

# ***Greenhouse Gas Measurement Technology***

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# Agenda

- Introduction
  - GHG
  - Regulatory
- Current Methods
  - Infrared Spectroscopy
  - GC FID
- Emerging Methods
  - Laser-Based Spectroscopy

## Greenhouse gases

Carbon Dioxide (CO<sub>2</sub>)

Methane (CH<sub>4</sub>)

Nitrous Oxide (N<sub>2</sub>O)

Sulfur Hexafluoride (SF<sub>6</sub>)

Hydrofluorocarbons (HFC)

Perfluorocarbons (PFC)

Carbon dioxide, methane, and nitrous oxide comprise 98% of the GHG problem

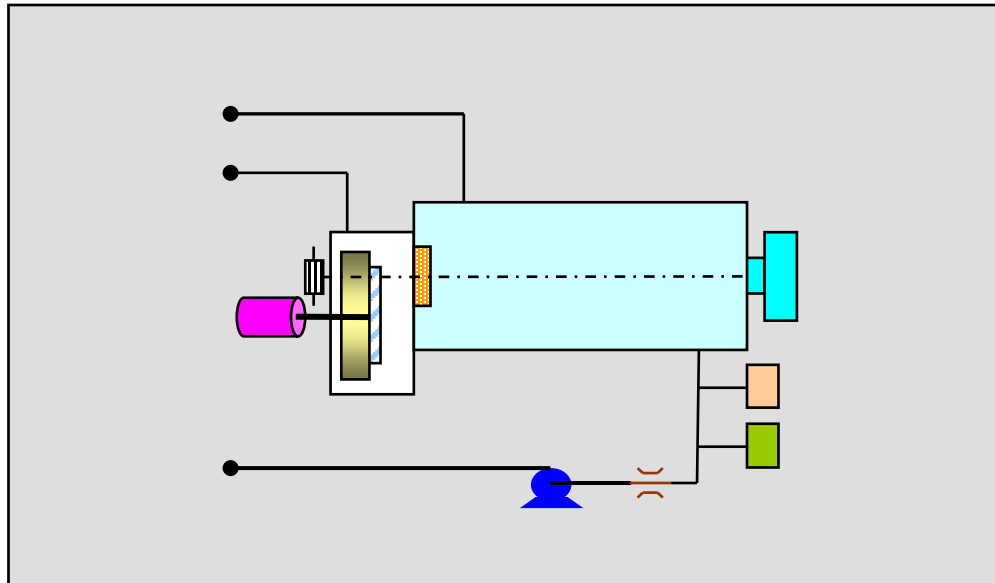
## Light-duty Vehicle Rule

- Proposed September 28, 2009
- Regulates GHG for all light duty vehicles starting with model year 2012
- Requires emission testing and control of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O
- GHG regulation of stationary sources would be triggered by PSD and Title V

# Carbon Dioxide Measurement

- **Infrared Spectroscopy**

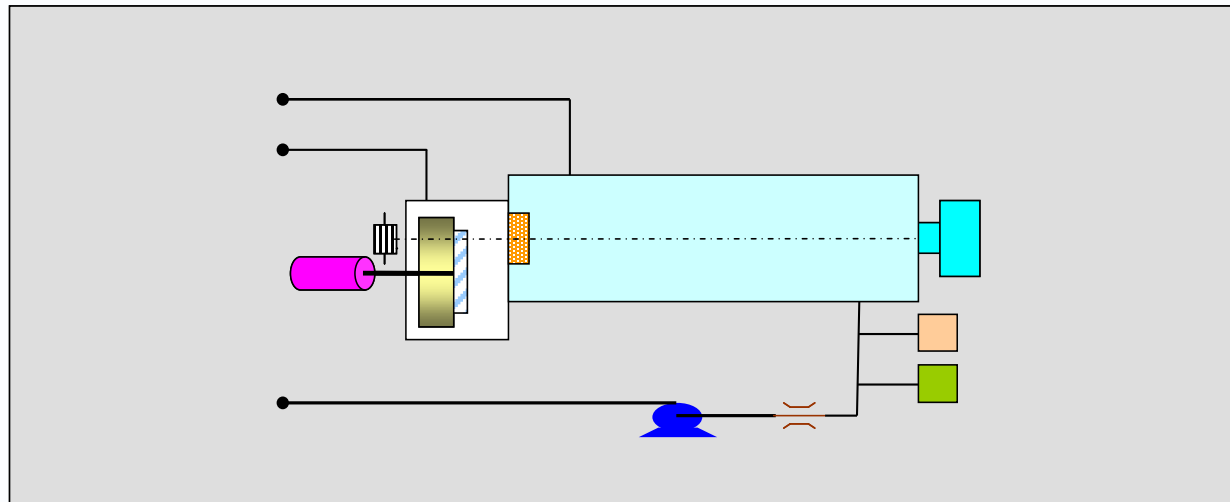
- Carbon dioxide ( $\text{CO}_2$ ) absorbs infrared radiation at a wavelength of 4.26 microns
- Sample is drawn into the instrument and flows through the optical bench
- Radiation from an infrared source is chopped and passed through a rotating optical wheel alternating between sample and reference filters.



