Greenhouse Gas Measurement Technology

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Agenda

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

Introduction

Greenhouse gases

- Carbon Dioxide (CO_2)
- Methane (CH_4)
- Nitrous Oxide (N_2O)
- Sulfur Hexafluoride (SF6)
- Hydrofluorocarbons (HFC)
- Perfluourocarbons (PFC)

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

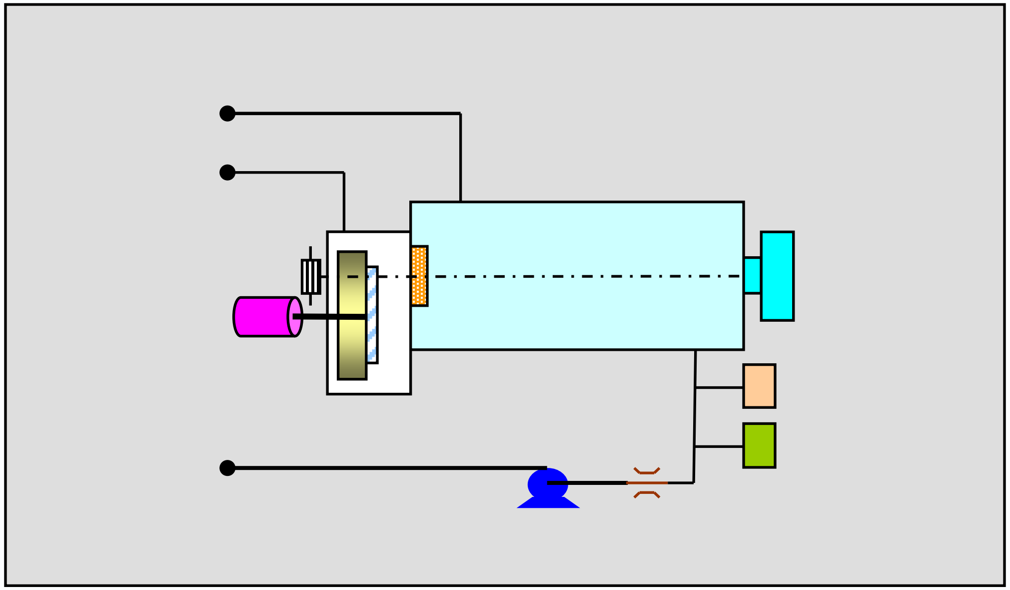
Regulatory

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_2, CH_4, and N_2O
- GHG regulation of stationary sources would be triggered by PSD and Title V

Carbon Dioxide Measurement

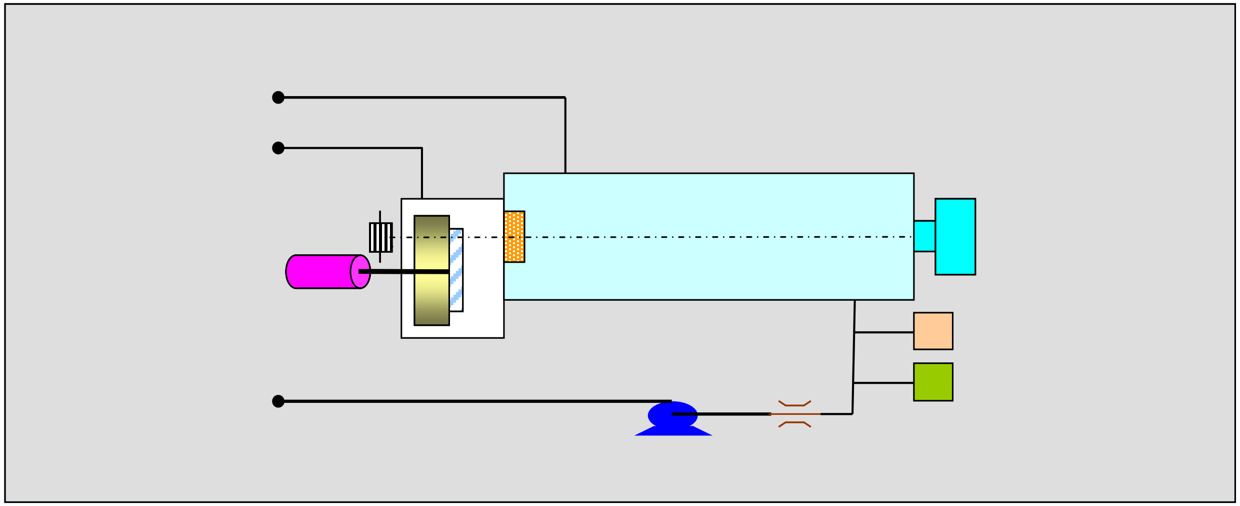
- **Infrared Spectroscopy**
- Carbon dioxide (CO_2) absorbs infrared radiation at a wavelength of 4.26 microns
- Sample is drawn into the instrument and flows through the optical bench
- Radiation from an infrared source is chopped and passed through a rotating optical wheel alternating between sample 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_2 in the sample cell



