OH DETECTION USING OFF-AXIS INTEGRATED CAVITY OUTPUT SPECTROSCOPY (OA-ICOS)

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Motivations

Why detect OH?

OH plays a critical role in atmospheric chemistry due to its high reactivity with chemical species such as volatile organic compounds (VOCs) and greenhouse gases (GHGs):

- Air quality impact
- Climate changes investigation

Need an adapted system that allows:

- Real time measurement (short OH life time ≤ 1 sec)
- High selectivity (interference-free from atmospheric H₂O, CO₂)
- High sensitivity (low OH concentration 10⁶ ∼ 10⁸ OH.cm⁻³)
- High spatial resolution (compact setup for in field measurements)
Outline

1 Introduction
   - Integrated Cavity Output Spectroscopy
   - ICOS expression
   - Off-Axis coupling to ICOS

2 Experiment details
   - Setup design
   - Calibration
      - Normalisation
      - ASE
      - Calibration
      - Validation
   - Improvement: Laser Amplitude Stabilization

3 Results and Outlook
   - Noise Equivalent Absorption Sensitivity
   - OA-ICOS system performances
In a typical Fabry-Perot cavity, the transmitted intensity, $I_T$, is calculated as the sum of the leaking radiations from Beer-Lambert law [1,2]. As Mie and Rayleigh scattering don’t occur in our case: $I = I_0 \times e^{-N\sigma(\lambda) \times L}$


In a high finesse optical cavity, the light trapped inside can make a great number of round-trips between the cavity mirrors.
Integrated Cavity Output Spectroscopy expression:

\[
I_T(\sigma(\nu)) = \sum_i I_i(\sigma(\nu))
\]

Molecule concentration

Absorber cross section from HITRAN database

Cavity length

Spectra measurement

Reflectivity: Calculated from calibration
**Introduction**

Off-Axis coupling to ICOS

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**Off-Axis ICOS**

An on-axis light injection will excite the fundamental $TEM_{(0,0)}$ modes, while high orders $TEM_{(m,n)}$ modes will be excited in the case of off-axis injection [3].

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Spectra SNR depends on the coupling to the cavity
Experiment details

Setup design

OA-ICOS applied to OH detection

Motivations
Outline of talk
Introduction
ICOS
ICOS expr.
Coupling
Exp. Details
Setup
Calibration
Normalisation
ASE
Validation
Amp. Stabilization
Results
NEAS
OA-ICOS perf.
Conclusion & Perspectives
Thanks

[Diagram of experimental setup]

Pure H₂O vapor
2.45 GHz Discharge
Pressure Gauge
Pump
PZT

Detector

L = 50 cm

M₁ & M₂:
R > 99.98%
R₀ = 1 m

Noise Eater TEM Messtechnik GmbH

Isolator
Optical Splitter
Collimator

AOM

Laser amplitude Stabilization

1434.35 nm

DFB

DRIVER + TEC

GBF

10 Hz
1 Vpp

Acquisition
The laser frequency is scanned at a rate of 10 Hz with a peak-to-peak amplitude of 1.00 V, allowing a scan over 1 cm$^{-1}$ around 6965.1939 cm$^{-1}$ to cross the OH transition line Q(2,5f) and the H$_2$O lines$^a$ near 6965.7 cm$^{-1}$.

\[ I_N = \frac{(I_0 - I_{Off})}{(I - I_{Off}) - 1} / L \]
Experiment details
Amplified Spontaneous Emission (ASE)

ASE may pass through cavity adding an additional background offset in cavity output intensity
Calibration: Interaction pathlength determination ($L_{eff} = \frac{L}{1-R}$)

The effective reflectivity is calculated from Voigt profile fit area:

$$R = 1 - \frac{N_{H_2O} \cdot S_{H_2O}}{A}$$

Normalized direct absorption signal of pure H$_2$O vapor at different pressure.
OA-ICOS absorption spectrum \((1 - I/I_0)\) of pure H\(_2\)O vapor at 0.75 mbar (black). A simulation spectrum based on the Beer-lambert law is shown in red for comparison with a \(L_{\text{eff}} = 1200\, \text{m}\).
Experiment details
Further improvement: Laser Amplitude Stabilization

Reduction of laser excess noise
Experiment details
Further improvement: Laser Amplitude Stabilization

Fluctuation in probe light limits the sensitivity. Intensity fluctuations (temperature, current): technical noise. The DFB laser power stabilization is implemented for reduction of laser excess noise.

