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

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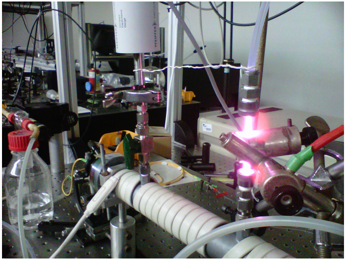

Motivations

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 $\leq 1\,\text{sec}$)
- High selectivity (interference-free from atmospheric H_2O, CO_2)
- High sensitivity (low OH concentration $10^6 \sim 10^8 OH.cm^{-3}$)
- High spatial resolution (compact setup for in field measurements)

Outline

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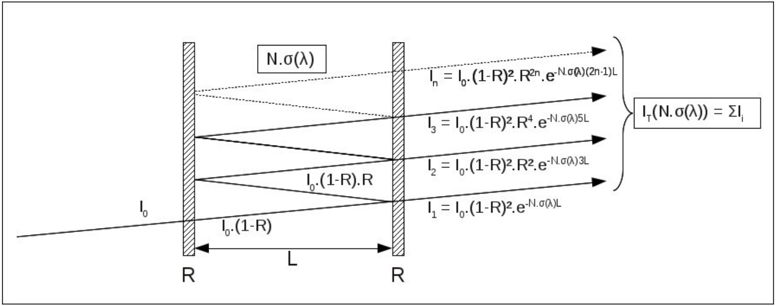
Introduction

Integrated Cavity Output Spectroscopy

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 :$\Rightarrow I = I_0 \times e^{-N\sigma(\lambda)\times L}$

[1] A. O'Keefe, J. J. Scherer, J. B. Paul, Chem. Phys. Lett. 307, 343-349 (1999)

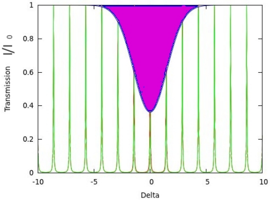
[2] A. O'Keefe, Chem. Phys. Lett. 293, 331-336 (1998)



In a high finesse optical cavity, the light trapped inside can make a great number of round-trips between the cavity mirrors.

Introduction

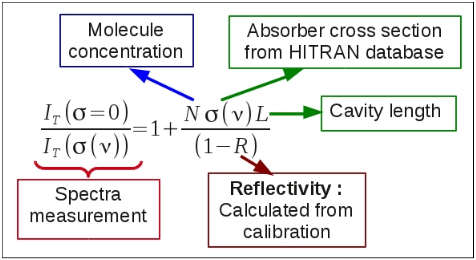
Integrated Cavity Output Spectroscopy expression



Intensity at cavity output is an infinite sum (integration) of leaking radiations intensity at each round-trip :

$$\Rightarrow I_T(\sigma(\nu)) = \sum_i I_i(\sigma(\nu))$$

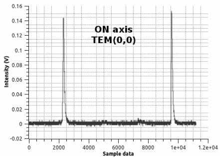
Integrated Cavity Output Spectroscopy expression :

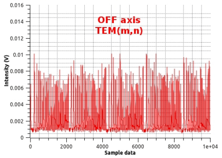


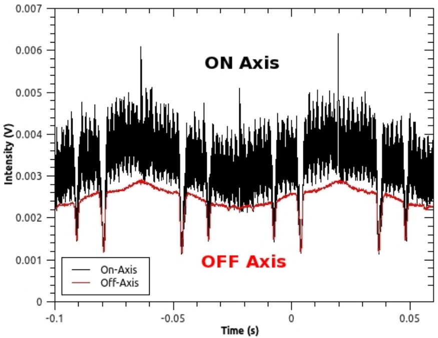
Off-Axis ICOS

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].

[3] H. Kogelnik, T. Li, Proceedings of the IEEE Vol. 54, N 10, 1312-1329 (1966)