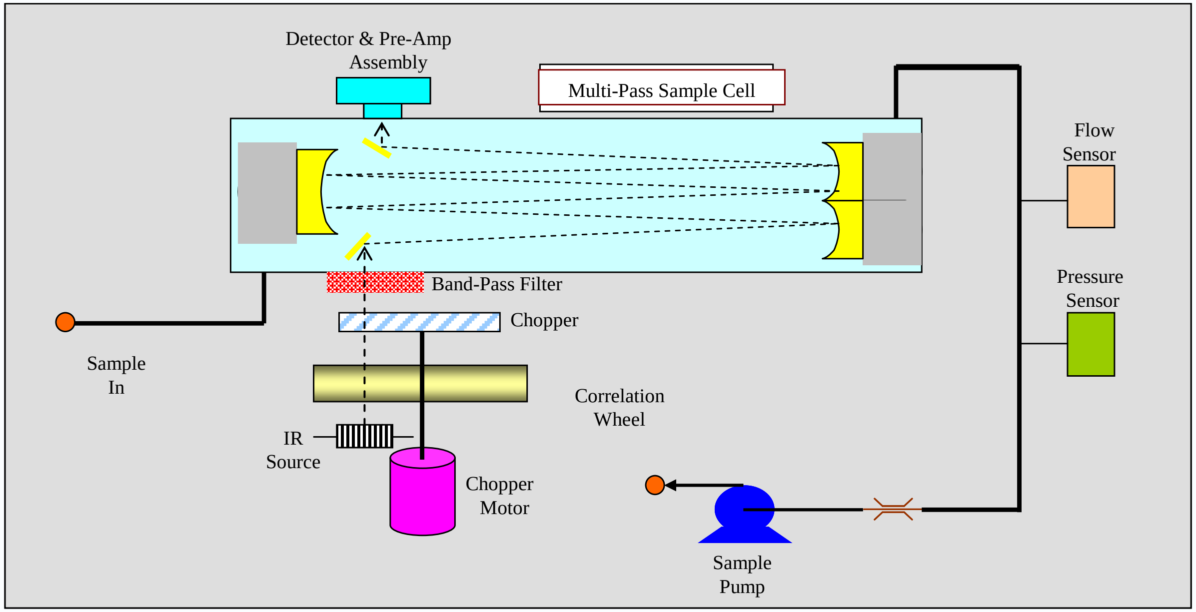
Nitrous Oxide Measurement

Infrared Spectroscopy

•Nitrous oxide (N_2O) absorbs infrared radiation at a wavelength of 4.49 microns

•Sample is drawn into the instrument and flows through the optical bench

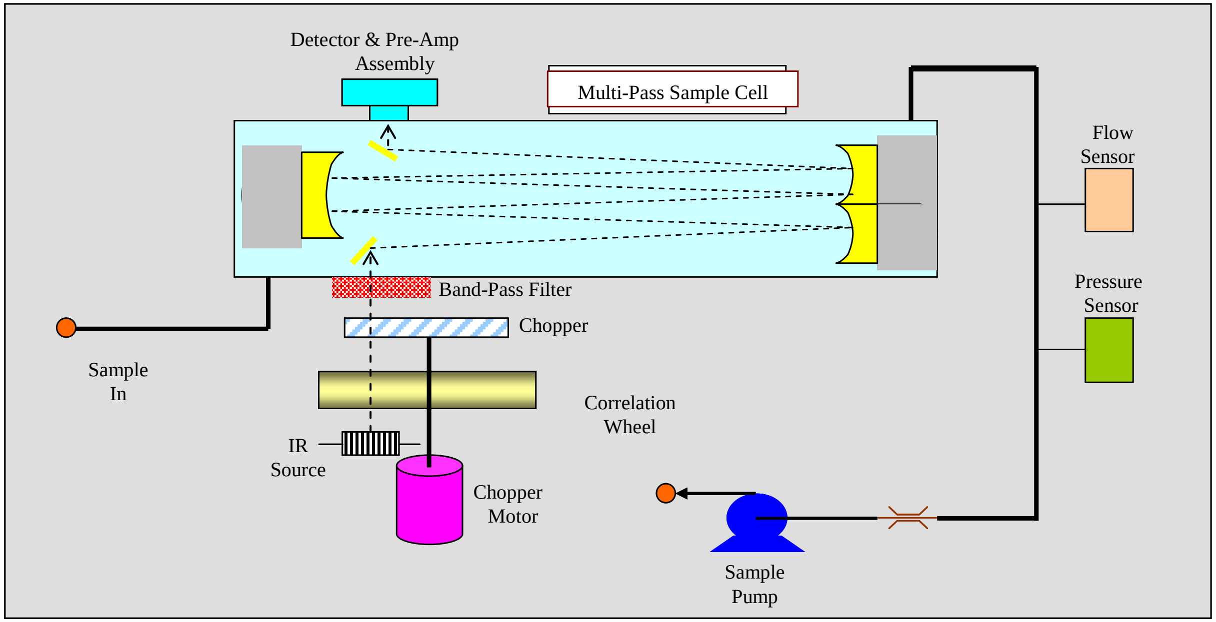
•Radiation from an infrared source is chopped and passed through a rotating optical wheel alternating between N_2O and N_2 gas filters.



Nitrous Oxide Measurement

Infrared Spectroscopy

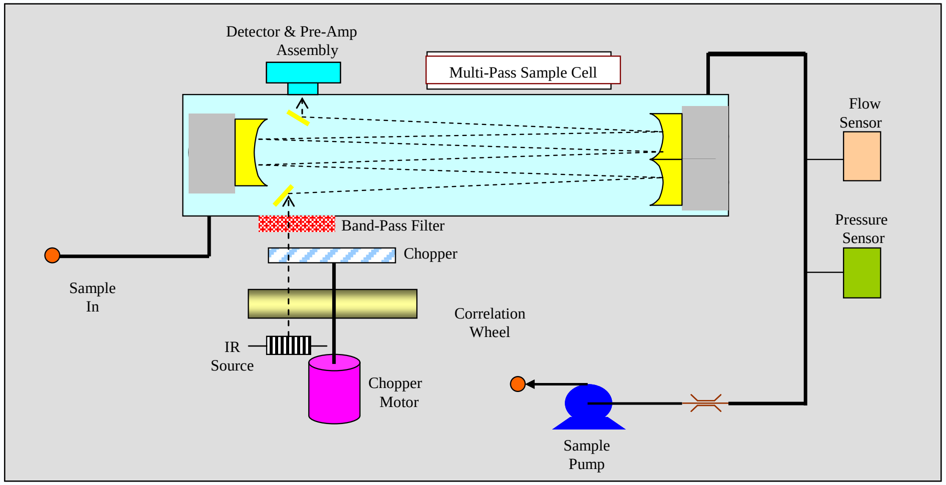
- Radiation passes through a narrow bandpass interference filter
- Radiation then enters the optical bench where absorption by the sample gas occurs
- The infrared radiation then exits the optical bench and falls on an infrared detector



Nitrous Oxide Measurement

Infrared Spectroscopy

- N_2O gas filter acts as a reference beam
  - Cannot be further attenuated by N_2O
- N_2 is transparent to IR radiation
  - Produces a beam which is absorbed by N_2O
- The chopped detector signal is modulated between the filters
  - amplitude related to the concentration of N_2O in the sample cell