# Carbon Dioxide Measurement

## Infrared Spectroscopy

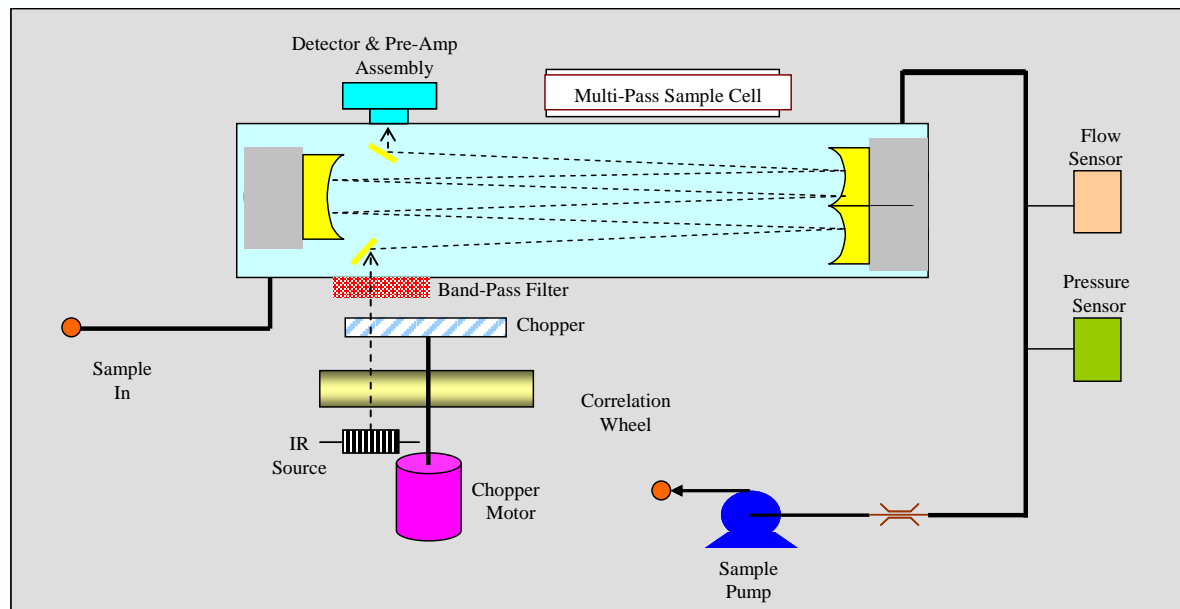
- Radiation then enters the optical bench where absorption by the sample gas occurs
- The infrared radiation then exits the optical bench and falls on an infrared detector
- The chopped detector signal is modulated between the filters
  - amplitude related to the concentration of CO<sub>2</sub> in the sample cell



# Nitrous Oxide Measurement

## Infrared Spectroscopy

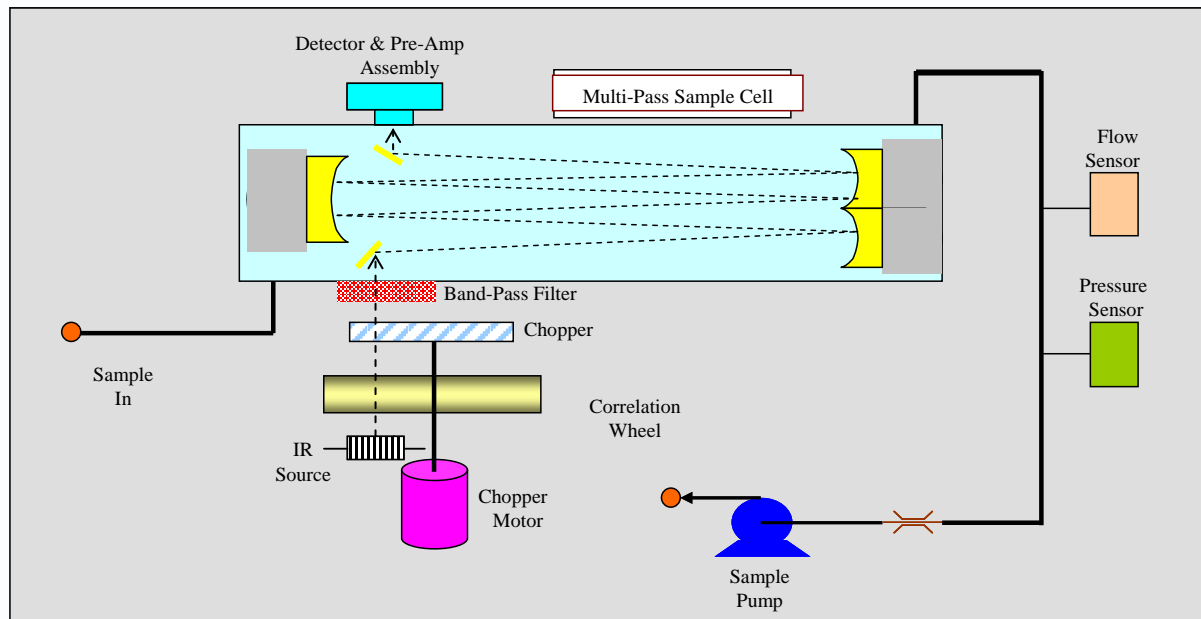
- Nitrous oxide ( $\text{N}_2\text{O}$ ) absorbs infrared radiation at a wavelength of 4.49 microns
- Sample is drawn into the instrument and flows through the optical bench
- Radiation from an infrared source is chopped and passed through a rotating optical wheel alternating between  $\text{N}_2\text{O}$  and  $\text{N}_2$  gas filters.



# Nitrous Oxide Measurement

## Infrared Spectroscopy

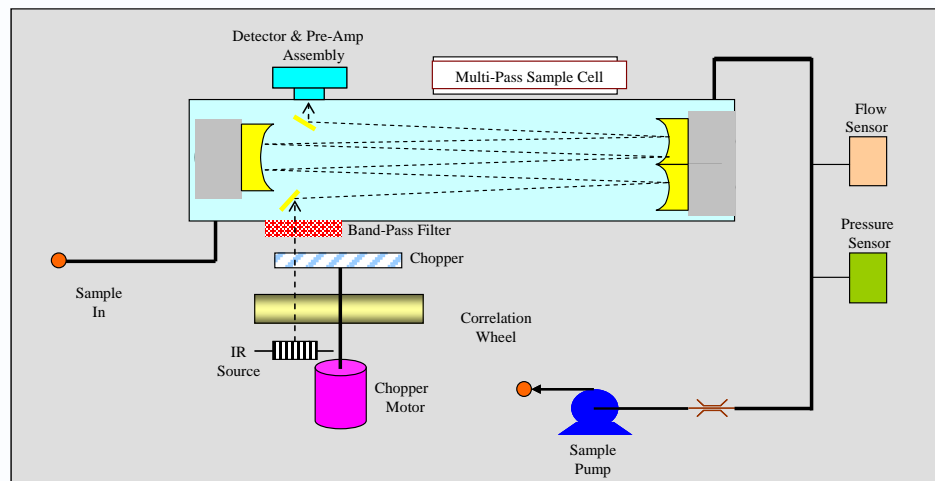
- Radiation passes through a narrow bandpass interference filter
- Radiation then enters the optical bench where absorption by the sample gas occurs
- The infrared radiation then exits the optical bench and falls on an infrared detector



# Nitrous Oxide Measurement

## Infrared Spectroscopy

- $\text{N}_2\text{O}$  gas filter acts as a reference beam
  - Cannot be further attenuated by  $\text{N}_2\text{O}$
- $\text{N}_2$  is transparent to IR radiation
  - Produces a beam which is absorbed by  $\text{N}_2\text{O}$
- The chopped detector signal is modulated between the filters
  - amplitude related to the concentration of  $\text{N}_2\text{O}$  in the sample cell



