# Off-axis integrated cavity output spectroscopy enhanced Faraday rotation techniques for OH detection at 2.8 μm

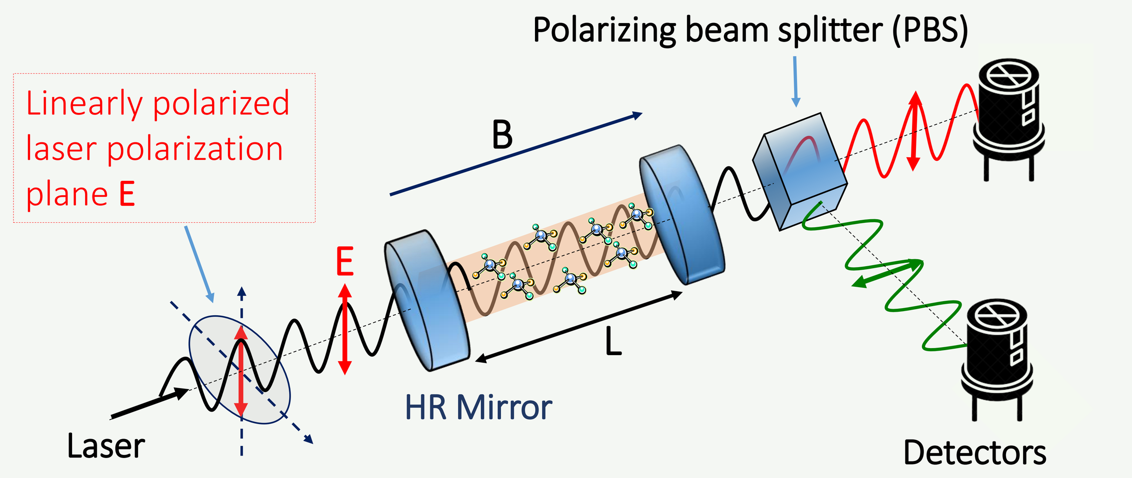
Minh-Nhut NGO[1], Tong NGUYEN-BA[1], Nicolas HOUZEL[1], Cécile COEUR[1], Weixiong ZHAO[2], Weidong CHEN[1]

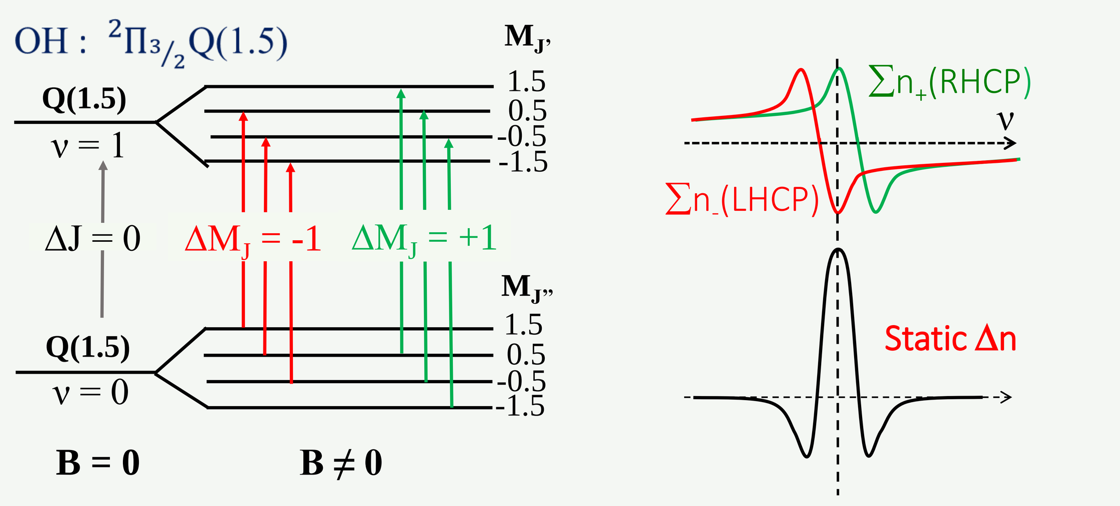
[1] Laboratoire de Physico-Chimie de l'atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France
[2] Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, China

## Abstract

OH radical is known as a major atmospheric oxidant playing a central role in the degradation of trace gases and pollutants in the atmosphere [1]. Measurement of total OH reactivity is crucial for understanding of the atmospheric oxidation capacity. In this paper, we report on the development of an optical instrument for interference-free measurement of OH radicals in laboratory based on a combination of off-axis integrated cavity output spectroscopy (OA-ICOS) and Faraday Rotation Spectroscopy (FRS) operating at 2.8 μm (OA-ICOS-FRS). OH radical concentrations in the range of ~$10^{12}$ molecule.cm$^{-3}$ were generated by microwave discharge of water vapor at low pressure and monitored by the OA-ICOS-FRS instrument, providing a limit of detection of ~$10^{10}$ molecule.cm$^{-3}$ within an integration time of 20 s. The performance of the system was evaluated by optical monitoring of the reaction of OH with $CH_4$. The oxidation rate coefficient $k_{OH-CH4}$=(4.8±0.5) × $10^{-15}$ cm$^3$.molecule$^{-1}$.s$^{-1}$ was obtained by measuring the decay time of the OA-ICOS-FRS signal during the oxidation of $CH_4$ by OH and this value is in good agreement with values reported in the literature. The developed instrument provides a suitable analytical tool for study of total OH reactivity in simulation chamber [2,3].

## Faraday effect and Cavity – enhanced absorption technique




### Spectral selectivity detection by FRS

The interaction of right-handed (RHCP) and left-handed (LHCP) circularly polarized light with the Zeeman split transitions results in the circular birefringence (MCB) around the absorption line of paramagnetic species, which causes a rotation of a linearly polarized laser light [4].

$$FRS\_signal \sim \Theta = \frac{\pi L_{eff}}{\lambda}\Delta n$$

- ✓ Absorption line intensity
- ✓ g-factor
- ✓ Magnetic field strength
- ✓ Optical path length
- ✓ Molecule concentration
- Avoid inference from $H_2O$, $CO_2$, ….

The polarization rotation unbalances the optical powers incident on two detectors ⇒ generates the FRS signal.

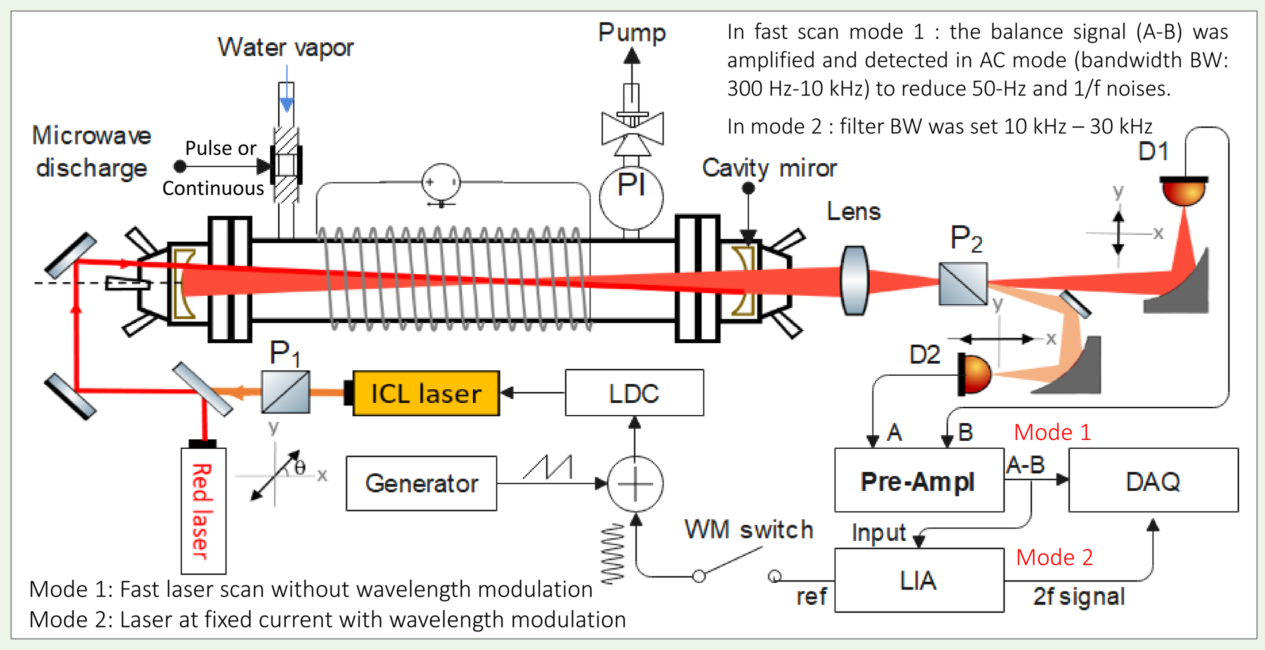
### Direct absorption measurement by ICOS

Concentration **C** is determined with the known value of mirror reflectivity **R** [5]:

$$\alpha(v) = C.\sigma(v) = \frac{1-R}{L}\left(\frac{I_0(v)}{I(v)} - 1\right)$$

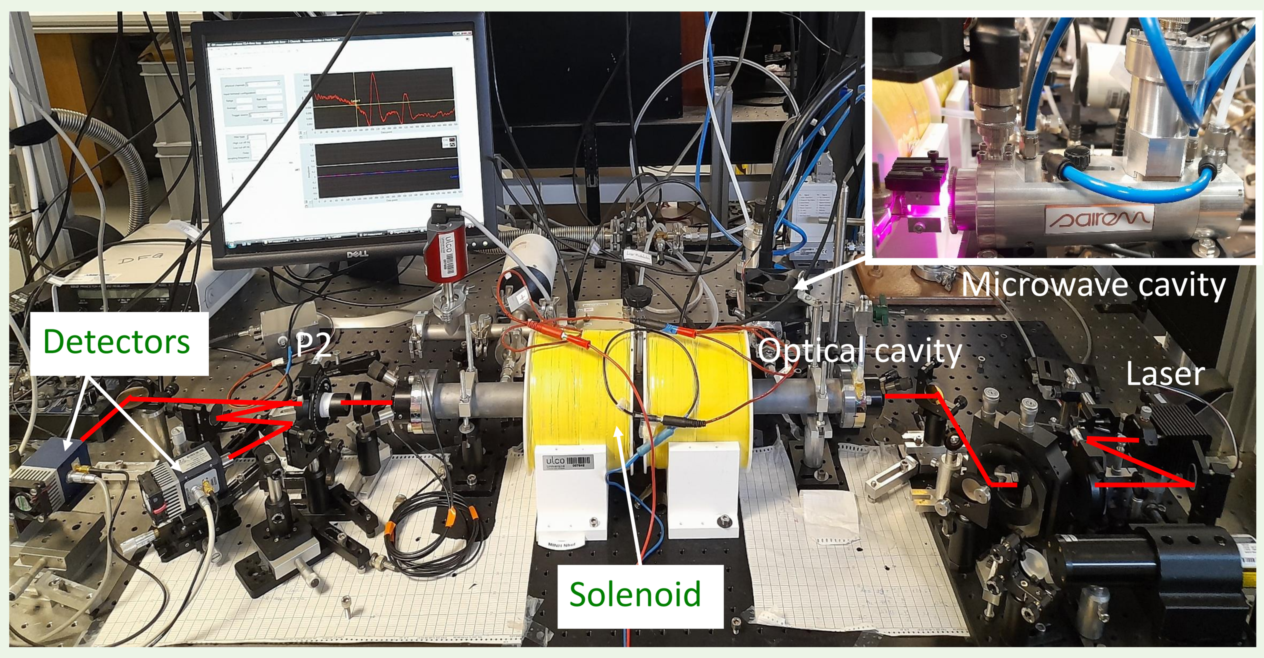
Δn - Difference in the indices of refraction for LHCP and RHCP, Θ - Faraday rotation angle, σ(v) - absorption cross-section, $I_0$(v) and I(v) transmitted light intensity with and without the absorbers, $L_{eff}$ = L/(1-R)