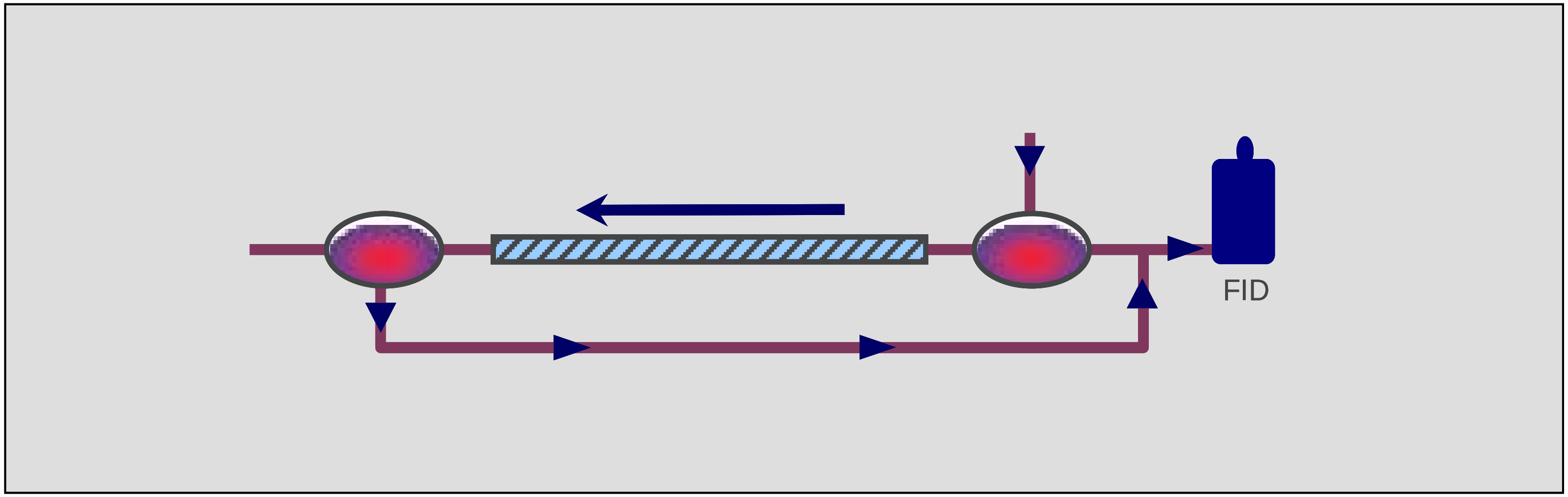
Methane measurement by GC FID

- 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

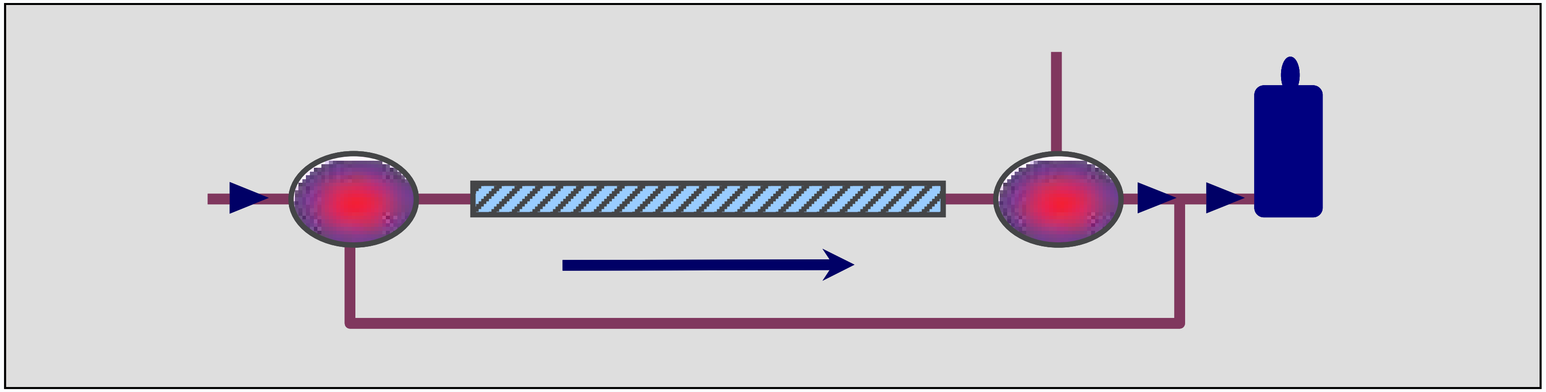
- Between analyses or in standby mode, valve is in the back-flush position
- Sample gas is continuously pulled through the sampling loop