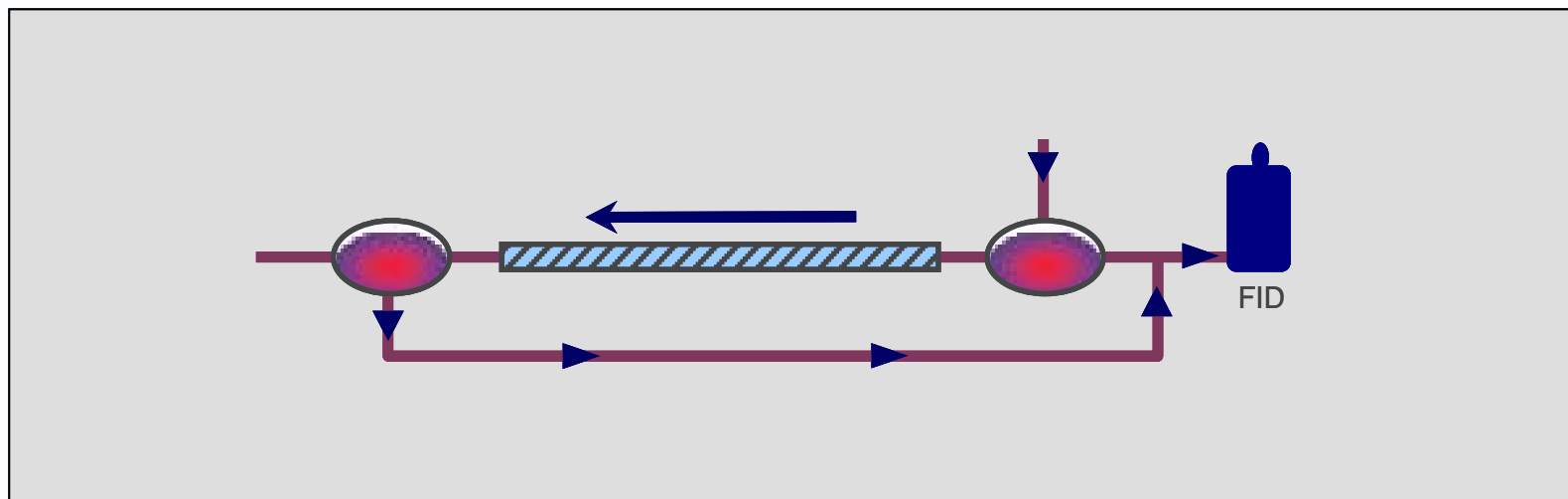
## Methane measurement by GC FID

- Based on the well developed science of gas chromatography
- Measures both methane and non-methane hydrocarbons
- Utilizes a column system developed specifically for this application
- Flame ionization detector
- Automated batch analyzer
  - Repeatedly collects and analyzes small amounts of the sample
  - Uses an eight port, two position, rotary valve
    - Introduce the gas sample into the analyzer
    - Control the flow through the chromatographic column.

# Methane Measurement

## Gas Chromatography FID

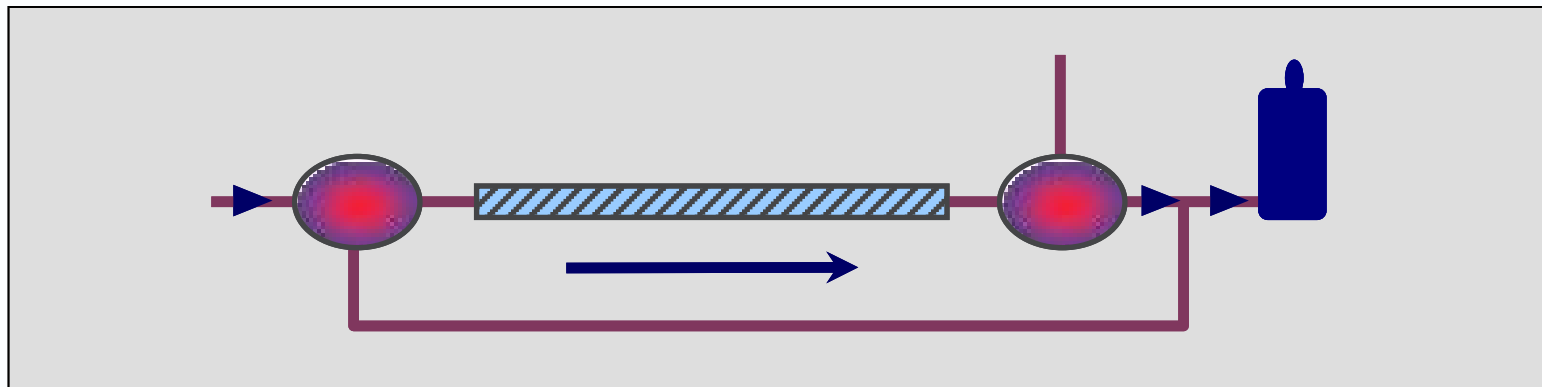
- Between analyses or in standby mode, valve is in the back-flush position
- Sample gas is continuously pulled through the sampling loop



