Sensor Development: Metrology Tools for Climate Science

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Our approach

- Both *in situ* monitoring and remote sensing require cutting-edge spectroscopic measurements.

- We develop novel techniques which allow for enhanced:
  - Spectral coverage
  - Portability
  - Sensitivity
  - Accuracy
  - Speed
  - Selectivity
Outline

• A series of new spectroscopic techniques
  • They offer a range of complexity, speed, and sensitivity

• Specifically I will discuss:
  • Photoacoustic sensor
  • Ultrasensitive cavity ring-down instruments
  • Multiplexed detection with optical frequency combs
NIST photoacoustic sensor

- Designed for routine monitoring of CO$_2$ concentrations

- Will be placed on the top of the Admin. Building at NIST (101).

Figure from HDR Architecture, Inc.
**Photoacoustic spectroscopy (PAS)**

- Zero background
- Optically broadband
- Relatively easy to implement
- High sensitivity
  - signal scales with laser power
- Wide dynamic range
Photoacoustic spectrometer at 1.6 µm

- Allows for routine, automated measurements of ambient CO$_2$
- Uncertainty of only 0.8 ppm (0.2%)

New 2 µm sensor

- Moved to 2 µm to probe stronger CO$_2$ transitions
  - Able to utilize recently developed laser technology
- Signal-to-noise ratios of ~14,000:1 for CO$_2$ at ambient levels
- Allows for simultaneous humidity measurements with the same laser
Future directions for the PAS instruments

• Dual species PAS instrument
  – Use fiber switches to probe numerous species simultaneously
  – Potential targets include CO$_2$, H$_2$O, NH$_3$, and CH$_4$ (and their isotopologues)

• Mid-infrared PAS
  – Would allow us to probe CH$_4$ and C$_2$H$_6$ simultaneously
  – Allows for source attribution of CH$_4$ emissions
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Cavity ring-down spectroscopy (CRDS)

Advantages:
• High effective pathlength and sensitivity
• Insensitive to laser intensity noise
• Small sample volume
The problem

• To record a spectrum you need to tune the laser frequency
• This generally requires thermal or mechanical tuning
  • This is usually non-linear and very slow
• Things are even more difficult with cavity-enhanced spectroscopy (discrete frequencies)
Frequency-agile, rapid scanning (FARS) spectroscopy

Method:
- Use waveguide electro-optic phase-modulator (EOM) to generate tunable sidebands
- Drive PM with a rapidly-switchable microwave (MW) source
- Fix carrier and use ring-down cavity to filter out all but one selected side band

Advantages:
- Overcomes slow mechanical and thermal scanning
- Links optical detuning axis link to radio-frequency (RF) standards
- Wide frequency tuning range (> 130 GHz = 4.3 cm⁻¹)

FARS operating principle

\[ \omega_c + \delta \]

\[ \omega_c + \delta + \omega_f \]

\[ \omega_c + \delta + 2\omega_f \]

cavity resonances

frequency scanning

Very high acquisition rates: scanning
Spectra of entire absorption bands

2 THz wide spectra recorded in 45 minutes

425 ppm of CO$_2$ in air

ECDL grating moved every 12 GHz

Each point is the average of 100 RDs
Lower finesse = faster rates

Finesse = 20,000
RD acq. rate = 8 kHz
$\sigma_v/\tau = 0.008 \%$
NEA = $1.7 \times 10^{-12}$ cm$^{-1}$ Hz$^{-1/2}$

Finesse = 60
RD acq. rate = 5 MHz
$\sigma_v/\tau = 4 \%$
NEA = $1.9 \times 10^{-8}$ cm$^{-1}$ Hz$^{-1/2}$

What if I want to scan faster?

• Entirely limited by the slow grating tuning

• So use higher bandwidth EOMs to reduce the number of grating steps
Even faster rates

Use recently developed W-band modulators (bandwidth up to 300 GHz!)