Methane Measurement

Gas Chromatography FID

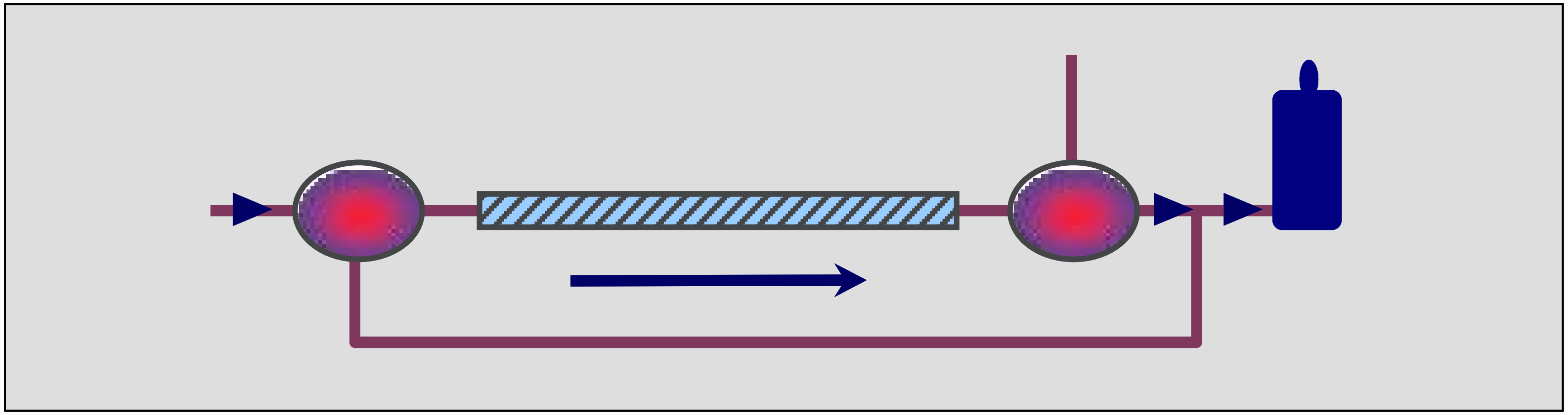
- The rotary valve is switched to the inject position
- Carrier inlet is connected to the sample loop
- Introduces the gas sample to a flowing stream of inert “carrier gas”
- The carrier gas sweeps the sample from the loop and into the front, or inject end, of the separation column, located in an oven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