Results of the use of laser amplitude stabilization. Spectra recorded without (black) and with (red) power stabilization. Allan variance curves: laser amplitude stabilization $\Rightarrow$ optimal averaging time $\geq 200$ s (red), compared to 100 s without (black). Noise equivalent sensitivity enhanced by a factor of $\sim 5$. 

![Graph showing Allan variance curves with and without laser amplitude stabilization.](image-url)
MDA (Minimum Detectable Absorption) per scan ($\text{MDA}_{ps}$) or per point ($\text{MDA}_{pp}$) & NEAS are deduced from data acquisition rate and SNR [4]:

$$\Rightarrow \text{MDA}_{ps} = \left(\frac{\Delta P}{P}\right)n\sqrt{n\sqrt{T_{\text{scan}}}}$$

$$\Rightarrow \text{NEAS} = \frac{\text{MDA}_{ps}}{L_{\text{eff}}\sqrt{N_{pts}}} \ & \ \text{MDA}_{pp} = \frac{\text{MDA}_{ps}}{\sqrt{N_{pts}}}$$


Where $n$ is the number of scans averaged, $T_{\text{scan}}$ the time of a scan, $L_{\text{eff}}$ the effective interaction pathlength and $N_{pts}$ the number of points per scan.

<table>
<thead>
<tr>
<th>System</th>
<th>(1-R) (ppm)</th>
<th>Pathlength (m)</th>
<th>NEAS (cm$^{-1} \times$Hz$^{-1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With</td>
<td>725</td>
<td>689</td>
<td>$1.1 \times 10^{-8}$</td>
</tr>
<tr>
<td>Without</td>
<td>725</td>
<td>689</td>
<td>$6.7 \times 10^{-8}$</td>
</tr>
</tbody>
</table>
Results and Outlook
OA-ICOS system performances

Performances

1. OH detection using an OA-ICOS setup with high sensitivity ($1 \times 10^{-10}$ cm$^{-1}$/Hz$^{1/2}$ with an effective absorption path length of $L_{eff} \approx 1.2$ km).

2. 1 $\sigma$ detection limit of $2.1 \times 10^{11}$ OH.cm$^{-3}$ achieved (signal-to-noise ratio (SNR) of 345).

3. Laser amplitude stabilization implementation $\Rightarrow$ improvement of the laser instrument stabilization time, and of the NEAS by a factor of $\sim 6$. 
## Results and Outlook

Typical performances of OA-ICOS in NIR

<table>
<thead>
<tr>
<th>Ref.</th>
<th>λ (nm)</th>
<th>(1-R) (ppm)</th>
<th>Pathlength (m)</th>
<th>NEAS (cm⁻¹×Hz⁻¹/2)</th>
<th>MDA&lt;sub&gt;pp&lt;/sub&gt; (Hz⁻¹/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5]</td>
<td>1565</td>
<td>40</td>
<td>27500</td>
<td>2.7×10⁻¹²</td>
<td>7.4×10⁻⁶</td>
</tr>
<tr>
<td>[6]</td>
<td>1565</td>
<td>165</td>
<td>4200</td>
<td>3.1×10⁻¹¹</td>
<td>1.3×10⁻⁵</td>
</tr>
<tr>
<td>☺</td>
<td>1435</td>
<td>396</td>
<td>1263</td>
<td>1.0×10⁻¹⁰</td>
<td>1.3×10⁻⁵</td>
</tr>
<tr>
<td>[8]</td>
<td>1573</td>
<td>4400</td>
<td>68</td>
<td>5.0×10⁻⁹</td>
<td>3.4×10⁻⁵</td>
</tr>
<tr>
<td>[7]</td>
<td>1605</td>
<td>160</td>
<td>1400</td>
<td>3.9×10⁻¹⁰</td>
<td>5.5×10⁻⁵</td>
</tr>
</tbody>
</table>

1. Implementation of frequency modulation in OA-ICOS ⇒ enhance sensitivity by up to 2 orders of magnitude.

![Graph of 2f signal OH at 6965.1939 cm⁻¹](image)

2. Using OA-ICOS for laboratory experiments to study the reactivity of atmospheric pollutants (OH measurement)
   - Simulation chamber (200 L) ⇒ determination of OH yields formed during the ozonolysis of VOCs.
   - Determination of OH rate constants
This work is supported by IRENI (Institute of Research in Industrial ENvironnement) program: