Comparison of FTIR and Diode Laser Based Spectroscopy for Trace Gas Detection

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Motivation

- Why detect methane
  - Pollutant gas, EPA exposure limit
  - NOAA: Study of carbon cycle
  - NASA: detection of methane flux from rice based agroecosystems

- Selection of optimum absorption line
  - Absorption line at $\nu = 3038.5$ cm$^{-1}$ ($\lambda = 3.29$ $\mu$m)
  - Line is not interfered by H$_2$O or CO$_2$ in ambient air
    - Lorentzian profile
  - Isolated spectral line is of interest for laser spectroscopy
  - Line strength sufficient for detection: $S = 8.92 \times 10^{-2}$ cm/mol
  - Readily accessible by mid-infrared sensor
GEISA Methane absorption line at 3038.5 cm$^{-1}$
(30 torr pure methane)
FTIR Technique

- Necessity of a "background spectrum" (no sample in the beam) which is indicative of instrumental and environmental contribution to IR spectrum.
- Transmittance spectrum: \( \%T = \frac{I}{I_o} \)
  - \( I \): Intensity measured with sample in beam
  - \( I_o \): Intensity from background spectrum
- Absorbance spectrum \( A = -\log_{10} T \)

- FTIR parameters for improving SNR
  - \( \text{SNR} \propto \text{Resolution} \)
  - \( \text{SNR} \propto (N)^{1/2} \) \( N \): Number of scans
  - \( \text{SNR} \propto (T)^{1/2} \) \( T \): Acquisition time

⇒ High resolution spectra are noisier than low resolution spectra
⇒ To increase SNR, an increased number of scans is necessary leading to a longer acquisition time
**FTIR Experiment**

- **Nicolet MAGNA IR 760 Spectrometer**
  - Spectral coverage: 400 - 4000 cm\(^{-1}\)
  - Resolution: 0.125 - 32 cm\(^{-1}\)
  - Minimum absorbance detectable: 10\(^{-4}\) - 10\(^{-5}\)
  - Weight: 100 lbs (vol = 0.5 m\(^3\))
  - Price: $75k

- **Experimental conditions**
  - Resolution: \(R = 0.125\) cm\(^{-1}\)
  - Number of scans: \(N = 100\)
  - Acquisition time: \(T = 30\) mn
  - Signal to Noise Ratio: \(\text{SNR} = 30\)

- **Absorption cell**
  - Length: \(L = 15\) cm to fit the spectrometer optical bench
  - Windows: \(D = 38.1\) mm
  - Material - Windows: CaF
    - Body: glass
FTIR of 30 torr pure methane
FTIR 3 torr pure Methane in 760 torr air
DFG Technique

- **DFG pump source requirement**
  - Methane absorption line: $\nu = 3038.5 \text{ cm}^{-1}$, $\lambda_i = 3.29 \mu\text{m}$
  - DFB Laser diode source: $\lambda_s = 1083 \text{ nm}$
  - Phase matching condition: $k_p = k_s + k_i \Rightarrow \lambda_p = 814.8 \text{ nm}$

- **PPLN crystal**

  - Quasi-phase matching condition $\Rightarrow \Lambda$ : Grating period
    \[
    \Lambda = \frac{2 \pi}{k_p - k_s - k_i} = \frac{1}{n_p - \frac{n_s}{\lambda_p} - \frac{n_i}{\lambda_i}} = 22.3 \mu\text{m}
    \]

  - Crystal with multiple grating periods from 21.5 to 22.4 with increments of 0.1 $\mu\text{m}$ is convenient

**Diagram:***

- Signal: SDL 1083 nm
- Pump: SDL 814.8 nm
- PPLN 22.3 $\mu\text{m}$
- $\lambda_i = 3.29 \mu\text{m}$
- Idler
DFG Experiment

- **DFG setup**
  - Spectral coverage: 1 cm\(^{-1}\), limited, target specific
  - Resolution: 0.5 - 20 Mhz
  - Minimum absorbance: 10\(^{-6}\)
  - Weight: 50 lbs (vol: 0.005 m\(^3\)), semi-portable
  - Price: $50k

- **Experimental conditions**
  - Number of sweeps: 10 to 1000
  - Acquisition time: T = 0.1 sec
  - Signal to Noise Ratio: SNR = 300

- **Absorption cell**
  - Same as for FTIR experiment
DFG of 3 torr pure methane
DFG vs FTIR at low pressure

Transmission (%)

Wavenumber (cm⁻¹)

FTIR (30 torr)

DGF (3 torr)
Comparison of DFG and FTIR characteristics

<table>
<thead>
<tr>
<th></th>
<th>FTIR spectrometer</th>
<th>DFG based sensor</th>
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</thead>
<tbody>
<tr>
<td>Spectral coverage</td>
<td>Typically, 400 - 4000 cm(^{-1})</td>
<td>Target specified, 1 cm(^{-1})</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.125 to 32 cm(^{-1})</td>
<td>0.5 Mhz - 20 MHz</td>
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<tr>
<td>Minimum absorbance</td>
<td>(10^{-4}) - (10^{-5})</td>
<td>(10^{-6})</td>
</tr>
<tr>
<td>detectable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acquisition time</td>
<td>Minutes</td>
<td>0.1 sec</td>
</tr>
<tr>
<td>Power consumption</td>
<td>60 W</td>
<td>50 W</td>
</tr>
<tr>
<td>Instrument dimension and weight</td>
<td>0.5 m(^3); 110 lbs</td>
<td>0.05 m(^3); 50 lbs</td>
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<tr>
<td>Price</td>
<td>75 k$</td>
<td>50 k$</td>
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</tbody>
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