# Methane Measurement

## Gas Chromatography FID

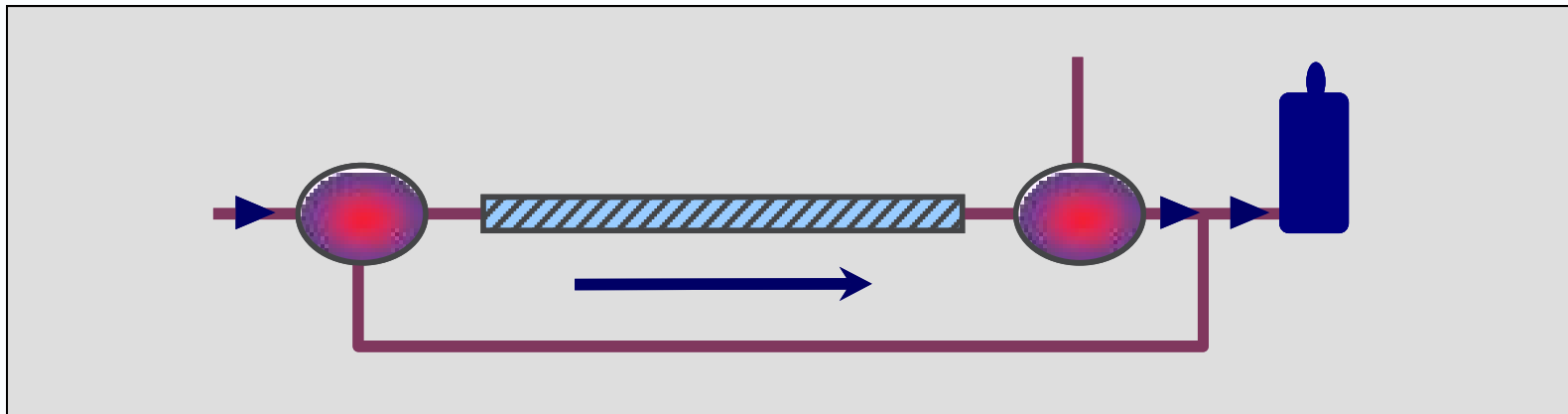
- The rotary valve is switched to the inject position
- Carrier inlet is connected to the sample loop
- Introduces the gas sample to a flowing stream of inert “carrier gas”
- The carrier gas sweeps the sample from the loop and into the front, or inject end, of the separation column, located in an oven operated at 65°C .