## OA-ICOS enhanced FRS setup for OH measurement




P1: linear polarizer, P2: Rochon prism, DAQ: data acquisition card, LIA: Lock-in amplifier ($f_m$ = 17.5 kHz, time constant = 200 μs)

Laser was injected into the cavity via off-axis coupling (un-resonant coupling)



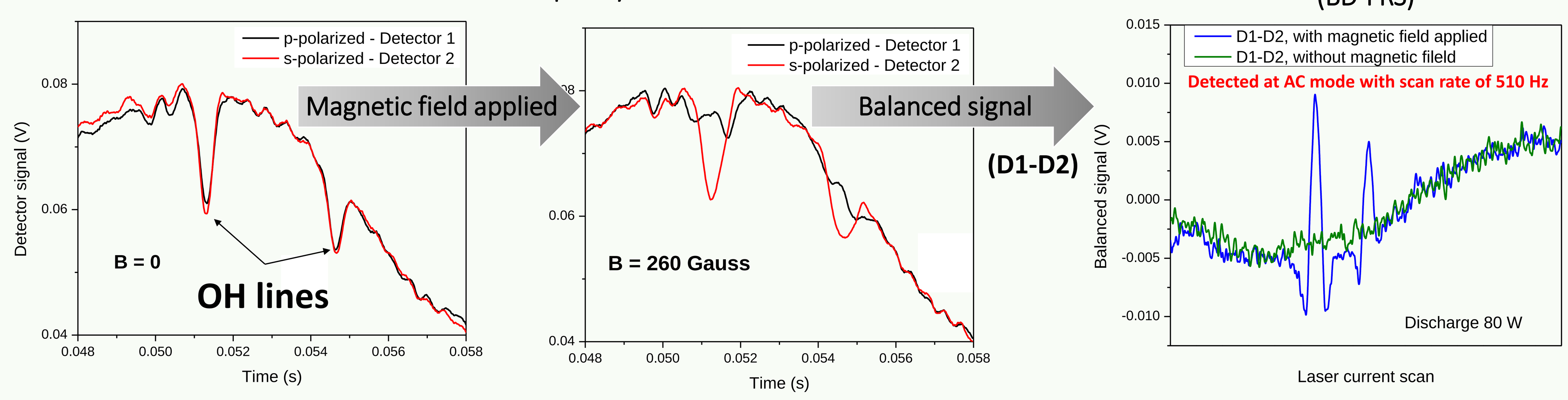

- ✓ **Light source** : DFB interband cascade laser (ICL) at 2.8 μm. Signal-mode, tuning range: ~11 nm. CW laser emission power: ~12 mW
- ✓ Mirror reflectivity: R = 0.9986 ⇔ Effective path length: $L_{eff}$ = 366 m determined using a known concentration of $CO_2$
- ✓ OH radical was produced by a 2.4 GHz microwave discharge of $H_2O$ vapor.

## Experimental details

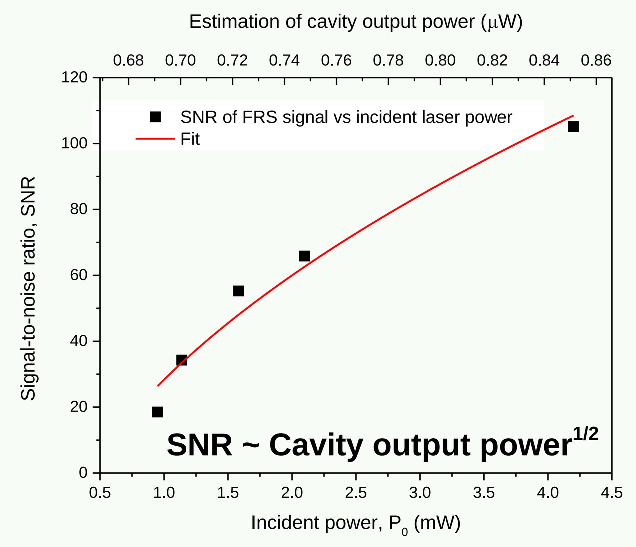
### Characterization of FRS signal from balanced detection based on ICOS approach

Time-integrated signal (ICOS signal) of two polarized cavity outputs, recorded by detectors D1 and D2 when the laser frequency was scanned across OH lines

FRS signal by Balanced detection (BD-FRS)




SNR of balanced signal vs laser power




### Faraday effect causing unbalance between p- and s-polarization compenents at cavity output, resulting in a difference in FRS signals

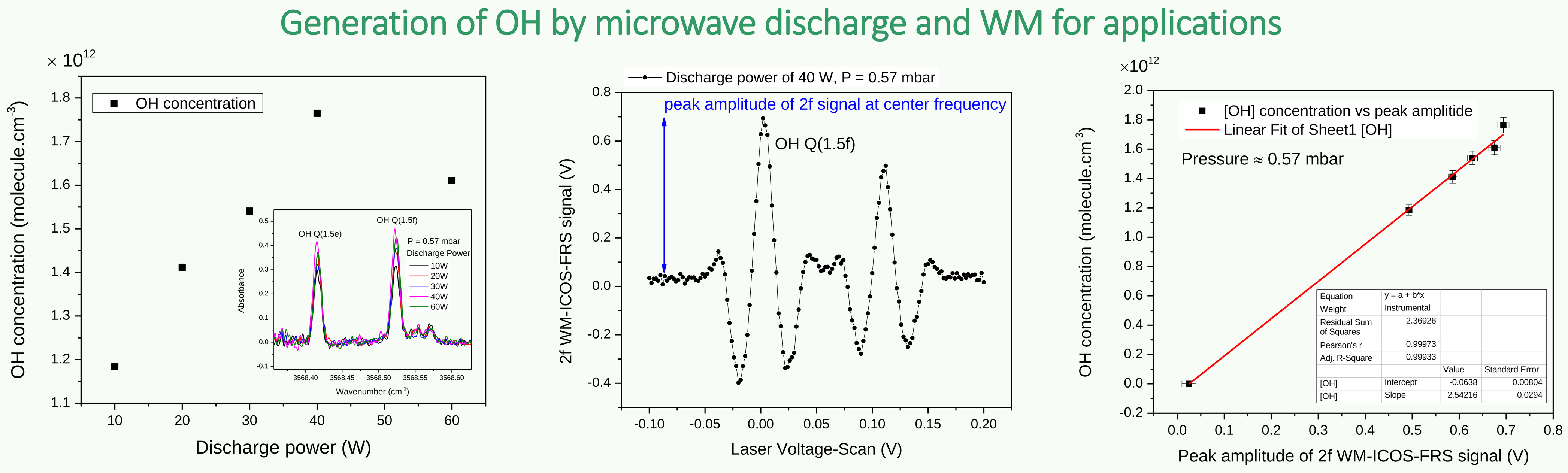
The detection limit can be further improved by increasing transmitted power through the cavity via serval approaches:

- Re-injection of laser into the cavity [6]
- Brewster injection cavity
- Resonant coupling as cavity ring-down technique [7]

OH detection can be performed based on measuring the **BL-FRS signal** in **AC mode** together with fast laser frequency tuning, showing advantages:

- Remove the **etalon effect** and the **interference from nearby non-paramagnetic species**
- White noise dominant in the balanced signal => improvement of SNR by simple **spectral average**
- Limit of detection (1σ): 9.3 × $10^9$ molecule.cm$^{-3}$ within 20 s integration time

### Generation of OH by microwave discharge and WM for applications



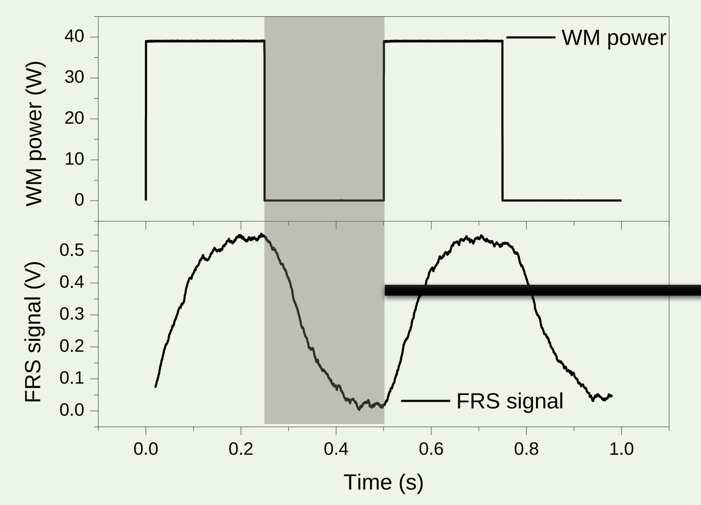

OH concentrations, determined from direct absorption by OA-ICOS, versus continuous discharge powers

2nd harmonic spectrum from LIA by applying wavelength modulation to the balanced FRS signal

Calibration of OH concentration versus peak-amplitude of 2f signal

Fast measurement of OH concentration in millisecond time scale can be performed by fixing laser current at center absorption frequency of the OH Q(1.5f) line and monitoring the peak BL-FRS signal value. As the BL-FRS signal is obtained in AC mode with fast laser scanning => it is necessary to apply wavelength modulation to BL-FRS and make demodulation using a LIA.

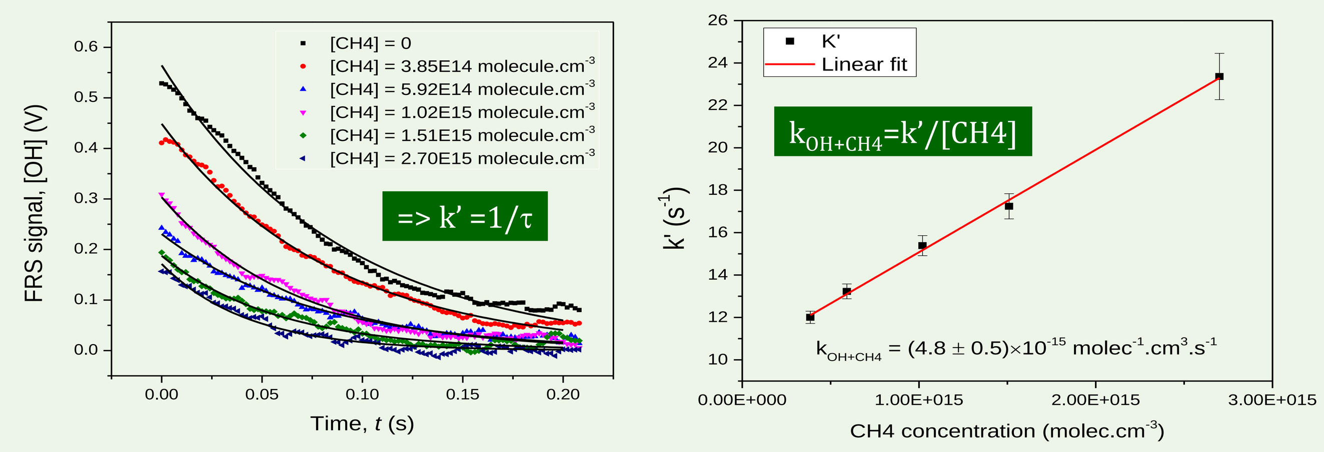
## On-line optical monitoring of $CH_4$ oxidation by OH




[OH] related to FRS signal, at laser frequency fixed at resonance frequency of OH Q (1.5f) line, versus **pulse WM** discharge power.

Window for measurement of Decay time τ

$[OH]_t = [OH]_0 \exp(-t/\tau)$




*left* : OH decay signal measured with different initial concentrations of $CH_4$.
*right* : Plot of the k' of the reaction of OH with $CH_4$ as a function of the initial $CH_4$ concentration at T = 293 ± 3 K.

## Conclusion & Perspectives

Development of a compact OA-ICOS-FRS instrument allowing interference-free detection of OH radical and validation via measurement of $CH_4$ oxidation by OH :

- ✓ Balanced detection with fast laser scanning
- ✓ Wavelength modulation (WM-FRS) with laser frequency fixed at OH signal peak for fast observation of OH decay
- ✓ Direct absorption (OA-ICOS) for absolute OH concentration determination

=> Study of the atmospheric OH reactivity with greenhouse gases and VOCs in atmospheric simulation chamber.

## References

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