High-sensitivity measurement of OH radicals using multi-pass enhanced Faraday Rotation Spectroscopy

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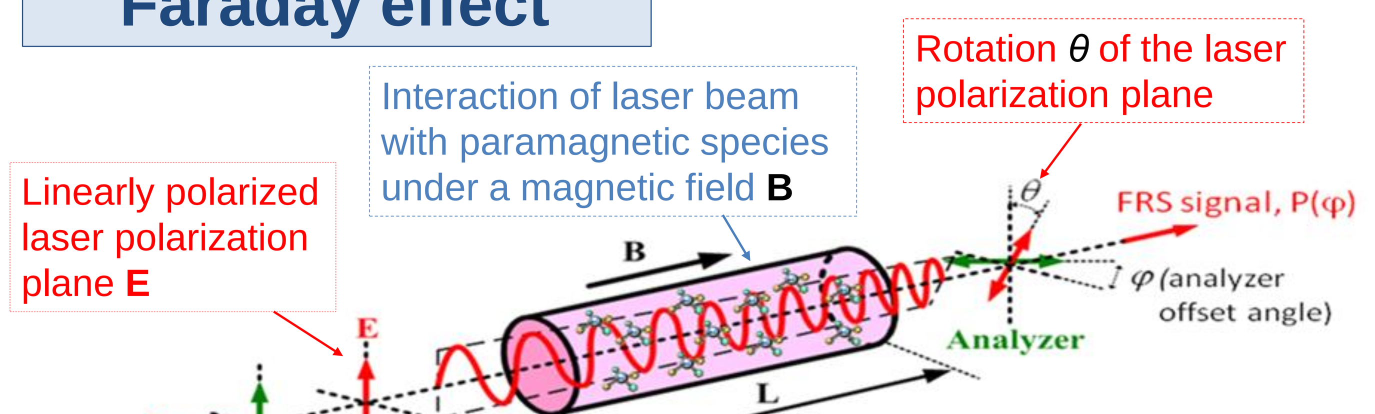
The hydroxyl radical (OH) is one of the dominant oxidising specie in the atmosphere and plays a critical role in atmospheric chemistry due to its high reactivity with trace polluants. Because of its very short lifetime (≤ 1 s) associated with very low atmospheric concentration (~10^6 OH radicals/cm^3), the development of analytical instrument allowing accurate, interference-free and ultra-high sensitivity in-situ direct measurement of absolute OH concentration presents a great challenge for atmospheric science and climate change research.

Faraday rotation spectroscopy (FRS) takes effect of the magnetic circular birefringence observed in the vincinity of Zeeman split transitions in paramagnetic species : when a longitudinal magnetic field is applied, the polarization axis of a linearly polarized light is rotated due to interaction with the sample. Measurement of this Faraday rotation angle allows for concentration retrieval of the target molecule.

We report on the recent development of a multi-pass enhanced Faraday Rotation Spectrometer for OH radicals measurement. The prototype instrument, using a 2.8 µm interband cascade laser (ICL) coupled to a multipass-cell with an effective optical absorption path-length of ~7.5 m, allowed us to achieve a 1σ (SNR=1) detection limit of (LoD) about 5x10^7 OH/cm^3. The LoD using multi-pass cell was improved more than one order compared to that using a single-pass cell of 25 cm.

OH free radicals detection based on Faraday Rotation Spectroscopy (FRS)

Faraday effect



$$P(\varphi) \sim \frac{P_0}{2}(1 - cos2\varphi + R_\Delta Lsin2\varphi)$$

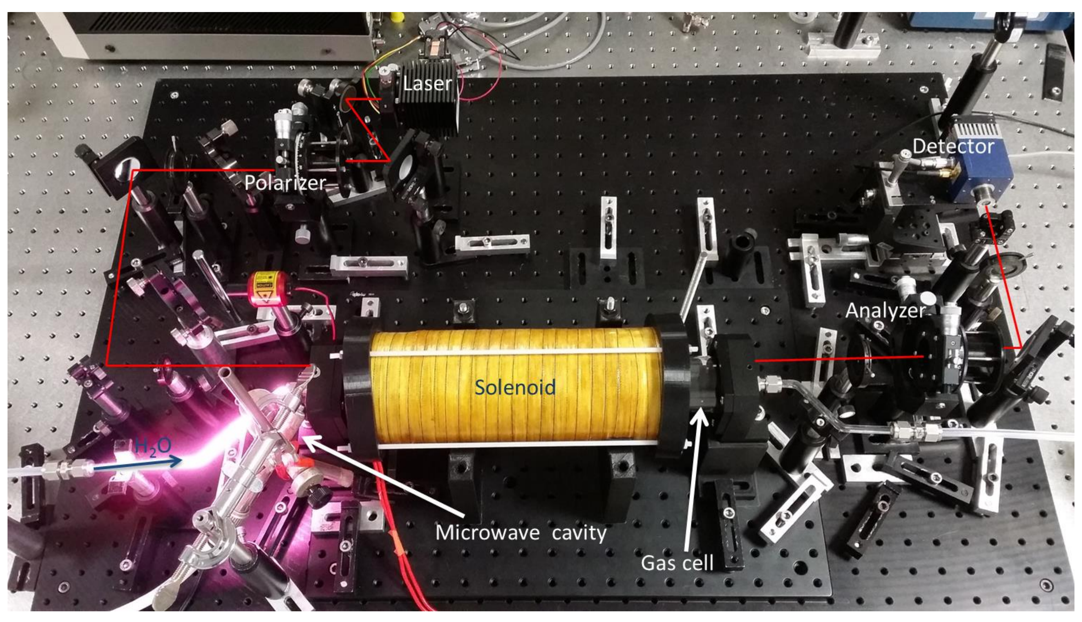
$$R_\Delta = k_0(n_+ - n_-)$$

The FRS relies on the Faraday effect resulting from an interation between incident light and a magnetic field in a paramagnetic species, which exhibits magnetic circular birefringence under the magnetic field applied in the light propagation direction :

→The refractive index is different for right-handed (RHCP, n_+) and left-handed (LHCP, n_-) circularly polarized waves travelling in the medium : $R_\Delta = k_0(n_+ - n_-)$, with k_0 is the wave vector

→The dispersion effects of paramagnetic molecules result in a rotation of the polarization plane of a linearly polarized laser beam → FRS signal P(φ)

FRS setup with AC field



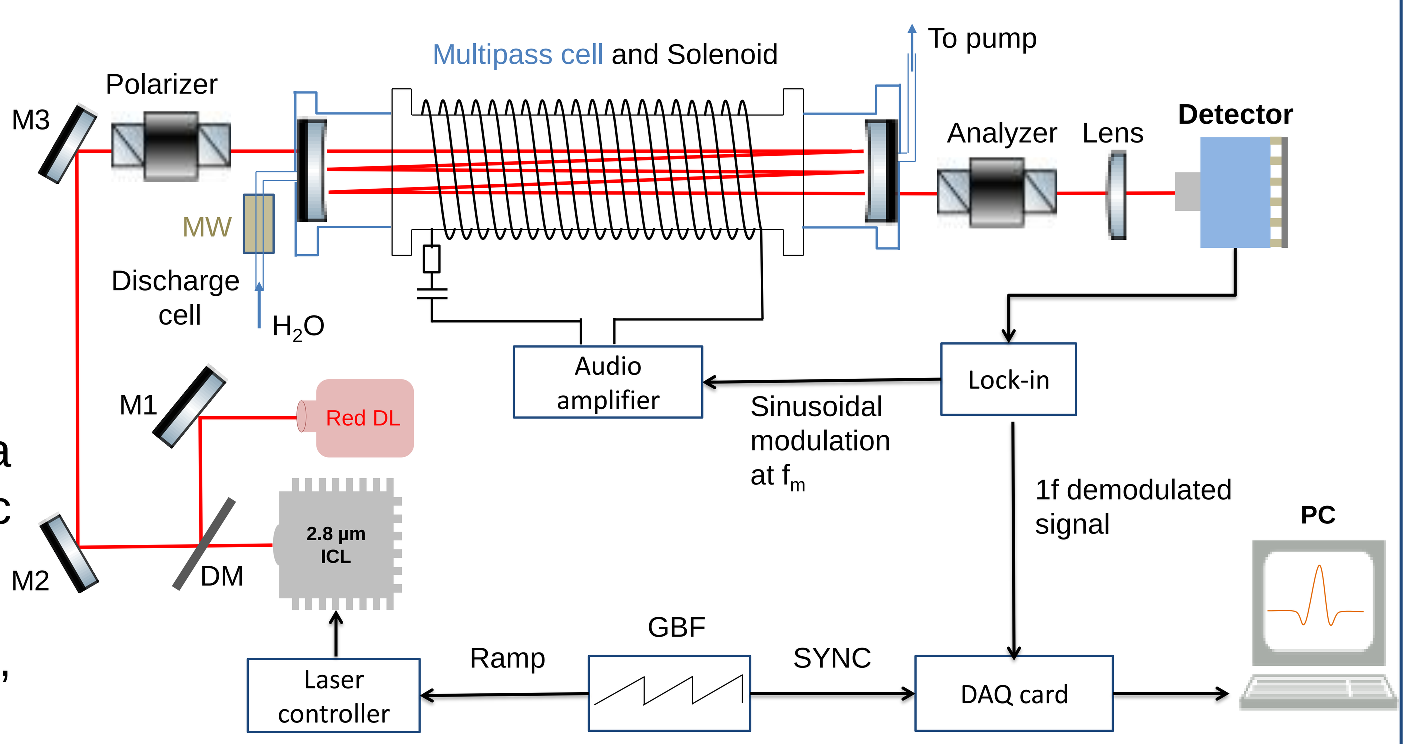
RT ICL laser operated at 2.8 µm (nanoplus)

- Single-mode T° tuning range : ~ 11 nm
- CW laser emission power : ~ 1.5 mW
- λ-tuning coefficients : 0.2 nm/mA & 0.25 nm/K

Polarizer : high extinction ration of ξ < 5x10^{-6}

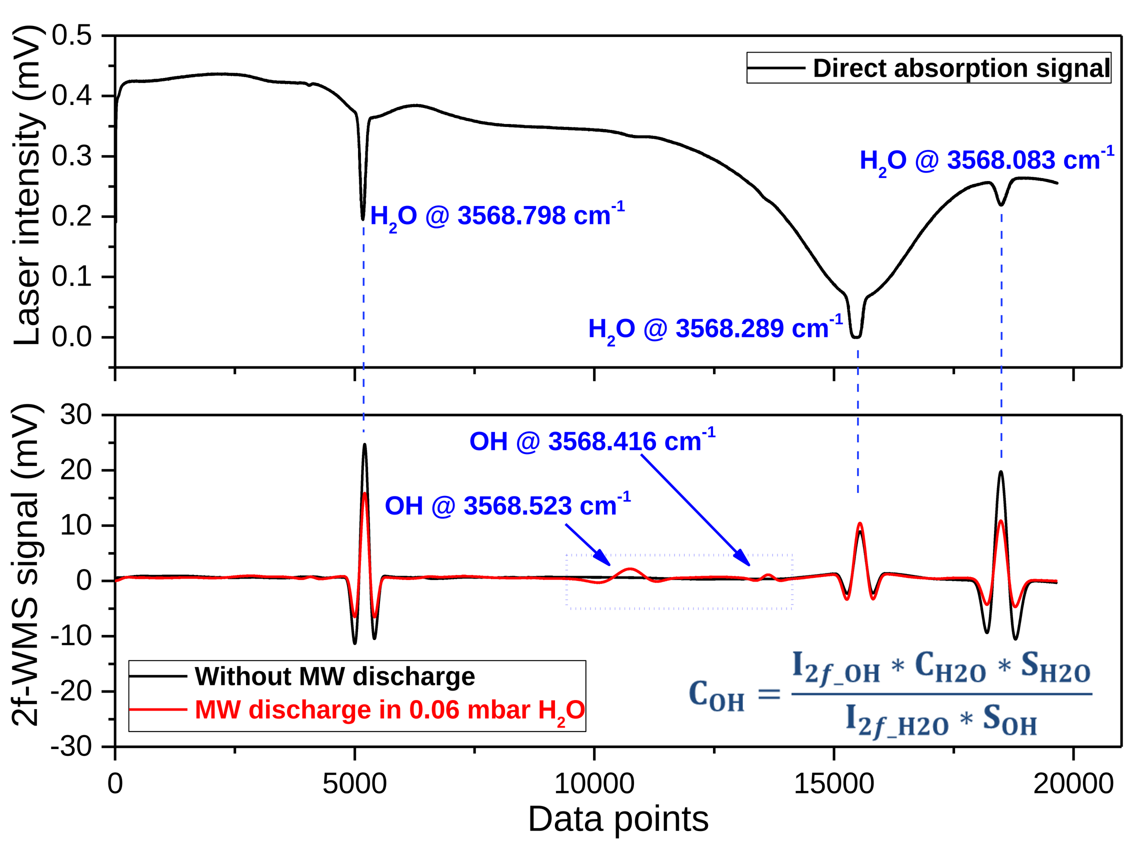
Solenoid : 25 cm long, operating in AC mode at a resonant frequency of 1.303 kHz, with a magnetic field of B ~ 95 $Gauss_{rms}/A_{rms}$

Multipass cell : 33 cm long, number of pass N : 23, effective path-length ~ 7.5 m, reflectivity R ~ 97 %



Experimental details

OH radicals calibration



OH radical was produced by a 2.45 GHz microwave (MW) discharge of H_2O vapor. 2f-Wavelength Modulation Spectroscopy (2f-WMS) was used for determination of the OH concentration [1].

Improvement factor in Limit of Detection : single-pass vs multipass cell

The signal to noise ratio (SNR) of FRS single-pass [2] :

$$SNR_{single-pass} = \frac{R_\Delta L\sqrt{P_0}}{\sqrt{2bd + c^2}}$$

R_Δ: difference of refractive index of RHCP and LHCP
L: absorption path length within the magnetic field
P_0: intensity of light incident at the analyzer
b : the detector and system noise
c : related to detector responsivity
d : the proportionality coefficient specific for the particular laser source

The signal to noise ratio (SNR) of FRS multi-pass :

The FRS signal strength after multi-pass cell is directly proportional to the **number of passes N** whereas the output optical power P_0 decays exponentially with **N** due to the power loss on the mirrors :

