (0.45µm) (Teflon for NH ₃ , HF, and HCl).	After 12 months, (if higher dust load every 3 to 6 months)
S2068	Complete fan kit	Expected after 2 to 3 years
S2009	External vacuum Rebuild Kit	Expected after ~15'000 hours (approx. 2 years cont. running)



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Customer Support

Arthur Schaeps

Manager Customer Support – Environmental

Remote Analyzer Health Check

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Health Check Service is a thorough evaluation and tune-up of your system.

Via a remote connection, a Picarro Customer Support engineer reviews, evaluates, and optimizes the performance of your analyzer optical, mechanical, electrical, and computer systems.

Software updates would be updated when appropriate and necessary.

- *Implement H₂O vapor interference correction*

*After a Health Check an instrument is eligible for a service plan**

**limitations might apply*

Picarro Customer Support

- For any Technical or Application question reach out to Customer Support:
 - e-mail: support@picarro.com
 - phone: +31 85 888 1650 (international) / +1 408 962 3991 (USA)

Please provide the following information:

- Serial number
- Description/overview of setup (analyzer/peripherals/experiment)
- EventLogs and Private Data from time that problem occurred
- Remote Access information (Teamviewer / Anydesk)