Image from Phase Sensitive Innovations
Even faster rates: single grating position

Allows for a 130 GHz ($4.3 \text{ cm}^{-1}$) to be recorded in 3 s.
Even faster rates: grating tuning

(30012) $\leftrightarrow$ (00001) CO$_2$ band

$1/c\tau$ ($10^{-6}$ cm$^{-1}$)

Detuning (THz)
What if I want higher sensitivity?

- To reduce $1/f$ noise, we want to make the measurement away from DC.
- Also need to rapidly compare ring-down time constants at different wavelengths.
Improving the sensitivity: Heterodyne measurements

- To do this we adapted the approach of Ye and Hall

APD

High Finesse Cavity

Heterodyne measurements: Our approach

- Replace their two AOMs with a single EOM
- This reduces the complexity and enables rapid scanning

Heterodyne measurements: Reaching the quantum-noise limit

- Utilized both a traditional InGaAs detector and an APD
- Able to reach the quantum-noise limit with the APD
- The traditional InGaAs allows for an NEA of $6 \times 10^{-14} \text{ cm}^{-1} \text{ Hz}^{-1/2}$
## Most sensitive spectrometers

<table>
<thead>
<tr>
<th>Technique</th>
<th>Ref.</th>
<th>Sensitivity (cm(^{-1}) Hz(^{1/2}))</th>
<th>Laser</th>
<th>Tuning range (nm)</th>
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<td>NICE-OHMS</td>
<td>Ye et al.</td>
<td>1E-14</td>
<td>cw-Nd:YAG</td>
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<tr>
<td>NICE-OHMS</td>
<td>Ehlers et al.</td>
<td>6E-12</td>
<td>Fiber laser</td>
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</tbody>
</table>

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Heterodyne measurements: Rapid scanning

- Able to record a 26 GHz-wide spectrum in 17 ms with 50 GS/s AWG
- Observed a weak CO$_2$ hot band transition (3.5E-25 cm molec.$^{-1}$) in an air sample

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What if I don’t want to scan?

• Then multiplex!
Multiplexed measurements: OFCs

OFCs have been used with a variety of detection schemes for spectroscopic measurements.

**Dispersive (VIPA)**

**Fourier Transform**

**Multiheterodyne**
Mode-locked femtosecond OFCs

Advantages:
- Wide bandwidth (octave-spanning)
- Can be self-referenced (absolute freq. axis)

Disadvantages:
- Essentially fixed repetition rate
- Low power per tooth (nW to µW)
- Large and expensive
An alternate approach: electro-optic modulators

Ideal for targeted measurements of selected species

Dual-drive MZM allows for power-leveling of the comb

Variable pitch

Pitch can be changed in <100 µs

Optical Power (10 dB/div.)

Detuning (GHz)

Multiheterodyne spectroscopy

Common mode (no need for phase locking)

Referencing

Multiheterodyne spectra

Acquired in 30 s (average of 10,000 spectra)

Where are we headed?

- The mid-infrared
- Probing the strongest molecular transitions allows for the lowest detection limits
Cavity ring-down spectroscopy in the mid-IR

- Instrument is up and running!

Detection limit of 3 ppt for $N_2O$
Conclusions

- Presented several new techniques for rapid, ultrasensitive detection of GHGs

  - Photoacoustic spectroscopy (PAS)
    - Relatively simply instrument allows for routine sensing

  - Frequency-agile, rapid scanning (FARS) spectroscopy
    - Use an EOM to step scan the laser frequency
    - Scanning rates limited only by the cavity response time

  - Heterodyne-detected cavity ring-down spectroscopy (HD-CRDS)
    - Make the measurement well above DC
    - Leads to quantum-noise-limited sensitivity

  - Multiheterodyne spectroscopy with EOM-generated optical frequency combs
    - Allows for multiplexed detection of several trace gases
    - Far lower costs and complexity than with femtosecond lasers
    - Inherently common-mode
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