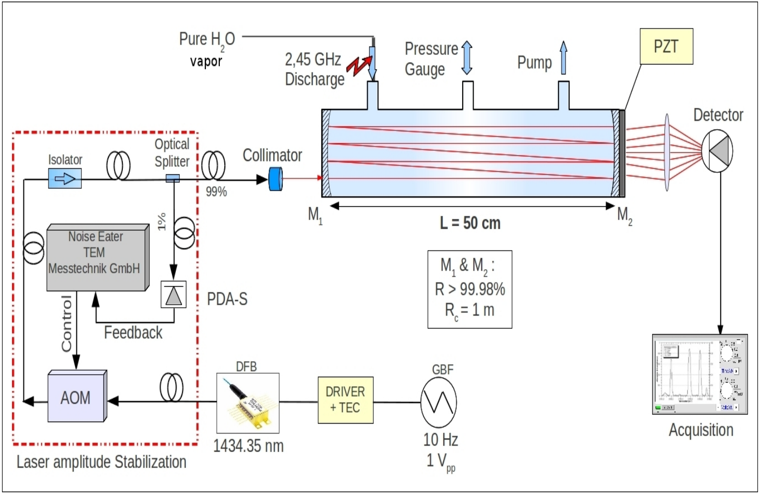




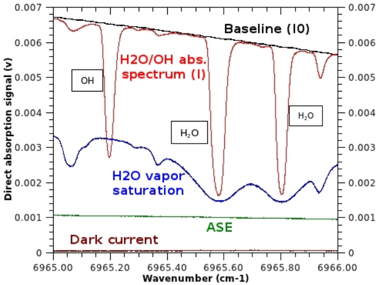


Spectra SNR depends on the coupling to the cavity

Experiment details
Setup design



Importance of offset level determination



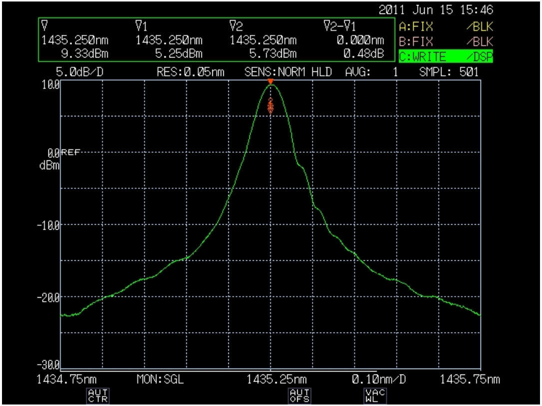
The laser frequency is scanned at a rate of 10 Hz with a peak-to-peak amplitude of 1.00 V, allowing a scan over 1 cm^{-1} around 6965.1939 cm^{-1} to cross the OH transition line Q(2,5f) and the H_2O lines[a] near 6965.7 cm^{-1}.

[a] The $9_{46} \leftarrow 10_{37}$ transition of the $2\nu 1$ band of H_2O at 6965.58 cm^{-1}
The $5_{41} \leftarrow 5_{32}$ transition of the $n1 + 2\nu 2$ band of H_2O at 6965.80 cm^{-1}.

Normalised spectrum

$$\Rightarrow I_N = \left(\frac{I_0 - I_{Off}}{I - I_{Off}} - 1\right)/L$$

Experiment details
Amplified Spontaneous Emission (ASE)

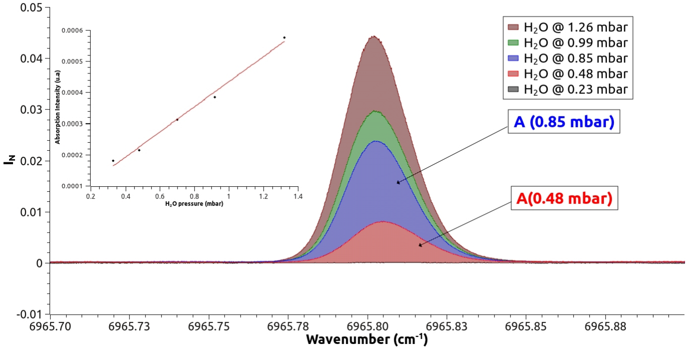


ASE may pass through cavity adding an additional background offset in cavity output intensity

Calibration : Interaction pathlength determination ($L_{eff} = \frac{L}{1-R}$)

The effective reflectivity is calculated from Voigt profile fit area :

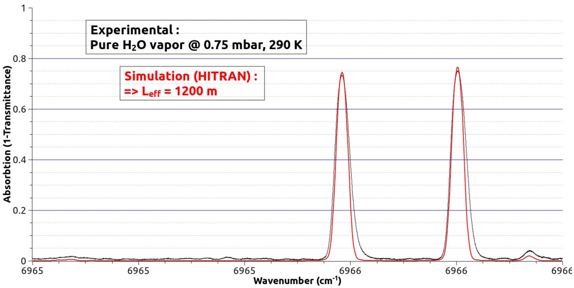
$$\Rightarrow R = 1 - \frac{N_{H_2O}.S_{H_2O}}{A}$$



Normalized direct absorption signal of pure H_2O vapor at different pressure

Calibration result : I_{off} choice validation

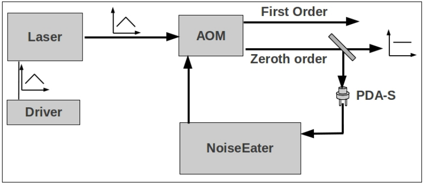
Effective interaction pathlength from calibration : $L_{eff} = 1263m$
Corresponding mirrors reflectivity : $R = 99.96\%$ (compared to manufacturer's $R \geq 99.98\%$)



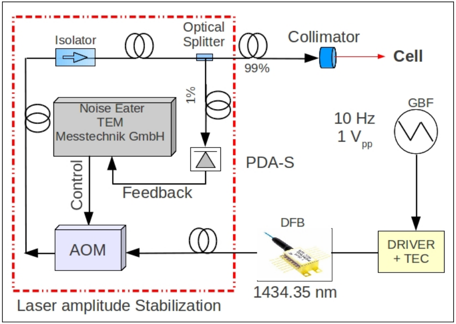
OA-ICOS absorption spectrum $(1 - I/I_0)$ of pure H_2O vapor at 0.75 mbar (black). A simulation spectrum based on the Beer-lambert law is shown in red for comparison with a $L_{eff} = 1200m$.

Experiment details

Further improvement : Laser Amplitude Stabilization



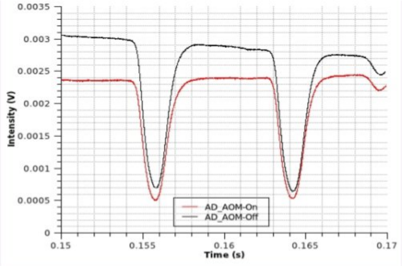
Reduction of laser excess noise

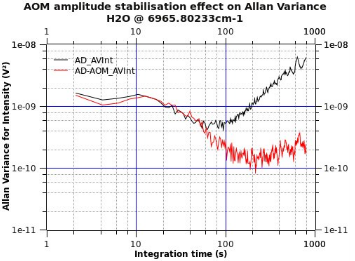


Experiment details

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 ⇒ optimal averaging time $\geq$ 200 s (red) , compared to 100 s without (black). Noise equivalent sensitivity enhanced by a factor of $\sim$ 5.

MDA (Minimum Detectable Absorption) per scan (MDA_{ps}) or per point (MDA_{pp}) & NEAS are deduced from data acquisition rate and SNR [4]:

$$\Rightarrow MDA_{ps} = \left(\frac{\Delta P}{P}\right)_n \sqrt{n}\sqrt{T_{scan}}$$

$$\Rightarrow NEAS = \frac{MDA_{ps}}{L_{eff}\sqrt{N_{pts}}} \;\&\; MDA_{pp} = \frac{MDA_{ps}}{\sqrt{N_{pts}}}$$

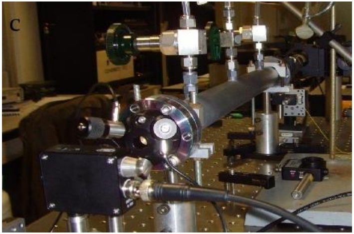
[4] E.J. Moyer et al., Appl. Phys. B 92, 467–474 (2008)

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

System	(1-R) (ppm)	Pathlength (m)	NEAS ($cm^{-1} \times Hz^{-1/2}$)
With	725	689	1.1×10^{-8}
Without	725	689	6.7×10^{-8}

Performances

1. OH detection using an OA-ICOS setup with high sensitivity (1×10^{-10} cm^{-1}/Hz$^{1/2}$ with an effective absorption path length of $L_{eff} \simeq 1.2km$).
2. 1 σ detection limit of 2.1×10^{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.



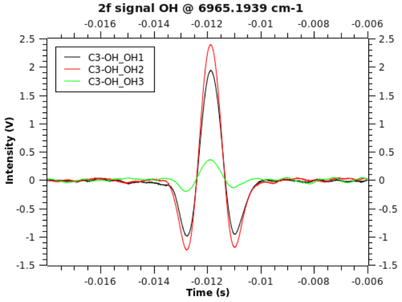
Ref.	λ	(1-R) (ppm)	Pathlength (m)	NEAS ($cm^{-1} \times Hz^{-1/2}$)	**MDA_{pp} ($Hz^{-1/2}$)**
[5]	1565	40	27500	2.7×10^{-12}	**7.4×10^{-6}**
[6]	1565	165	4200	3.1×10^{-11}	**1.3×10^{-5}**
☺	1435	396	1263	1.0×10^{-10}	**1.3×10^{-5}**
[8]	1573	4400	68	5.0×10^{-9}	**3.4×10^{-5}**
[7]	1605	160	1400	3.9×10^{-10}	**5.5×10^{-5}**

[5] G.S. Engel et al., Appl. Opt. 45, 9221 (2006)
[6] D.S. Baer et al., Appl. Phys. B 75, 261 (2002)
[7] V.L. Kasyutich et al., Appl. Phys. B 85, 413 (2006)
[8] W. Zhao et al., Appl.Phys. B 86, 353 (2007)

Conclusion

Perspectives

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



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

Thanks

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