Methane Measurement

Gas Chromatography FID

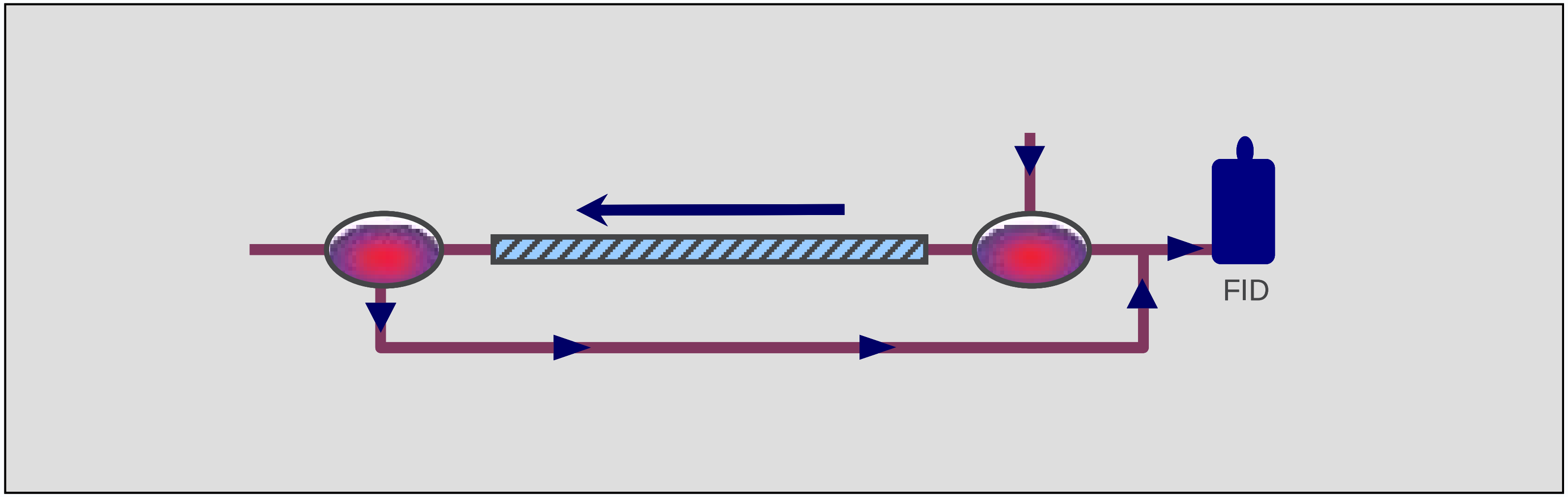
- Methane moves faster than other organic compounds
  - Due to its low molecular weight and high volatility
- First to emerge from the column
- Flows back through the rotary valve to the flame ionization detector, or FID
- Methane peak is detected and measured



