Development and Application of a Real-Time Optical Sensor for Atmospheric Formaldehyde

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- Motivation and Technology Issues
- Infrared Diode Laser-based Gas Sensors
- Formaldehyde Concentration Measurements
- Summary and Outlook

Wide Range of Gas Sensor Applications

- Urban and Industrial Emission Measurements
  - Industrial Plants - Fenceline perimeter monitoring
  - Combustion Sources
  - Automobile
- Rural Emission Measurements
  - Agriculture
- Environmental Monitoring
  - Atmospheric Chemistry
  - Volcanic Emissions
- Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Life Support
- Chemical Analysis and Industrial Process Control
  - Petrochemical and Semiconductor Industry
- Medical Diagnostics
### Air Composition

<table>
<thead>
<tr>
<th>Main Components</th>
<th>Trace Components</th>
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<tbody>
<tr>
<td>Nitrogen 78%</td>
<td>Methane 1.7 ppm</td>
</tr>
<tr>
<td>Oxygen 21%</td>
<td>CO 0.4 ppm</td>
</tr>
<tr>
<td>Water 0.8%</td>
<td>N₂O 0.3 ppm</td>
</tr>
<tr>
<td>CO₂ 0.03%</td>
<td>O₃ 0.03 ppm</td>
</tr>
<tr>
<td></td>
<td>H₂CO 0.001 ppm</td>
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<td>...</td>
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</table>

### Existing Methods for Trace Gas Detection

#### Non-Optical
- Mass Spectroscopy
- NMR
- Chemical
- Electro Chemical

- Gas Chromatography
- Galvanic
- Fourier Transform
- Gas Filter Correlation

#### Optical
- Non-Dispersive
- Dispersive

- Microwave Spectroscopy
- Laser Spectroscopy
Absorption Spectroscopy

**Beer – Lambert’s Law**

\[ I(v) = I_0 \cdot e^{-\alpha(v) \cdot P_s \cdot L} \]

- \( \alpha(v) \): absorption coefficient [cm\(^{-1}\) atm\(^{-1}\)]
- \( L \): path length [cm]
- \( v \): frequency [cm\(^{-1}\)]
- \( P_s \): partial pressure [atm]

**Molecular Absorption Coefficient**

\[ \alpha(v) = C \cdot S \cdot g(v - v_0) \]

- \( C \): total number of molecules of absorbing gas/atm/cm\(^3\)
  [molecule/cm\(^3\) atm\(^{-1}\)]
- \( S \): molecular line intensity [cm \cdot molecule\(^{-1}\)]
- \( g(v - v_0) \): normalized lineshape function [cm]. (Gaussian, Lorentzian, Voigt)

Difference Frequency Generation

**Nonlinear Crystal** with \( \chi^{(2)} \)

\[ \omega_1 = \omega_p - \omega_s \]

**Mid-IR Power**:

\[ P_1 = C \cdot P_{\text{PUMP}} \cdot P_{\text{SIGNAL}} \cdot L \cdot h(\gamma_H) \]

- \( C = (\epsilon \cdot d_{\text{eff}})^2 \)
- \( \mu = k_s / k_p \), \( \zeta = L/b \)

**Example**: for PPLN at 3.5 \( \mu \)m

- \( C \sim 450 \mu W / \text{cm W}^2 \)
- \( \sim 3 \mu W \) for 6mW and 540mW LD pump sources
Design Features of CW DFG Sensor

- Adequate Mid-infrared DFG Power
- High Sensitivity (ppb concentrations)
- High Selectivity (<30 MHz)
- Wavelength Tunable (Single or Multiple Trace Gases)
- Fast Data Acquisition and Analysis
- Room Temperature
- Non-invasive, Point or Remote Monitoring
- Compact, Lightweight and Robust
- Power Efficient
- No Consumables, Low Maintenance and Cost Effective

Diode Laser Based H₂CO Sensor

[Diagram showing a diode laser-based H₂CO sensor with various components such as DFB-DL, DBR-DL, 10 Fiber Amplifier, Er3⁺ Fiber Amplifier, PPLN, and a Ge-filter.]
H₂CO Calibration of Dual Beam DFG Sensor

![Image of the H₂CO Calibration setup]

- **7.26 ± 4.7 ppb**
  - (4.5% lower)
- **58.2 ± 0.4 ppb**
  - (8% lower)
- **31.8 ± 0.8 ppb**
  - (10% lower)
- **19.3 ± 0.8 ppb**
  - (12% lower)
- **7.1 ± 0.17 ppb**
  - (pseudo-ambient)

**Parameters:**
- Using **S = 5.44 × 10⁻²⁰ cm mol⁻¹**
- **P = 40 torr**
H$_2$CO Detection in Ambient Air at 3.53 $\mu$m

![Graph showing transmission data with wavenumbers and concentrations.]

Concentration: $(8.49 \pm 0.57)$ ppbv

Goodness of fit:

$\chi^2 = 3.4272 \times 10^{-10}$

$\sigma = 1.852 \times 10^{-5}$

9 Day H$_2$CO Detection at 3.53 $\mu$m in Houston

![Graph showing H$_2$CO concentration over 9 days with PFSIA measurements and rain periods.]

11/29/99 to 12/8/99
Map of the Greater Houston Area

Texas Natural Resources Conservation Commission Monitoring Site, Houston
Nine Days of Continuous HCHO Data

Rice University Data (Deer Park, Texas)

Five Days of Continuous Channel View HCHO Data
**HCHO Data Comparison TTU-Rice**

![Graph comparing HCHO concentrations between TTU and Rice](image)

**Summary**

- **Diode Laser Based Trace Gas Sensors**
  - Compact, tunable, robust (alignment insensitive), fieldable
  - High sensitivity (<2×10^-4 to 10^-5) and selectivity (10–300 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: \( \text{H}_2\text{CO}, \text{NH}_3, \text{CH}_4, \text{NO}_2, \text{N}_2\text{O}, \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{NO}, \text{HCl}, \text{SO}_2, \text{C}_2\text{H}_5\text{OH}, \text{isotopic species of } ^{12,13}\text{C}, ^{16,17,18}\text{O}, ^{35,37}\text{Cl} \)

- **Applications in Trace Gas Detection**
  - Environmental monitoring: \( \text{H}_2\text{CO}, \text{CO}, \text{CH}_4 \) (EPA, NASA, NCAR, NOAA,)
  - Industrial process control and chemical analysis
  - Medical diagnostics (NO, CO, CO\(_2\), NH\(_3\))

- **Future Directions**
  - Fiber lasers and amplifiers
  - Longer mid-IR wavelengths with orientation patterned GaAs and QC lasers, detection of complex molecules
  - Cavity enhanced and cavity ringdown spectroscopy