High-resolution Difference-frequency Laser Spectroscopy
for Environmental Applications

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OUTLINE

⇒ Motivation
⇒ Infrared spectrometer based on laser difference-frequency generation
⇒ Spectroscopic performances
⇒ Trace gas measurements by laser absorption spectroscopy
⇒ Conclusion & outlook
Motivation

- Spectroscopic investigation of molecular line parameters;
- Environmental monitoring of trace gas, in particular volatile organic compounds, by laser absorption spectroscopy
Laser difference-frequency spectrometer

Spectral coverage

3.5-6.5 μm (DFG in QPM-PPRTA and AgGaS₂)
8-19 μm (DFG in GaSe)

cw power conversion

10-500 μW/(W²·cm)

Spectral purity of the DFG source

< 1 MHz (~ 10⁻⁴ cm⁻¹)
FT-IR Spectrum of $C_2H_2$ (Q branch of the $v_4$ band)

DFG Spectrum of $C_2H_2$ in the $v_5$ band

Transmission (%)

Wavenumber (cm$^{-1}$)

Resolution:
- FT-IR: 0.2 cm$^{-1}$
- DFG: ~0.002 cm$^{-1}$
High-resolution DFG spectrum of $\nu_7$ C$_2$H$_4$ (@ 3.1 mbar & L=10 cm)
DFG spectrum of $\text{C}_2\text{H}_4$ of the $v_7$ band

The Geisa-based simulated spectrum

Frequency (cm$^{-1}$)
High-resolution Laser DFG Absorption Spectra
The concentration of the absorbing species \( C \) is given by:

\[
C = \ln \left( \frac{I_0}{I} \right) (\omega) (\sigma_S, \% (v, \ell) (l))
\]

Then the concentration:

\[
I(v) = I_0 \exp (\omega) (\sigma_S, \% (v, \ell) (l))
\]

The Beer's Law:

Laser Absorption Spectroscopy

Trace Gas Detection Using
High-resolution DFG spectra of ethylene of the $v_7$ band
Absorption line selection

- **Strong** for highly sensitive detection
- **Isolated** for highly selective measurement

Selecting a strong absorption line for high sensitivity which at the same time should be isolated from interfering lines due to other gas species or from the same species.
FT-IR absorption spectrum of C$_2$H$_2$ @ ~40 mbar (R=2 cm$^{-1}$ with 64 scans)
The inset spectrum was obtained @ ~3 mbar (R=0.2 cm$^{-1}$ with 16 scans)
(q) using $\nu_5$-D11 and $\nu_5$-D13 lines

77 ppm CH$_2$ measurement
Simulated spectra of CO$_2$ and C$_2$H$_2$ @ atmospheric pressure
C²H₂ trace at atmospheric pressure

Spectrum of the $\nu$ ($R(9)$ transition of $\nu$)
Spectrum of calibrated 1% CO$_2$ and C$_2$H$_2$ mixture around 679.5 cm$^{-1}$ @ atmospheric pressure
Comparison of $\text{C}_2\text{H}_2$ trace detection using the P(21), Q(11) and R(9) lines of the $\nu_5$ band

<table>
<thead>
<tr>
<th>Rotational assignment</th>
<th>Transition frequency</th>
<th>Line strength</th>
<th>Absorption coefficient</th>
<th>Measured concentration-path</th>
<th>Pressure (Torr)</th>
<th>MDC* (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_5\text{ band})</td>
<td>(cm$^{-1}$)</td>
<td>(cm/mol.)</td>
<td>(ppm$^{-1}$ m$^{-1}$)</td>
<td>(ppm m)</td>
<td></td>
<td></td>
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<tr>
<td>P (21)</td>
<td>679.7095</td>
<td>1.32E-19</td>
<td>6.65E-4</td>
<td>96.1</td>
<td>760</td>
<td>84.7</td>
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<td>Q (11)</td>
<td>729.7380</td>
<td>1.08E-18</td>
<td>2.68E-2</td>
<td>7.7</td>
<td>126</td>
<td>2.4</td>
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<tr>
<td>R (9)</td>
<td>752.6589</td>
<td>6.82E-19</td>
<td>2.88E-3</td>
<td>43.2</td>
<td>760</td>
<td>20.7</td>
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</tbody>
</table>

* MDC is the 3$\sigma$-detection-limited minimum detectable concentration in ppb (part per billion, 10$^{-9}$ atm.) using an optical path of 100-m.
Figure 1: Atmospheric absorption spectrum and benzene spectrum. The spectrum shows bands for CO₂ and H₂O, with specific wave number values for v₁₄ and v₄.
DGF spectrum of C$^6$H$_6$ in the $^4\Pi$ band
**Figure 5**

- R(9) of the $\nu_4 + \nu_20 - \nu_20$ band
- R(6) of the $\nu_4$ band
- Residual

$173.1$ ppm $C_6H_6$ in $40$ mbar air

- Voigt line-shape fit
Pressure dependence of the linewidth of the $C_6H_6$ line of the n4 R(6) branch @ 676.6258 cm$^{-1}$

Preliminary result: $\gamma_{\text{air}}$ (FWHM) = 0.23855 cm$^{-1}$/atm @ 291 k

$\gamma_{\text{air}}$ (FWHM) = 2.3855E-4 cm$^{-1}$/mbar @ 291 k
SUMMARY

Laser absorption spectroscopy for environmental applications

⇒ High sensitivity and selectivity in the fundamental infrared region.
⇒ Measurements of trace amounts of various hydrocarbons: acetylene ($v_5$ band), benzene ($v_4$ band) and ethylene ($v_7$ band) with a minimum detectable concentration of <ppm.

OUTLOOK

In situ and real time BTEX detection by means of diode laser based DFG employing QPM-GaAs crystal for the 8-16 μm region.