Methane Measurement

Gas Chromotography 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

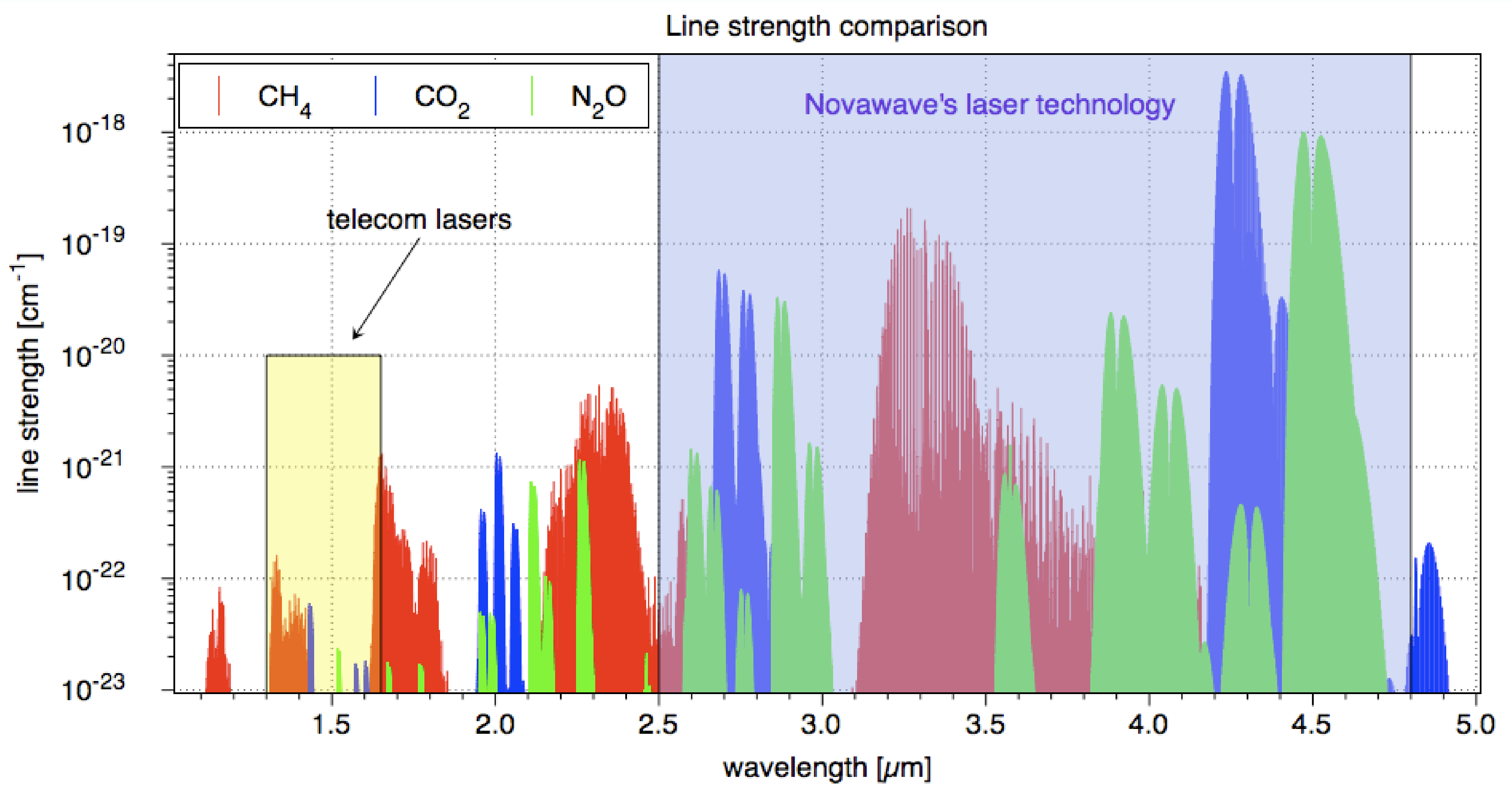


Laser-Based Measurement of GHG

- 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



Laser-Based Measurement of GHG

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

Non-Linear Optics (NLO's)

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

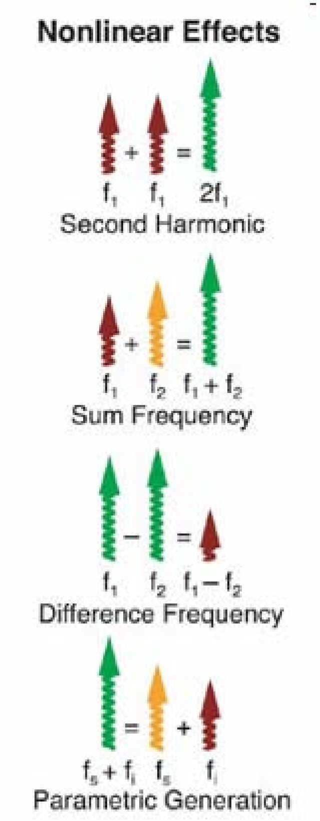
<u>Methods</u>

- Difference Frequency Generation (DFG): $\nu3=\nu1-\nu2$
- Sum Frequency Generation (SFG): $\nu3=\nu1+\nu2$
- Harmonic Generation (SHG, THG…): $\nu3=2\nu1,\ 3\nu1,\ 4\nu1$
- 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

<u>Materials</u>

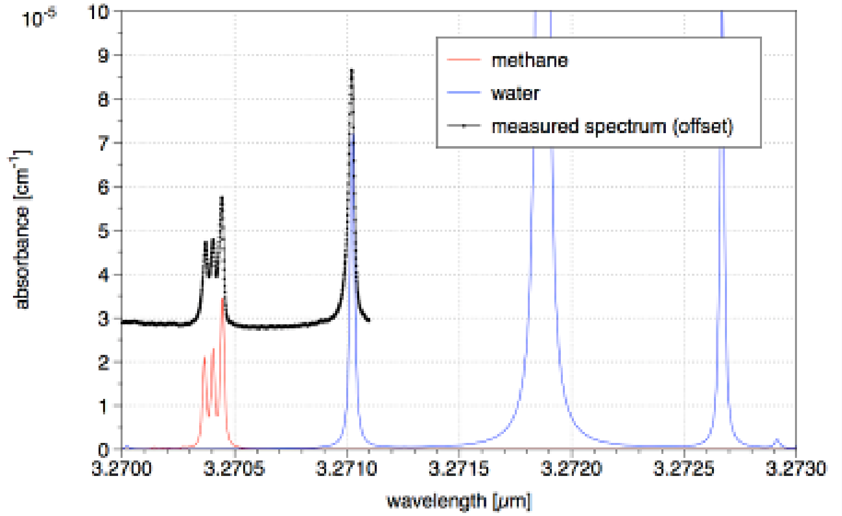
- Bulk Crystals: LBO, BBO, KDP, KTP, LT, LiNbO3
- Periodically Poled Media: PPLN, PPKTP, PPXX
- Patterned/Engineered Media: OPGaAs