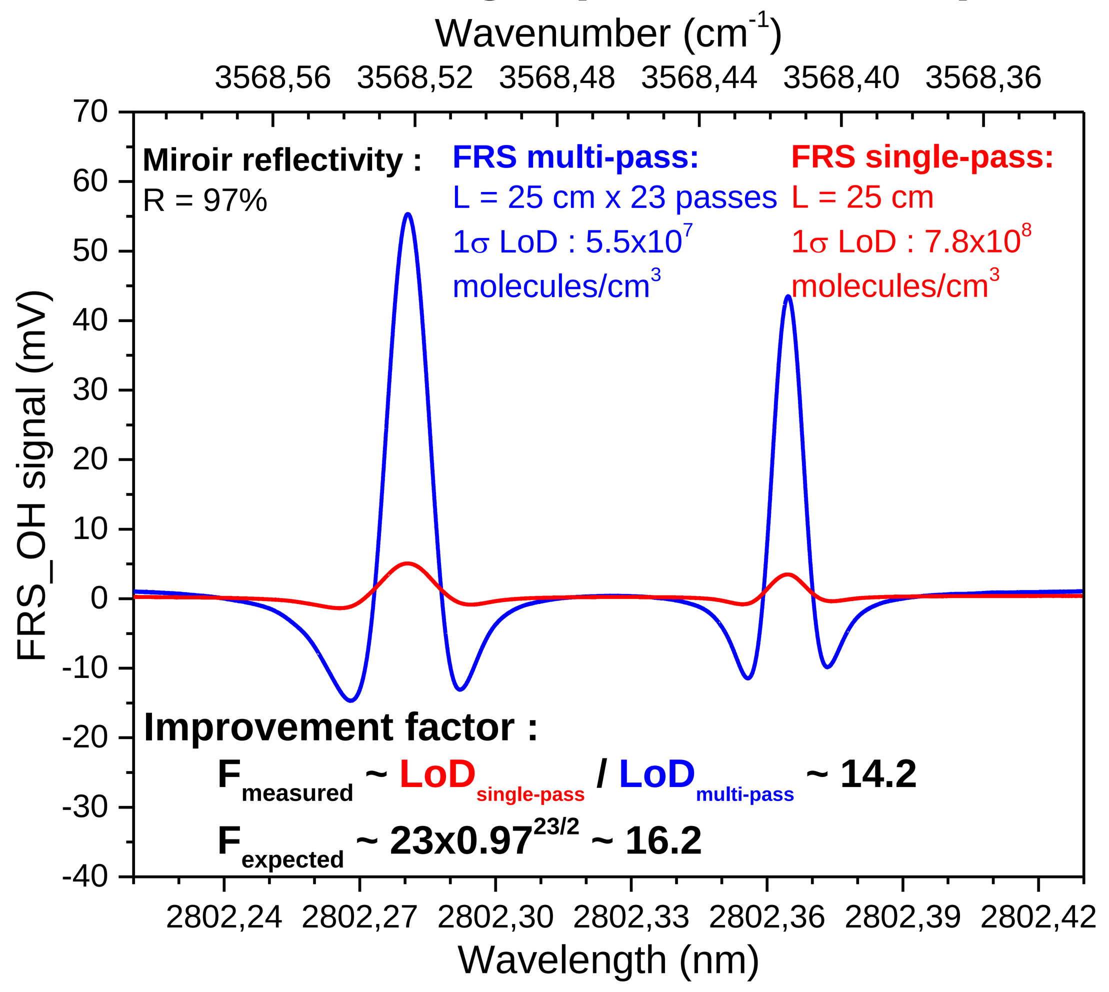
$$SNR_{multi-pass} = \frac{R_\Delta L N\sqrt{P_0 \boldsymbol{R^N}}}{\sqrt{2bd + c^2}}$$

N : number of passes
R : the power reflectivity on the mirror

The signal to noise ratio (SNR) improvement factor **F** :

$$\boldsymbol{F} = \frac{SNR_{multi-pass}}{SNR_{single-pass}} = \boldsymbol{N}\sqrt{\boldsymbol{R^N}}$$

FRS-OH : single-pass vs multi-pass



FRS-OH spectrums were obtained by scanning the current with a 1 Hz ramp, with an alternative magnetic field B at 104 $Gauss_{rms}$ and a lock-in time constant of 5 ms.

Conclusions & Perspectives

A compact multi-pass enhanced Faraday Rotation Spectrometer for OH radicals measurement was developed in laboratory. The SNR improvement factor (**F**) of the FRS multi-pass is directly proportional to the number of pass **N** and to the square root of the exponentially with N of the mirror reflectivity. A good agreement of $F_{measured}$ and $F_{expected}$ was demonstrated.

→ ***Further improvement in LoD by using cavity-enhanced FRS approach in order to achieve necessary detection sensitivity for field application.***

Acknowledgements

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[2] R. Lewicki, J. H. Doty, R. F. Curl, F. K. Tittel, and G. Wysocki, Proc. Natl. Acad. Sci. U. S. A. **106** (2009) 12587–12592