# Methane Measurement

## Gas Chromatography FID

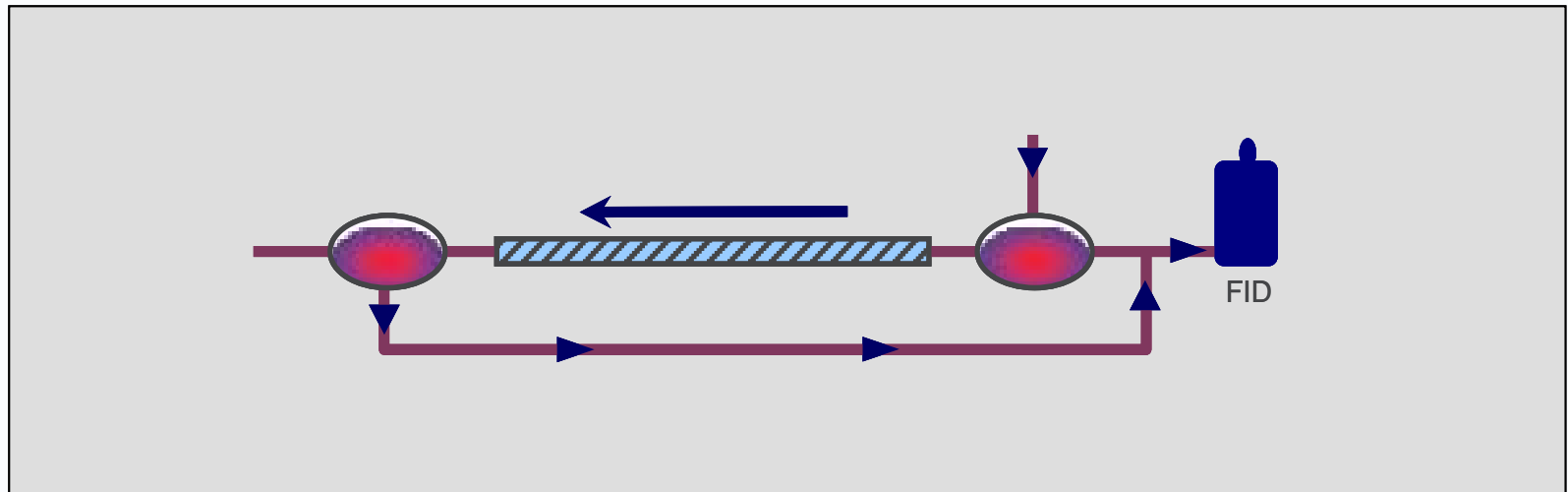
- Methane moves faster than other organic compounds
  - Due to its low molecular weight and high volatility
- First to emerge from the column
- Flows back through the rotary valve to the flame ionization detector, or FID
- Methane peak is detected and measured



# Methane Measurement

## Gas Chromatography FID

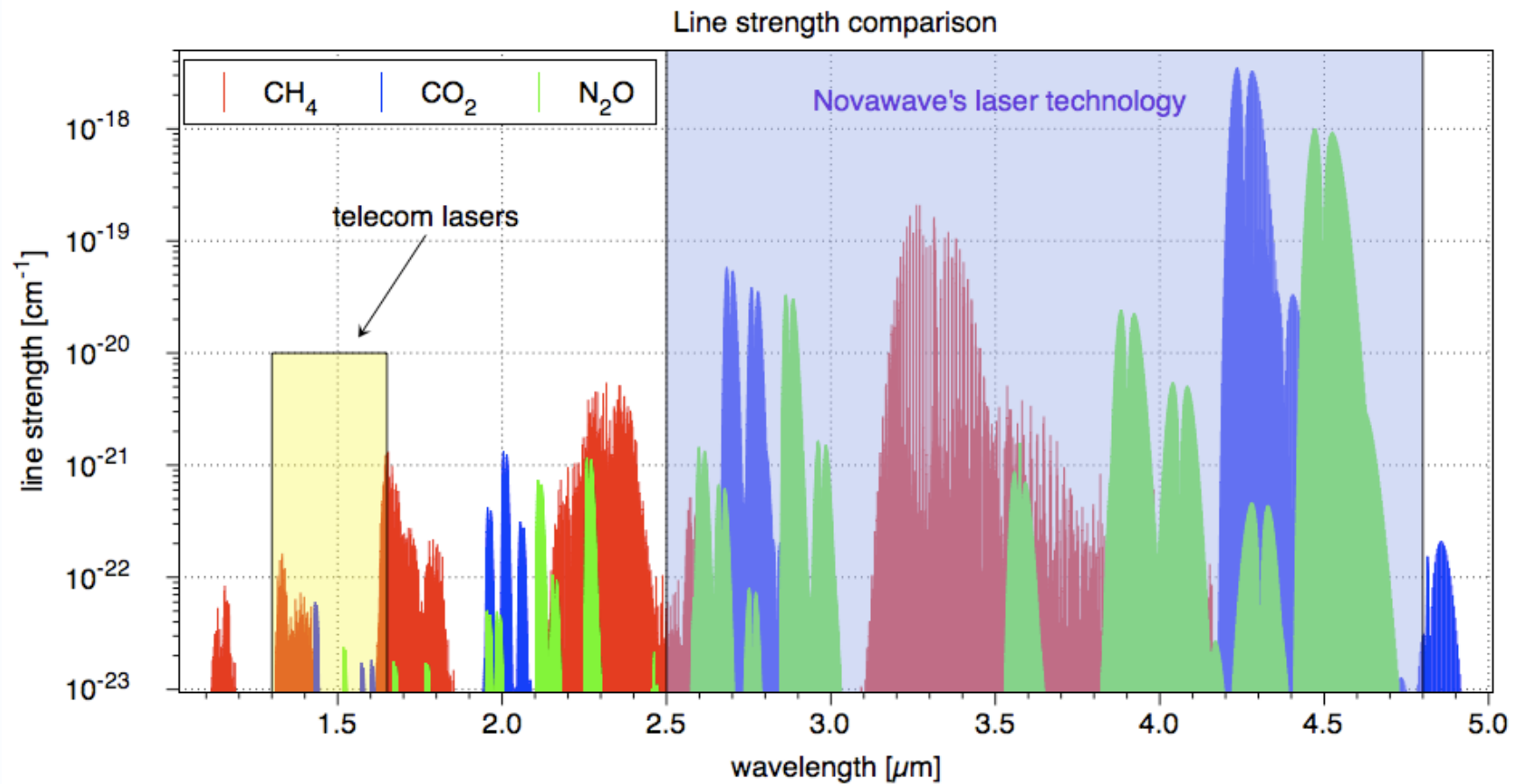
- Direction of carrier gas flow through the column is reversed
- Sample loop has been switched out of the carrier stream and back into the sampling system.
- With the reversal of carrier flow, non-methane hydrocarbons are "back-flushed"
- Carried to the FID for measurement



- Most laser based analyzers utilize the near infrared region at ~1.5 microns
  - Many species do not have lines in NIR limiting applications
  - Ultra-sensitive techniques are required in this region necessitating high power usage
  - 10-10000X less sensitive than MIR region

# Laser-Based Measurement of GHG

Mid-IR absorption intensity is 10-10000x that of commonly used (telecom) near-IR



*Existing MIR lasers are either not readily available, too expensive, or not fieldable*

*What's needed is a low-cost, mass produced MIR laser sensor platform that is intrinsically versatile and robust*

- *Sensitivity*
- *Stability*
- *Specificity*
- *Simplicity*

# Non-Linear Optics (NLO's)

*Frequency converting telecom laser technology to hit the spectral "sweet-spots" from the UV to MIR*

## Methods

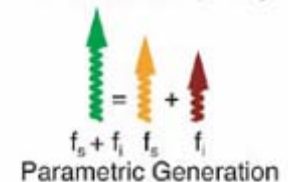
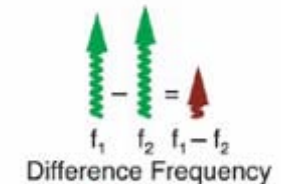
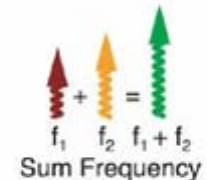
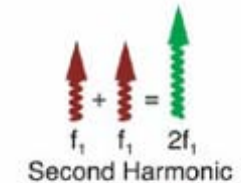
- Difference Frequency Generation (DFG):  $\nu_3 = \nu_1 - \nu_2$
- Sum Frequency Generation (SFG):  $\nu_3 = \nu_1 + \nu_2$
- Harmonic Generation (SHG, THG...):  $\nu_3 = 2\nu_1, 3\nu_1, 4\nu_1$
- Hybrids of the above

*Suitable combinations of the above effectively enable novel new laser systems that access the BEST spectral region for the target of interest*