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. CH_4 vs H_2O, CO vs. N_2O, C_xH_y vs $C_{x\ n}H_{y\ n}$

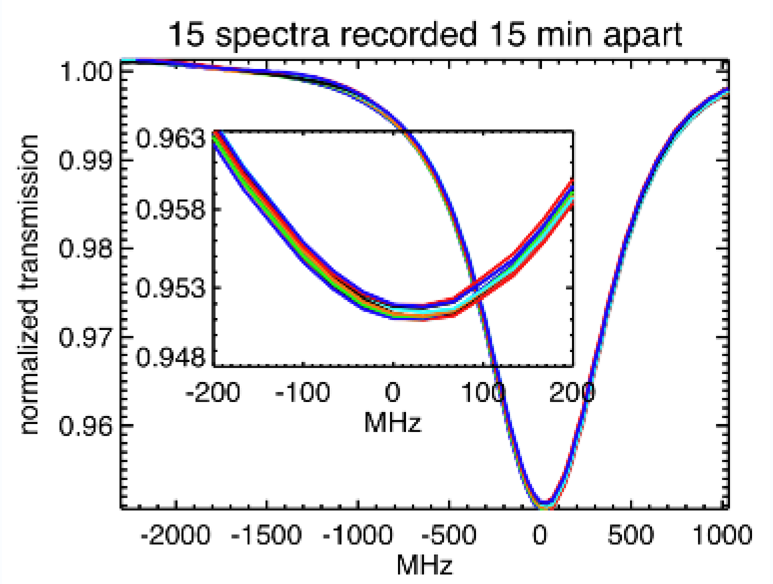
- Single-line resolved absorption/emission provides a highly quantitative deduction of concentrations: ppb to ppt detection limits



MIR Lasers: Stability

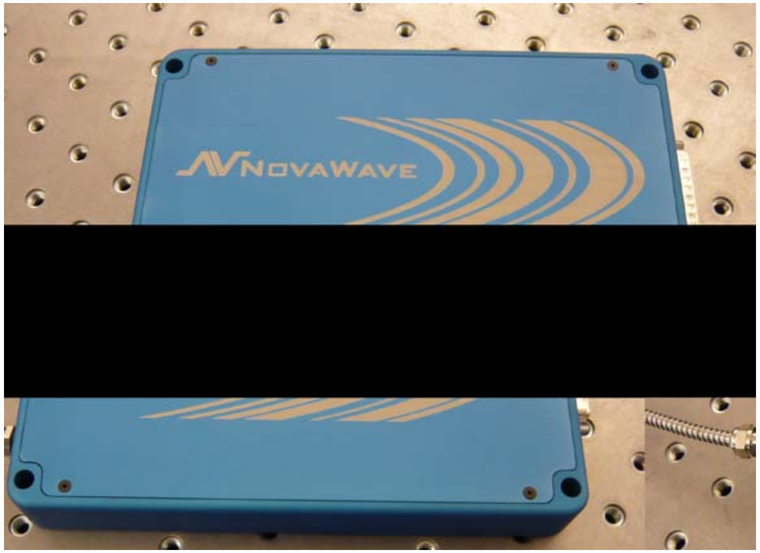
- High fidelity sensing at ppb limits is possible due to the intrinsic stability and narrow linewidth of the laser source

- 15 consecutive methane absorption spectra recorded over a several hour period. Drift of ~0.0003nm 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_4, N_2O, CO_2, CO

Thank you for your time and attention

Questions?