## Materials

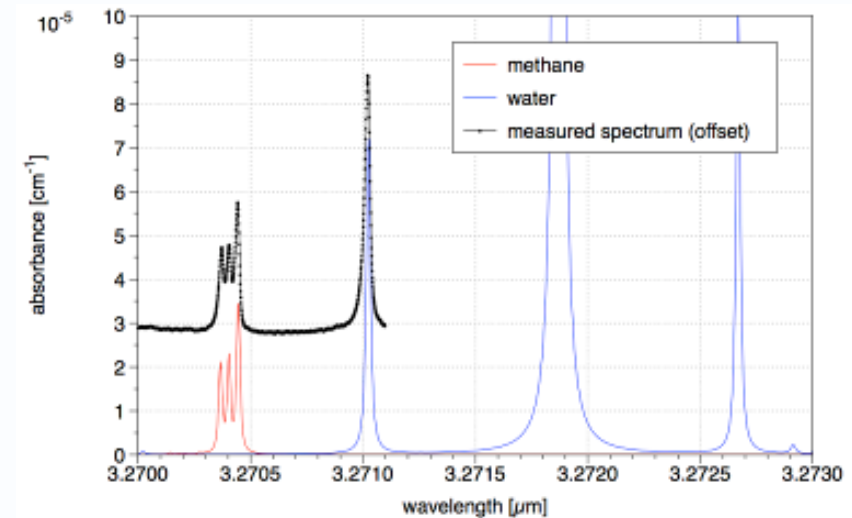
- Bulk Crystals: LBO, BBO, KDP, KTP, LT, LiNbO<sub>3</sub>
- Periodically Poled Media: PPLN, PPKTP, PPXX
- Patterned/Engineered Media: OPGaAs

## Nonlinear Effects



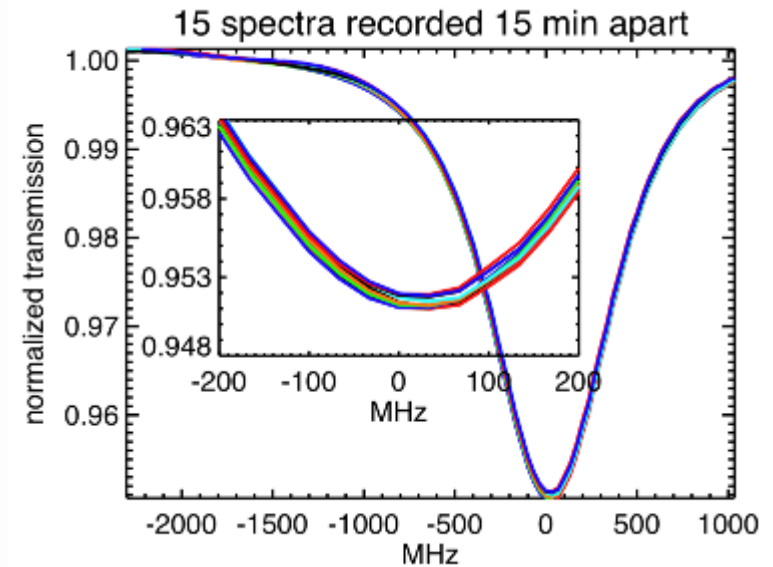
# MIR Lasers: Sensitivity and Specificity

- Approximately 100,000x spectrally narrower than the best NDIR filter
  - Spectral “fingerprints” can be resolved with extremely high specificity and fidelity
  - Interferences eliminated, e.g.  $\text{CH}_4$  vs  $\text{H}_2\text{O}$ ,  $\text{CO}$  vs.  $\text{N}_2\text{O}$ ,  $\text{C}_x\text{H}_y$  vs  $\text{C}_{x-n}\text{H}_{y-n}$
- Single-line resolved absorption/emission provides a highly quantitative deduction of concentrations: ppb to ppt detection limits



# MIR Lasers: Stability

- High fidelity sensing at ppb limits is possible due to the intrinsic stability and narrow linewidth of the laser source
- 15 consecutive methane absorption spectra recorded over a several hour period. Drift of  $\sim 0.0003\text{nm}$  is 20-100x less than the intrinsic absorption linewidth.



# MIR Lasers: Simplicity

- No moving parts
- Room temperature operation
- “Off the shelf” telecom lasers
- Single mode, tunable laser light
- Insensitive to vibration and thermal influences: all fiber-coupled architecture
- Low power consumption, Low thermal load: passive cooling architectures



# Summary



- Provides an immediate, commercially viable means of producing laser-based analyzers for a large range of applications and markets
  - Sensitive
  - Specific
  - Stable
  - Simple
- Current pipeline includes CH<sub>4</sub>, N<sub>2</sub>O, CO<sub>2</sub>, CO

Thank you for your time and attention

Questions?